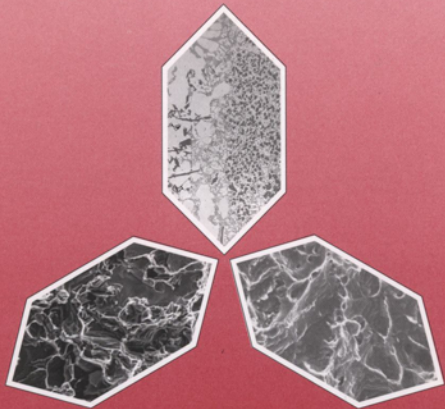




SURFACE MODIFICATION TECHNOLOGIES XV

Edited by

T.S. Sudarshan, J.J. Stiglich, and M. Jeandin



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**The Materials
Information Society**

Surface Modification Technologies XV

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Proceedings of the Fifteenth International Conference on
Surface Modification Technologies
held in Indianapolis, Indiana
November 5–8, 2001

Editors (Proceedings)

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**Fifteenth International Conference on
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Foreword

The Fifteenth (15th) International Conference on Surface Modification Technologies was hosted by “ASM International” and held in Indianapolis, Indiana, between 5th and 8th of November, 2001. Due to the incidents of September 11th, 2001 international travel was severely restricted and several papers were withdrawn due to the uncertainty in people’s minds about their safety and the love of family. Over 11 countries were represented at this meeting and this proceedings is a complete compilation of all the papers that were presented. The meeting was co-sponsored by Institute of Materials (IOM), U.K., and the proceedings is co-published by ASM and IOM.

The papers in this proceedings reflect significant work by the authors and was unfortunately diminished by the poor audiences due to the tragic events. The dedication of the authors and the session chairs in pulling off their individual sessions must be commended under the difficult and uncertain atmosphere that prevailed throughout this meeting. The papers included in these proceedings were peer reviewed and corrected prior to publication. We would like to thank the numerous reviewers for their time, patience and assistance.

We would also like to acknowledge the generous use of the communication facilities and the time released by our employers in the compilation of this volume that ensured its publication.

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Thermally Sprayed Materials

The PROTAL Process: An Economical Alternative for Producing a Clean Interface in a Thermal Spraying Application

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Abstract

Surface preparation prior to thermal spraying is a key step to ensure good adhesion of the coating. Usually, two successive stages are implemented, a surface degreasing using a solvent and surface roughening using grit blasting.

The PROTAL® process combines the surface preparation and the coating deposition in one step and produces a clean interface without contamination.

PROTAL® also allows the realization of metallurgical or chemical bonding between coating and substrate by thermal spraying in a normal atmosphere. The substrate is cleaned by ablation of the contaminated surface using a Neodyne-YAG laser. Short pulses of ten nanoseconds allow the cleaning of the surface without significant heating of the substrate. Using the PROTAL® process the mechanism of adhesion of the coating is changing from mechanical to chemical bonding. The PROTAL® process shows economical, environmental and

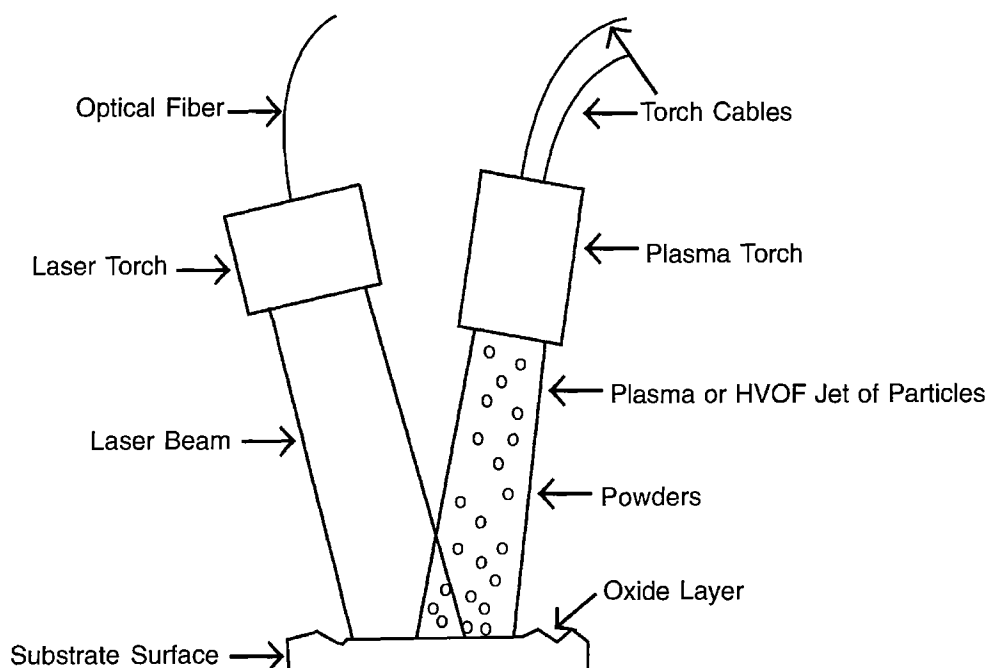


Fig. 1: Principle of the PROTAL® process.

technological advantages, especially during coating deposition on titanium and aluminum alloys.

1.0 Introduction

Surface preparation prior to thermal spraying is a key step in ensuring good adhesion of the coating onto the part to be coated. Usually, substrates initially are degreased and grit blasted, mainly with corundum. These steps are necessary to eliminate the superficial contamination (machining oil, handling, etc.) and to form a rough surface, which provides mechanical bonding between the substrate and the coating. It is well known that residues of grease and oxide layers prevent close contact between the impinging particles and the substrate. Also, the surface roughness significantly influences the adhesion of the thermal sprayed coatings.

Removing and recycling of solvents, as well as operator and environmental protection, are two major disadvantages of surface degreasing. The main drawback of the grit blasting technique with corundum is surface contamination by the abrasive particles which significantly degrade the mechanical properties of the interface and increase the risk of cracks.²

The PROTAL® process is a substitute for the degreasing and the grit blasting operations, particularly in the case of materials sensitive to the formation of stable

oxides (aluminum and titanium alloys, etc.).³⁻⁶ The objective of the laser treatment is to evaporate the grease, eliminate the oxide layer and to ablate the substrate surface.

These factors allow the metallurgical or chemical bonding between the substrate and the coating. The PROTAL® process is covered by the European Patent EP 0580534 B1.

2.0 Process Description

The laser aided PROTAL® process combines the preparation of the substrate and the thermal spraying in a single operation (Figure 1). There is no need for the pretreatment degreasing and grit blasting with corundum or white cast iron. Contamination free interfaces between coating and substrate can be realized.

With the PROTAL® process the substrate is cleaned with a high energy laser pulse. A laser beam with a wavelength of 1.064 μm and a very short pulse duration of only 10 ns evaporates the layer of grease, detaches the oxide layers and removes the uppermost atomic layer by means of ablation, without heating the base metal to any appreciable degree. The impact area of the laser is normally $18 \times 8 \text{ mm}$. A surface area of 1 m^2 can be treated with an energy density of 1.5 J cm^{-2} in just one minute. A few nanometers of the substrate are removed with this process. The resultant activated surface is now

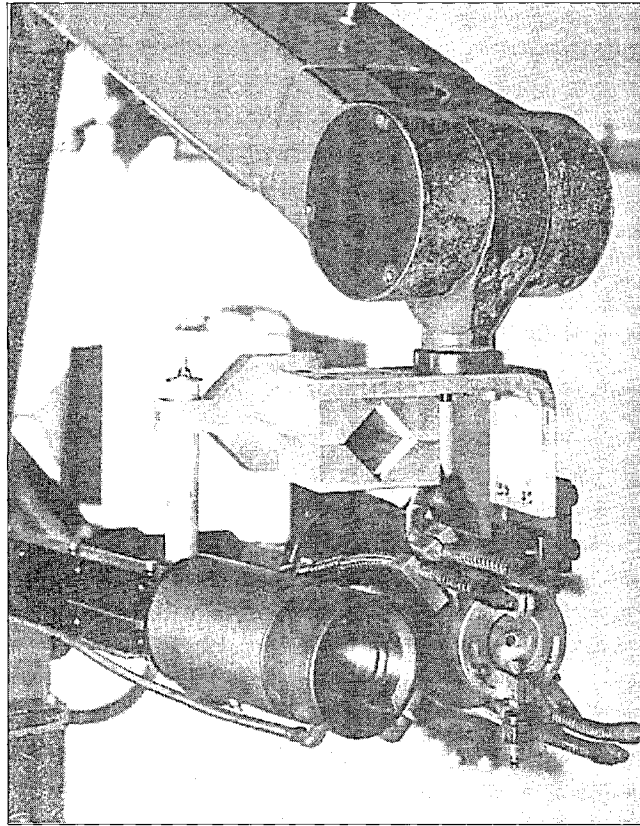


Fig. 2: A picture of the PROTAL® with an F 4 plasma spray gun, mounted on a robot arm.

coated by using HVOF (High Velocity Oxy-Fuel) or a plasma torch process with ceramic or metallic materials.

3.0 Metallurgical or Chemical Bonding

The grit blasting process results in the mechanical interlocking of the coating with the substrate, because of the roughening of the surface period. With the PROTAL® process, the substrate is cleaned and activated by the laser. The smooth, very clean surface facilitates the formation of a chemical/metallurgical bond between the sprayed particles and the substrate. This results in an adhesive strength which is comparable to or higher than that of the conventional process, especially in comparison with the surface roughness.

The PROTAL® process is especially interesting for coating deposition on a reactive material such as aluminum or titanium alloys. A Δt equal to zero (Δt represents the time between laser preparation and the impact of the particle) can be achieved during the process and an oxide free interface can be obtained by spraying in the ambient atmosphere.

In the case of an aluminum alloy a critical Δt from 100 ms was experimentally determined. The critical Δt

is defined by a reduction of ten percent in the measured bond strength according to the EN 582 standard (correspond with ASTM C 633-79). The EN 582 is the conventional method for the determination of the bond strength by thermal sprayed coating. Sprayed samples of 25 mm diameter are assembled with a high strength glue and test on a uniaxial tensile testing machine. For titanium alloys this value of Δt is about 3 s. For this reason the laser system is mounted with the thermal spray torch as one unit on a robot arm (Figure 2). This enables the time between the preparation of the surface and the application of the coating to be reduced to 20-40 ms, which is ideal for this application.

4.0 Economic and Ecological Advantages

PROTAL® can be described as a “green” process. The elimination of solvent and grit material makes the process attractive. The low level of energy consumption (max. 3 kW) and the saving of time, because the operation of surface preparation and coating are done simultaneously, are advantages of the PROTAL® process. For a production of rolls in the case of the print industry

Table 1. Adhesion Strength of EN 582 for Plasma Sprayed Coatings with Conventional and PROTAL® Surface Preparation

Substrate	Coating Material	Surface Preparation	Bond Strength (MPa)
Ti6Al4V	Cu	Grit Blasting, $R_a = 5 \mu\text{m}$	60
Ti6Al4V	Cu	Laser 0.75 J/cm^2 , $R_a = 0.2 \mu\text{m}$	55
Ti6Al4V	Ni20Cr	Grit Blasting, $R_a = 5 \mu\text{m}$	60
Ti6Al4V	Ni20Cr	Laser 0.75 J/cm^2 , $R_a = 0.2 \mu\text{m}$	55
Ti6Al4V	$\text{Al}_2\text{O}_3/13\%\text{TiO}_2$	Grit Blasting, $R_a = 5 \mu\text{m}$	80
Ti6Al4V	$\text{Al}_2\text{O}_3/13\%\text{TiO}_2$	Laser 0.75 J/cm^2 , $R_a = 0.2 \mu\text{m}$	80
Ti6Al4V	WC-Co	Grit Blasting, $R_a = 5 \mu\text{m}$	60
Ti6Al4V	WC-Co	Laser 0.75 J/cm^2 , $R_a = 0.2 \mu\text{m}$	80
Carbon Steel	Ni20Cr	Grit Blasting, $R_a = 6 \mu\text{m}$	70
Carbon Steel	Ni20Cr	Laser 1 J/cm^2 , $R_a = 0.2 \mu\text{m}$	80
Aluminum	$\text{Al}_2\text{O}_3/13\%\text{TiO}_2$	Grit Blasting, $R_a = 8 \mu\text{m}$	40
Aluminum	$\text{Al}_2\text{O}_3/13\%\text{TiO}_2$	Laser 1.5 J/cm^2 , $R_a = 0.2 \mu\text{m}$	40
Aluminum	Ni20Cr	Grit Blasting, $R_a = 8 \mu\text{m}$	40
Aluminum	Ni20Cr	Laser 1.5 J/cm^2 , $R_a = 0.2 \mu\text{m}$	40
Inconel 718 (HVOF)	$\text{Cr}_3\text{C}_2\text{-NiCr}$	Grit Blasting, $R_a = 6 \mu\text{m}$	90
Inconel 718 (HVOF)	$\text{Cr}_3\text{C}_2\text{-NiCr}$	Laser 1.5 J/cm^2 , $R_a = 0.5 \mu\text{m}$	90

the preparation costs prior plasma spraying can be reduced of a factor two and more.

5.0 Bond Strength and Coating Examples

Typical results of bond strength measured according EN 582 procedure are given for different material substrates in Table 1 for the case of air plasma spraying (APS) and HVOF. Similar bond strengths are obtained with the PROTAL® process but with a very smooth surface in contrast with the rough surface after grit blasting.

Figures 3 and 4 show typical coating cross sections obtained by the PROTAL® process. Both cases show absolute contamination free interfaces. The thickness of the electroless deposit chemical nickel can be reduced, because the risk of perforation by grit blasting does not more exist.

TEM investigation has shown that for the coating system copper on aluminum copper diffusion of 200 nanometers is obtained by using the PROTAL® process. This is only possible if no diffusion barrier (oxide layer)

is present on the surface prior to impact of the melted particles.

6.0 Summary and Conclusions

The PROTAL® process is a “green” technology for thermal spray coating deposition and allows the realization of metallurgical/chemical bonding. High bond strength can be obtained on a smooth substrate. The possibility of coating thin metallic foils is a further advantage of this process.

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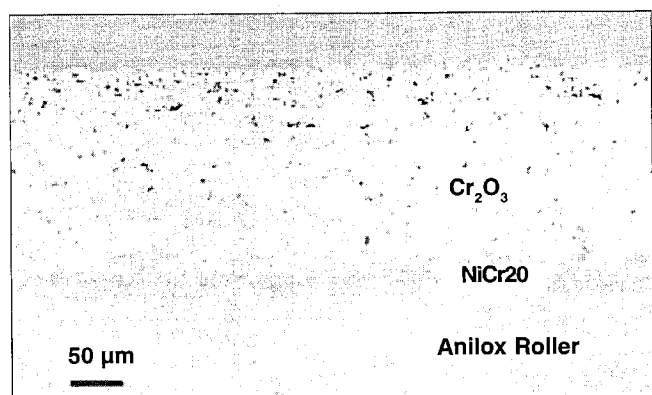


Fig. 3: PROTAL® application for the printing industry. Anilox roller with Cr_2O_3 ceramic coating and bond coat NiCr20.

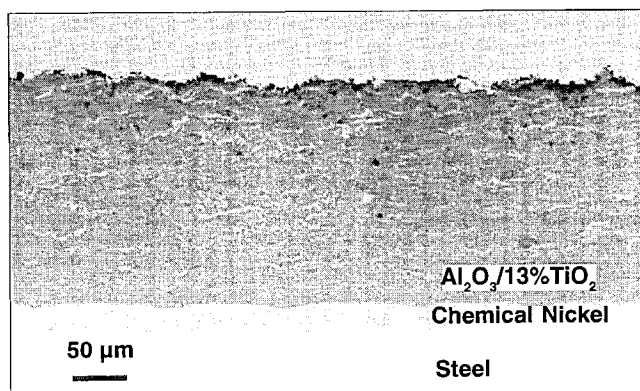


Fig. 4: Ceramic coating on chemical nickel deposit using the PROTAL® process.

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Application of In-Process Reaction to the Fabrication of $\text{MgAl}_2\text{O}_4/\text{Al-Si}$ Composite Coating by HVOF Spraying

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Abstract

It is known that thermodynamically unstable hard particles such as WC in composite spray materials are ready to decompose to W_2C and tungsten during the thermal spray process. Reactive thermal spraying based on in-process reactions has been recently focused on the fabrication of composite coatings containing nitrides or carbides as a reinforcement. In the present study, instead of DC and RF

plasma spraying, reactive HVOF spraying characterized by high flame velocity and low flame temperature was applied to the formation of *in situ* composite coatings. Granulated particles of $\text{SiO}_2/\text{Al-Mg}$ were sprayed onto an aluminum substrate to fabricate the composite coatings. Through the reduction of SiO_2 accompanied by an exothermic reaction, the composite coatings are expected to consist of MgAl_2O_4 and Al-Si alloy matrix. However, the sprayed coatings actually consist of MgAl_2O_4 , Al-Si and additional Mg_2Si . This is

because the formation rate of Mg_2Si is much faster compared with that of MgAl_2O_4 , although MgAl_2O_4 is more thermodynamically stable than Mg_2Si . The amount of formed MgAl_2O_4 decreases with an increase in the spraying distance, although it gives a longer in-flight period of droplets. Hence, the in-process reaction such as MgAl_2O_4 formation mainly occurs on a substrate.

1.0 Introduction

Thermal spraying, which is one of the major surface coating processes for anti-wear and anti-corrosion applications, is characterized by a wide selection of thermal sources, spray materials and substrates. Practical applications of composite coatings with WC/Co cermet powder as a spray material have been proven by thermal spraying. However, this powder is commonly expensive and tends to decompose due to thermodynamically unstable WC to W_2C and tungsten, so that the coating is degraded by lowering the hardness. Many researchers have noticed the effectiveness in reactive thermal spraying for the fabrication of composite coatings, in which stable compounds are formed by in-process reactions during the spraying. Plasma spraying, which utilizes the reactions of molten droplets with atmospheric gases^{1, 2} and the mutual reactions with constituents in spray materials,³ is a major reactive spraying method. However, there have been no studies concerning *in situ* composite coatings fabricated by HVOF spraying. This is because the flame velocity is extremely fast and its temperature is relatively low compared with plasma spraying. These features of HVOF spraying are definitely disadvantages in reactive thermal spraying.

According to previous works with respect to reactive DC plasma spraying, *in situ* reinforcements such as TiN ,¹ Ti_2AlN ,² and CrN ⁴ are formed during the spray process. The size and the volume fraction of each reinforcement, which affect the mechanical and adhesive properties of coatings, can be controlled through the process parameters. However, the operating plasma gas is limited to nitrogen as a reactant in conventional DC plasma spray systems, because of the optimum gap distance for the generation of the discharged arc. Besides nitrides, *in situ* composite coatings containing carbides are formed with CH_4 as a carrier gas,⁵ although carbide formation is limited. In reactive RF plasma spraying, many reactant gas species such as N_2 , O_2 , and CH_4 can be employed as a plasma gas. There have been some studies concerning RF plasma sprayed coatings with *in situ* nitride,^{6, 7} and carbide.⁸

It is worth noting that the *in situ* formation of reinforcements has been employed in liquid processing of metal matrix composites (MMC). For example, MMC

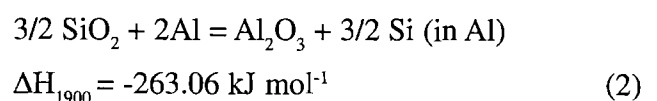
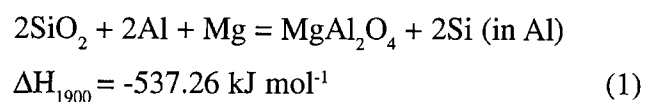
containing TiC precipitates as a reinforcement were formed by utilizing the reaction of titanium (Ti) powder with graphite in molten aluminum (Al).^{9, 10} They are fundamentally based on the formation of TiC from Ti and graphite. The same idea with an exothermic reaction has also been applied to a SiO_2/Al system, in which the formation of Al_2O_3 occurs by the reduction of SiO_2 particles or blocks immersed in molten Al.¹¹⁻¹³ It is known that the wettability between SiO_2 and molten Al plays an important role in the rapid reaction.¹³ Applying in-process reactions to the surface modification of Al substrates, we have also proposed a novel process using an electrical discharge machine.^{14, 15} A graded surface layer containing TiC precipitates is formed in a TiAl matrix by the reactions of a green-compacted Ti electrode with an Al substrate and decomposed carbon from a working fluid of kerosene.

In the present study, the formation of *in situ* composite coatings is performed by HVOF spraying which is characterized by a higher deposition rate than that of plasma spraying. Instead of the reaction of molten droplets with atmospheric gases, composite coatings containing a thermodynamically stable reinforcement of MgAl_2O_4 are formed by the reaction of SiO_2 and molten Al-Mg in a spray material. It can be noticed that this spraying is a typical example of high temperature droplets sprayed on an Al substrate with a low melting point. We also discuss the splat/substrate interfacial temperature which may be high enough to cause partial melting of the substrate surface.

2.0 Methods

2.1 Material Design

In HVOF spraying, in-flight droplet temperature is relatively low just before their impingement on a substrate. In-flight time, during which droplets can react with each constituent, is short due to the fast droplet velocity. Both the low temperature and short in-flight time of droplets are expected to restrict the required in-process reactions. In order to overcome these difficulties, we designed a composite spray material based on the following reactions in granulated particles of a $\text{SiO}_2/\text{Al-Mg}$ system:



where Al-2.5 wt.% Mg particles with an average diameter of 43 μm were used. In addition to the formation

of MgAl_2O_4 by Eqn. (1), Al_2O_3 also appears by Eqn. (2) after the consumption of Mg. Alloying of magnesium (Mg) with molten pure Al is known to lower the surface energy,¹⁶ which improves the wettability with ceramics such as Al_2O_3 . Inexpensive fine SiO_2 particulates with an average diameter of 50 nm were supplied as an oxygen source to form stable and high performance reinforcements of MgAl_2O_4 and/or Al_2O_3 . In order to obtain the eutectic composition (Al-12 wt.% Si) in an Al-Si system as a matrix of the composite through the in-process reactions, the premixing ratio of SiO_2 to Al-Mg was selected to be 0.246 by weight. Then, the adiabatic instantaneous reaction causes a temperature rise in the reacted particle of 593 K due to the exothermic reactions of Eqns. (1) and (2). According to the above consideration, granulated particles composed of SiO_2 and Al-2.5 wt.% Mg were prepared through a mixing, drying and sieving step with sodium silicate ($\text{SiO}_2 \text{ Na}_2\text{O}$) as a binder.

2.2 HVOF Spraying

Pure Al (A1050) sheets were the substrate with a thickness of 3 mm. The substrate was mirror-polished before spraying for the splat collection, while it was pretreated by shot-blasting for the coating formation. The splat collection and the coating formation were performed by lifting a substrate to the flame center using an air cylinder, and maintaining the substrate position for a certain time depending upon the purpose. The substrate was forcibly cooled from the back-side during the process by chilled air to prevent it from melting. The substrate temperature was continuously recorded by a thermocouple inserted at the substrate center. Although the spraying distance was usually fixed at 285 mm, to examine where the in-process reaction occurs, it was changed from 220 to 350 mm.

Prior to spraying, the in-process reactions were confirmed by differential thermal analysis (DTA) heated to 1273 K with a heating rate of 0.17 K s^{-1} in an Ar atmosphere. The constituents were identified by XRD with $\text{CoK}\alpha$ radiation after heating at a given temperature. It is important to discuss where the in-process reaction occurs, that is, during flight or on the substrate, to control coating microstructure by changing the spray parameters. The sprayed particles were collected to study the in-process reaction, and their cross-sections were examined by SEM and EPMA. With the same objectives, the splats were collected on a substrate, and analyzed for elemental distribution by EPMA and their constituents by XRD. The cross-section of coatings with different spraying distances was also examined through the same procedures.

3.0 Results and Discussions

3.1 In-Process Reaction of Granulated Particles During Flight

As a typical example, an elemental distribution for a granulated particle composed of fine SiO_2 particulates and an Al-Mg core particle with a $\text{SiO}_2\text{Na}_2\text{O}$ binder is shown in Figure 1. The $\text{SiK}\alpha$ image corresponds to fine SiO_2 particulates adhered on an Al-Mg particle. Although the adhesion of SiO_2 particulates is not so uniform, the existence of SiO_2 particulates is approved on all core Al-Mg particles. Furthermore, sodium (Na) in a binder is also weakly detected on the granulated particles.

At first, we must investigate whether the expected in-process reactions of Eqns. (1) and (2) occur or not on the granulated particles. DTA scans were carried out on the granulated $\text{SiO}_2/\text{Al-Mg}$ particles heated to 1273 K, as shown in Figure 2. The DTA scan is characterized by an endotherm of Al fusion and the exothermic reaction due to MgAl_2O_4 formation at about 1100 K, which is confirmed by the XRD pattern taken just after the reaction. However, the formation of Mg_2Si is not identified on the XRD pattern. After the formation of MgAl_2O_4 through the reduction of SiO_2 by molten Al-Mg alloy, there exist diffraction peaks of Al, MgAl_2O_4 , and silicon (Si), as expected from Eqn. (1).

The granulated particles were sprayed and collected at d_s of 1000 mm to elucidate whether they react with each constituent during flight. The Al-Mg core in granulated particles naturally melts by flame heating. The cross-section of sprayed particles was observed by SEM and EPMA, as shown in Figure 3. The intensity of $\text{SiK}\alpha$ is detected even inside the particle, that is to say, SiO_2 on a granulated particle surface reacts with molten Al-Mg alloy during flight. However, most of the adhered SiO_2 particulates are not only uniformly covered on the particles, but also exist like a lump on the surface in places. Hence, the progress of the expected in-process reaction is not so intensive during the flight, because of the relatively low droplet temperature and a short in-flight period in HVOF spraying.

3.2 Splat Formation on an Al Substrate

When granulated $\text{SiO}_2/\text{Al-Mg}$ particles are sprayed onto an Al substrate, circular splats are formed as shown in Figure 4. The existence of Si is localized on the splat as recognized in a $\text{SiK}\alpha$ image, however, that of Mg is widely distributed on the splat. Since the molten droplets are rapidly solidified after impingement and flattening on a substrate, the in-process reaction is not expected to proceed. However, XRD patterns on the splats exhibit

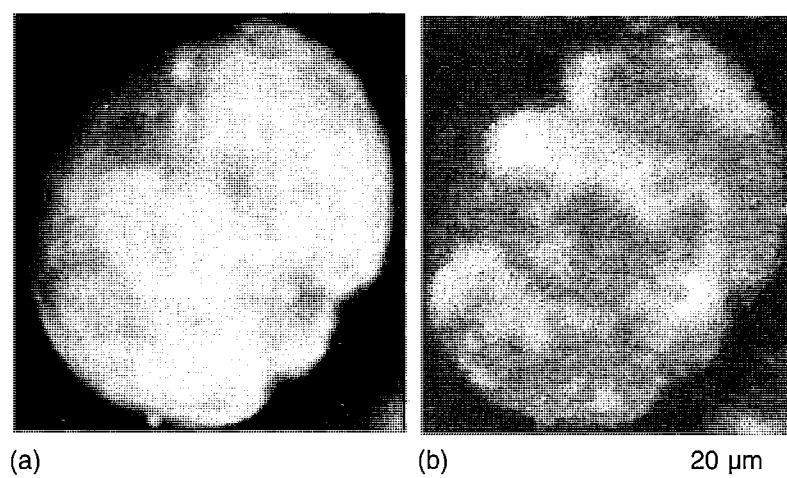


Fig. 1: Characteristic x-ray images of a granulated $\text{SiO}_2/\text{Al-Mg}$ particle (a) $\text{AlK}\alpha$ and (b) $\text{SiK}\alpha$ image.

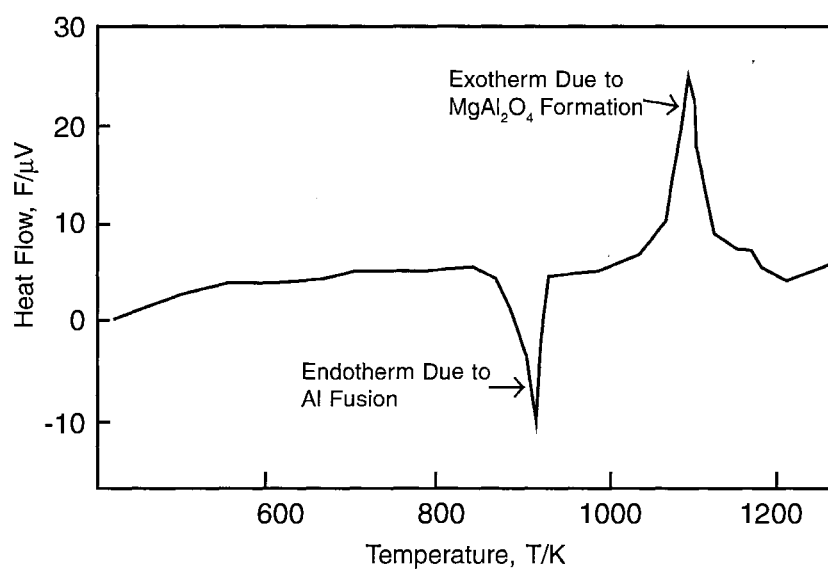


Fig. 2: DTA scan of granulated $\text{SiO}_2/\text{Al-Mg}$ particles heated to 1273 K with heating rate of 0.17 K s^{-1} in an Ar atmosphere.

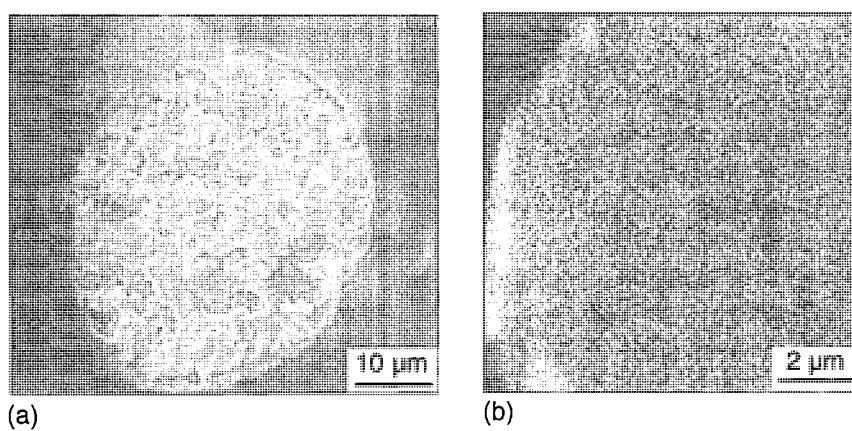


Fig. 3: (a) Scanning electron micrograph and (b) $\text{SiK}\alpha$ image of a sprayed $\text{SiO}_2/\text{Al-Mg}$ particle cross-section.

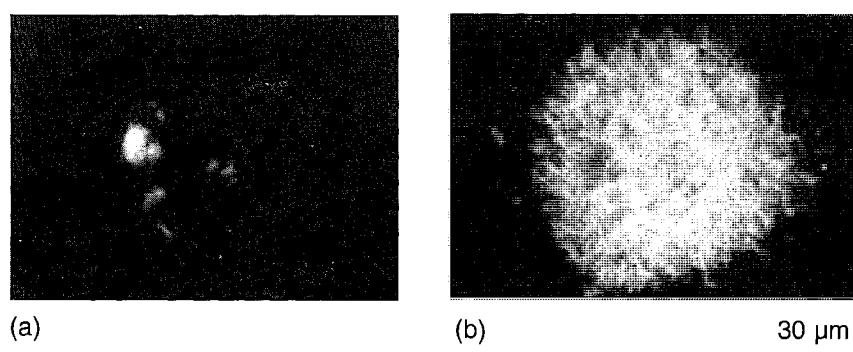


Fig. 4: Characteristic x-ray images showing an elemental distribution of a splat surface sprayed on an Al substrate (a) $\text{SiK}\alpha$ and (b) $\text{MgK}\alpha$ image.

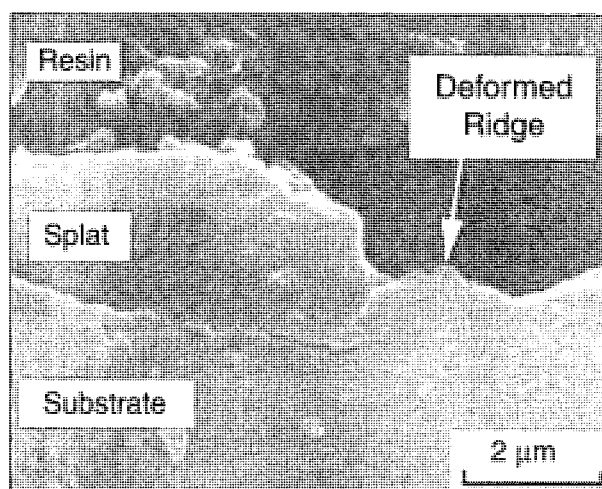


Fig. 5: Scanning electron micrograph showing a splat cross-section sprayed on an Al substrate. Note: A deformed substrate ridge appears at the outer periphery of the splat.

the formation of MgAl_2O_4 and Mg_2Si , though they are not so intense. This disagreement in the in-process reaction is mainly caused by a difference in the solidification rate.

The cross-section of splats was observed by SEM, as shown in Figure 5. The cross-sectional microstructure of a splat is distinguished from that of the substrate. There are no pores within a splat or at the splat/substrate interface. The sinking splat outer periphery in a substrate

is interesting. It is the feature of high temperature droplets impinging onto a substrate with a low melting point. The droplets with high in-flight velocity, which is achieved in HVOF spraying, may cause the deformation of a substrate surface through their heavy collisions. However, the plunge of splat periphery into a substrate mainly results from the slight surface melting of the substrate. We call this feature a deformed substrate ridge. An elemental distribution on the splat cross-section is

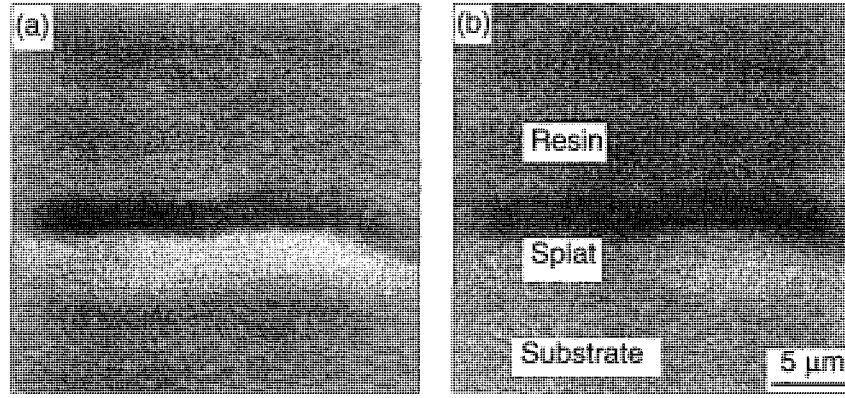


Fig. 6: Characteristic x-ray images of splat cross-section sprayed on an Al substrate (a) OK α and (b) MgK α image.

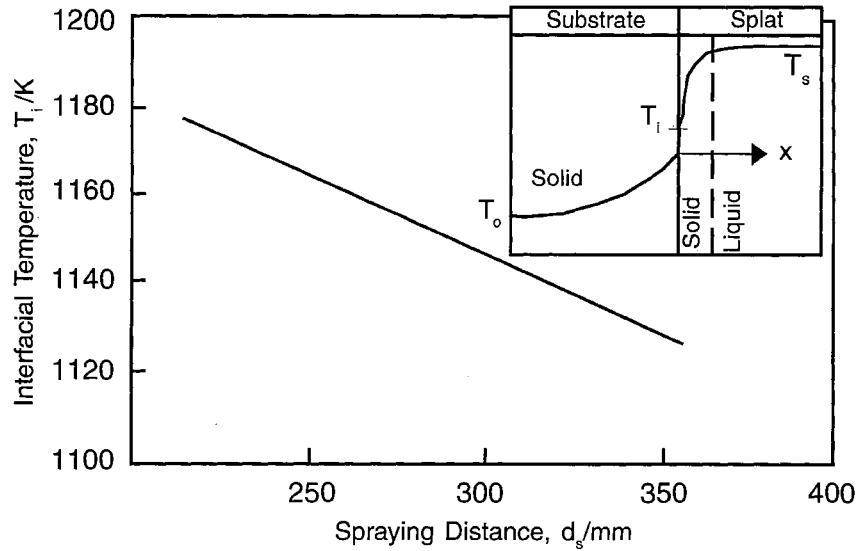


Fig. 7: Calculated interfacial temperature between a splat and a substrate as a function of spraying distance.

shown in Figure 6, in which an OK α image exhibits oxygen diffusion into the splats, the same as that of Mg.

Now, we estimate the interfacial temperature at a flat Al substrate surface impinged by a molten droplet. The general differential equation for heat conduction in the case of one-dimensional heat flow is:

$$\frac{\partial T}{\partial t} = (k/\rho C_p) \frac{\partial^2 T}{\partial x^2} \quad (3)$$

where k is the thermal conductivity, ρ the density and C_p the heat capacity. After some solidification has occurred in a splat, the temperature profile in the substrate and the splat is schematically drawn at the top

of Figure 7, in which we assume the condition of no thermal contact resistance at the splat/substrate interface. The substrate is initially at room temperature (T_o) and the molten splat is superheated by ΔT above the melting point depending on the spraying distance. The heat flux into the splat/substrate interface from the molten splat must equal the flux away from the interface into the substrate. The substrate is semi-infinite in the negative x -domain with the interfacial temperature (T_i), which is determined by the thermal properties of both the splat and the substrate as listed in Table 1. For the calculation, we made two additional assumptions. First the effective

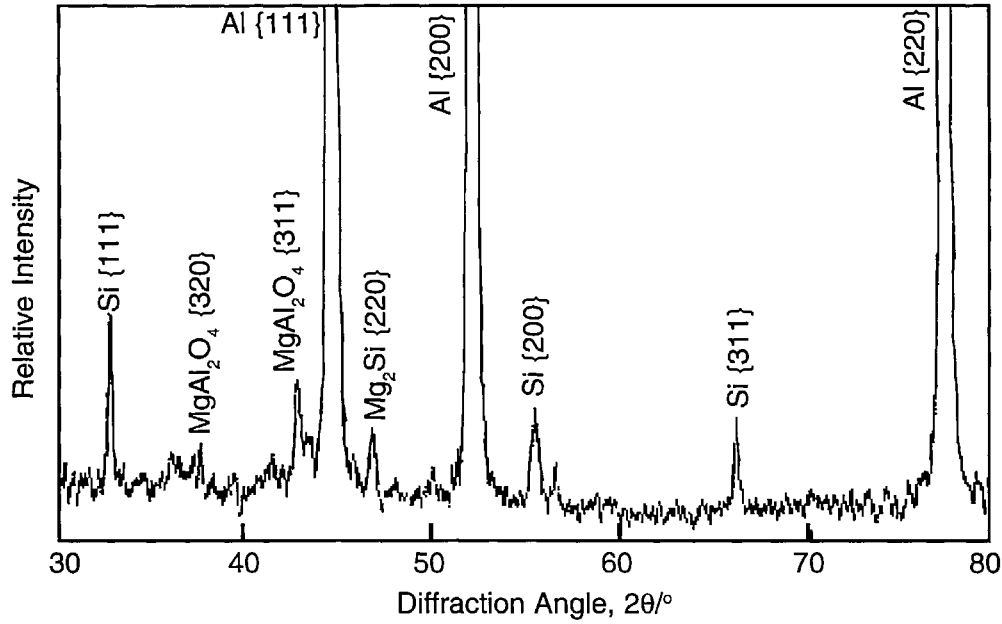


Fig. 8: X-ray diffraction pattern of coating surface sprayed with granulated $\text{SiO}_2/\text{Al-Mg}$ particles (spraying distance = 285 mm).

Table 1. Thermal Properties of Splat and Substrate

Items	Splat	Substrate
Thermal Conductivity ($\text{J m}^{-1} \text{K}^{-1} \text{s}^{-1}$)	$k' = 55.9^*$	$k = 238$
Density (kg m^{-3})	$\rho' = 2469^*$	$\rho = 2700$
Heat Capacity ($\text{J K}^{-1} \text{mol}^{-1}$)	$C_p' = 50.6^*$	$C_p = 34.0$
Heat of Fusion (J mol^{-1})	$H_f = 10470$	-
Melting Point (K)	$T_m' = 850$	$T_m = 933$

* k' , ρ' , and C_p' are the values at 2000 K based on the rule of mixtures.

heat of fusion (H_f') is the sum of the latent heat of fusion (H_f) and the superheat in the liquid phase, that is,

$$H_f' = H_f + C_{p(\text{Al-Si})\text{liq}} \Delta T \quad (4)$$

Secondly the in-flight droplet temperature (T_s) just before impingement is expressed by Eqn. (5), which is the approximation based on the experimental data by Legoux et al.¹⁷

$$T_s = -0.8 d_s + 2373 \text{ (K)} \quad (5)$$

where d_s is the spraying distance in mm. The temperature distribution within the semi-infinite substrate is given by Eqn. (6).¹⁸

$$(T - T_i)/(T_s - T_i) = \text{erf} [-x/\{2(kt/\rho C_p)^{1/2}\}] \quad (6)$$

According to Geiger and Poirier's method,¹⁸ T_i is calculated as shown in Figure 7 as a function of d_s . The estimated T_i linearly decreases with d_s . The estimated T_i

within the range of examined d_s is much higher than the melting point of the substrate (850 K) at each d_s . Since the above calculation does not involve substrate melting, that is, a temperature drop due to the latent heat of Al fusion, all of the actual interfacial temperatures become lower compared with the calculated values. Hence, this particular spraying is characterized by slight surface melting due to the impingement of high melting point droplets.

3.3 In-Process Reaction During Splat Layering

With the $\text{SiO}_2/\text{Al-Mg}$ granulated particles, the composite coatings were fabricated by HVOF spraying at a spraying distance (d_s) of 285 mm. A typical XRD pattern on the coating surface is shown in Figure 8, in

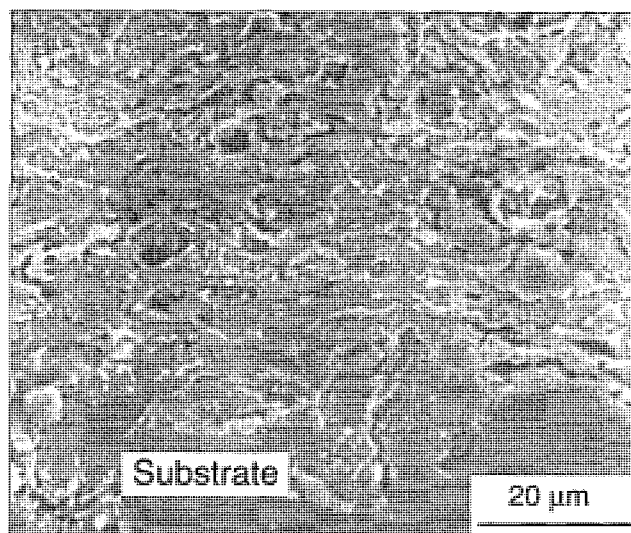


Fig. 9: Scanning electron micrograph showing a cross-section microstructure of coating sprayed on an Al substrate (spraying distance = 285 mm).

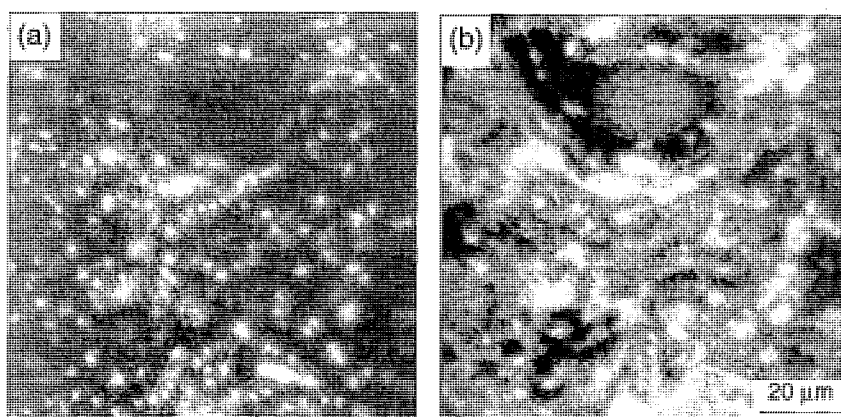


Fig. 10: Characteristic x-ray images of coating cross-section sprayed on an Al substrate (spraying distance = 285 mm) (a) SiK α and (b) MgK α image.

which the coating is composed of MgAl_2O_4 , Mg_2Si , and Al-Si. Hence, *in situ* composite coatings can be fabricated by HVOF spraying accompanied by the in-process reaction of SiO_2 reduction.

Coating microstructure was observed on the cross-section after etching with 5 wt.% NaOH aqueous solution, as shown in Figure 9. The picture exhibits a wavy layered microstructure and a complex splat/substrate interface, which gives good adhesive strength.

An elemental distribution was also examined on the coating cross-section, as shown in Figure 10. The distribution of Si becomes rather discrete in a matrix compared with that of Mg. However, a few splats exhibit weak intensity of SiK α and MgK α , implying that the in-process reaction does not occur in all the splats.

In order to discuss whether the in-process reaction proceeds during flight or on a substrate, the coatings were fabricated with different d_s . According to the

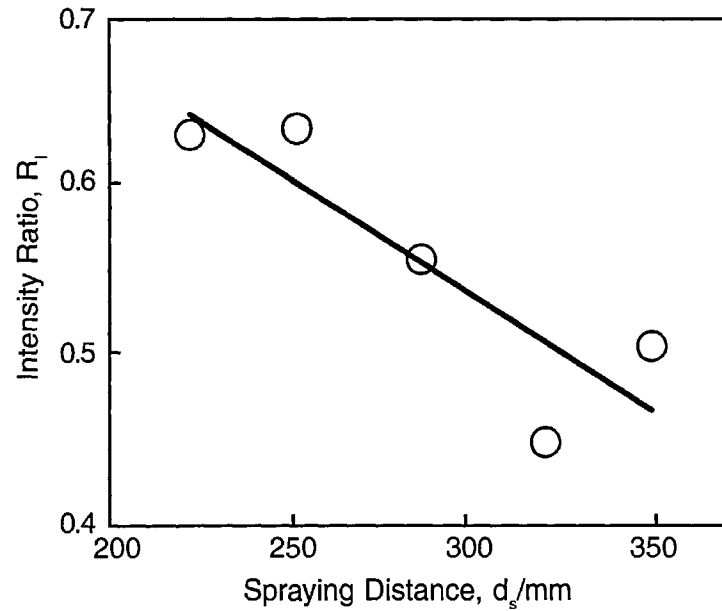


Fig. 11: Diffraction intensity ratio of MgAl_2O_4 {311} to the sum of MgAl_2O_4 {311} and Mg_2Si {220} on coating surfaces as a function of spraying distance.

corresponding XRD patterns, the intensity ratio (R_I) of MgAl_2O_4 expressed by Eqn. (7) was calculated.

$$R_I = I_{\text{MgAl}_2\text{O}_4\{311\}} / [I_{\text{MgAl}_2\text{O}_4\{311\}} + I_{\text{Mg}_2\text{Si}\{220\}}] \quad (7)$$

The intensity ratio of R_I is shown in Figure 11 as a function of d_s , in which the R_I decreases linearly with an increase in d_s . Semi-stable Mg_2Si formed more at longer d_s , which provides a longer reaction time for the droplets. Consequently, the in-process reaction mainly proceeds on the substrate due to the flame heating in this composite system.

4.0 Conclusion

With granulated $\text{SiO}_2/\text{Al-Mg}$ particles, the formation of composite coatings was performed by HVOF spraying which is characterized by high in-flight velocity and low droplet temperature. The following results were obtained.

1. Composite coatings composed of MgAl_2O_4 , Mg_2Si in an Al-Si matrix are fabricated by reactive HVOF spraying, in which the in-process reaction based on SiO_2 reduction by molten Al-Mg is expected to increase the droplet and/or splat temperature.
2. The exothermic in-process reaction mainly proceeds during splat deposition on a substrate rather than during flight.

3. The impingement of high temperature droplets on a low melting point substrate causes deformed substrate ridges immediately adjacent to an outer splat periphery due to the slight surface melting of substrate.

5.0 Acknowledgments

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Wear Resistant Coatings

Finite Element Modeling of Coating Architectures for Aluminum Die Casting

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Abstract

This paper will focus on the use of finite element modeling (FEM) in the development of a multilayer or graded coating “architecture” engineered to extend die life for the aluminum pressure die casting industry. The complexity of failures seen in the die casting industry, i.e. heat checking, erosive wear, soldering, and corrosion/oxidation, dictates the need for a multilayer system. The non-linear thermal-

mechanical FEM employed is a two-step procedure starting with a global analysis of the entire die to determine strain fields of critical areas that are then applied to a localized model in which the coating is optimized. FEM provides a predictive capability for the optimization of the coating architecture while reducing the “trial and error” approach of physical experiments. FEM is being used to determine the architecture of the intermediate layers, or compositionally graded layers, that will help minimize the residual and thermal stresses resulting from the die casting process.

1.0 Introduction

1.1 Overall Methodology for the Development of a Surface Engineered Coating

Finite element modeling (FEM) is being used as an integral part of an overall research program focused on engineering a coating system for use in the aluminum pressure die casting industry.¹ Due to the complexity of the failures, it is unlikely that a monolithic coating or thin film would provide the optimum system for any specific die casting application. For this reason a specially engineered multi-layered or graded “architecture” will be considered. Each layer of the “architecture” will provide a specific function, e.g., adhesion to the substrate, accommodation of thermal and residual stresses, wear and corrosion/oxidation resistance and non-wettability with the molten metal. The coating architecture refers to the nature, form, thickness and compositional gradient of each layer that composes the total coating system. This initial research program will concentrate on developing a coating system for dies used in die-casting aluminum alloys. The success of the multi-layered coating system depends on the synergy of the properties and functions of each layer. The outer layer of the coating architecture, along with being corrosion/oxidation and wear resistant, must be non-wettable with molten aluminum. Wettability tests such as sessile drop and dunk tests will provide three or four films that are non-sticking with aluminum. These coatings can then be used in the finite element modeling (FEM) of the coating system. FEM provides a predictive capability for the optimization of the coating architecture. Systematic finite element modeling will predict the optimal coating architecture that results in a minimum level of contact stresses and thermally induced stresses.²⁻⁴ FEM allows a reduction in the number of coating systems tested experimentally. In order to develop a fundamental understanding of the die casting process, the modeling will initially concentrate on axisymmetric die geometries for the sake of simplicity. Along with the material properties of the coatings, the temperature and pressure profiles that adequately represent a die casting process are key to using FEM as a tool to predict the stresses involved. The finite element analysis consists of a two-step nonlinear thermal-mechanical procedure, which includes a global analysis of the entire die to assess critical strain fields that are then applied to a local model in which the coating system is optimized. Ultimately the coating architectures will be deposited using various physical vapor deposition (PVD) processes and then tested in the laboratory and in the field.

1.2 Methodology of Two-Step Global-Local Finite Element Procedure

Finite element modeling (FEM) is being used as a predictive tool to reduce the number of trial and error experiments in the development of a non-sticking, wear resistant, and corrosion/oxidation resistant coating for dies used in aluminum pressure die casting. Ultimately the goal is to investigate possible mechanisms that result in thermal fatigue and to reduce the onset of any failure modes in the coating. This assumes that fatigue in the steel cannot be completely prevented, but die life may be extended by applying a fatigue resistant coating system. The non-linear thermal-mechanical finite element analysis being employed incorporates temperature dependent nonlinear material behavior to determine the optimal geometry, and compositional gradients of a multi-layered coating system architecture. Minimal thermal stress criteria during mechanical and thermal loading cycles will be used to determine the coating system architecture and composition.

A major consideration in the design of the multi-layered coating architecture is the overall thermal and mechanical response of the die. Of particular importance is the transient total strain field created at the surface of the die cavity during a simulated shot cycle or a repeated number of shot cycles. The non-linear FEM therefore consists of a two-step procedure (Figure 1).

Step 1- Global Model: A transient thermal-mechanical analysis of the die and aluminum casting is performed over a number of shot cycles. The thermal loading consists of a specific time-dependent temperature profile applied to the interior of the die cavity. This simplifying assumption eliminates the need for modeling the solidification of the aluminum and the detailed heat transfer from the aluminum into the die with a finite element discretization. In this model we ignore the effects that the die coating system has on the overall thermal and mechanical response of the die. This assumption is justified since the thickness dimension of the coating is very small (usually on the order of microns) compared with the overall die dimensions (usually on the order of centimeters or meters).³ The boundary conditions include convective heat transfer on the external surfaces of the die exposed to the air and specified time dependent temperatures on the inner walls of the die in contact with the casting part to simulate the thermal loading during a shot cycle. Note, a more detailed analysis may be performed by explicitly modeling the molten cast metal with additional finite elements. This detailed analysis would include additional elements to model the injection and solidification of the aluminum part (neglecting the fluid flow of the

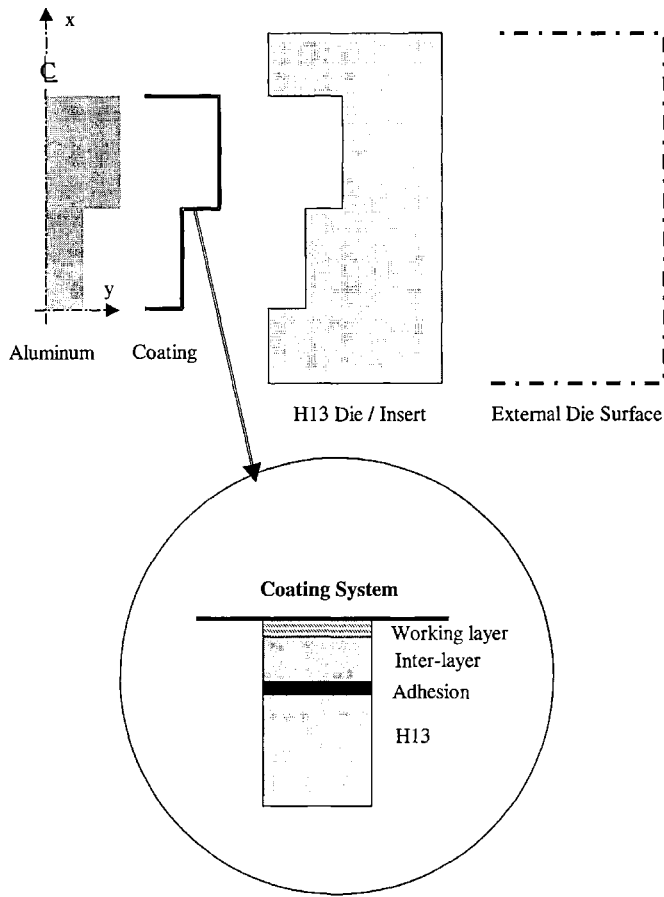


Fig. 1: Finite element analysis methodology includes a two-step procedure in which the entire die is modeled in a global analysis. Then critical strain fields are applied to a local analysis to optimize the coating architecture. Note, the die geometry in this finite element model is assumed to be axisymmetric.

aluminum), and the part ejection and lube phase during the shot cycle.

Step 2- Local Model: A number of transient thermal-mechanical “local” analyses for a specified number of critical points on the surface of the die cavity are performed over a number of shot cycles. These critical points are at surface locations where strains are significantly different from the free thermal expansion of the die material. These analyses are essentially one-dimensional, since the stresses in the different layers are uniform within each layer unless it is a functionally graded material (FGM). Because the dimensions of the analyses are on the order of microns, the applied strain boundary conditions and temperature loads are spatially uniform and time dependent. The local analysis of the die coating is used to analyze the stresses generated in the coating system during a simulated process cycle.

2.0 Methods

Ultimately the performance and reliability of the coating architecture must be verified by field and service testing, but a two-step finite element analysis is being developed to simulate processing conditions in an effort to reduce the number of possible experimental coating systems investigated. It is well known that the residual stress due to the deposition process present in a coating, is an important consideration since the stress often controls the mechanical properties, microstructural stability, and film-substrate adhesion of thin films. It is frequently thought to be the cause of malfunction or failure of technologically important coating systems.² The two-step global-to-local FEM procedure has been used to analyze the residual stresses generated in the coating system during a simulated aluminum pressure die-casting. Initial results of the parametric analysis are being used to describe the methodology and ultimately will be used to predict an optimal coating architecture with minimized residual stresses and an optimal stress distribution. The commercial software MARC 2000 by MSC Software Corporation was used in this finite element analysis.

3.0 Results and Discussion

3.1 Global Analysis

The global analysis of a casting die was performed, using a coupled non-linear thermal-mechanical FEM. If the coated system is only subjected to free thermal expansion, the total strain of the substrate, $\epsilon_{\text{Total, substrate}}$, is

$$\epsilon_{\text{Total, substrate}} = \alpha_{\text{substrate}} (T - T_0) \quad (1)$$

where $\alpha_{\text{substrate}}$ is the coefficient of thermal expansion (CTE) of the die bulk (substrate) material, T is the current temperature of the die, and T_0 is the datum stress-free temperature of the die. In multilayered thin films on thick substrates, the strain calculated from equation (1) is the strain in the substrate and in all the layers of the coating system, so long as the thin film approximation holds true, i.e. the total film thickness is much less than the substrate thickness.³ In this work, the order of the layers has no significance on the thermal strain provided they are subject to the same thermal profile. Because the coating system is much smaller than the massive die the strain is based on the CTE of the substrate only. Now with the global analysis, an investigation of restrained thermal expansion due to factors such as die geometry can be explored. The coating system is ignored during the global analysis because the coating has a negligible

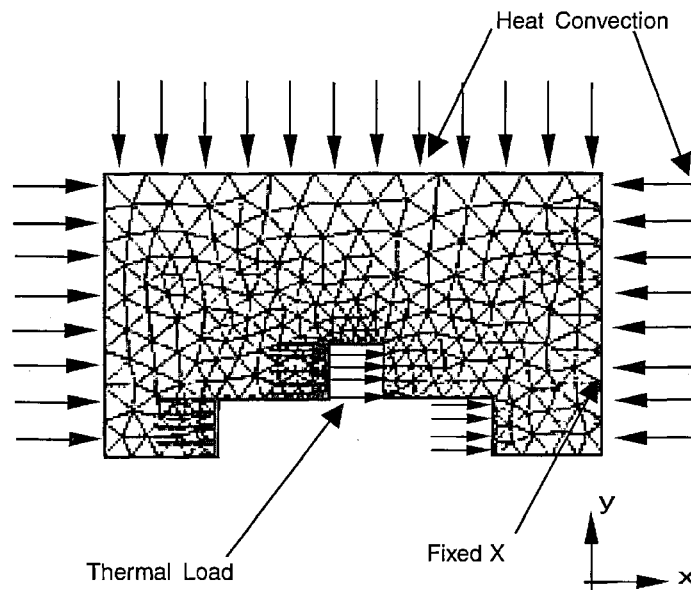


Fig. 2: Global mesh with applied boundary conditions of fixed x-direction, time-dependent cyclic thermal profile along the interior of the die cavity, and heat convection along the exterior of the die. Note that the model is rotated 90° counterclockwise since the axisymmetric axis is on the x-axis.

effect on the overall thermal-mechanical response of the die.

A hypothetical axisymmetric model of a die (Figure 2) allows the study of planar surfaces, sharp corners, and concave/convex rounded corners. As seen in Figure 2, 3-node triangular solid elements were used in the mesh. Also the boundary conditions are outlined in Figure 2, namely the die is fixed in the x-direction at the base (essentially on rollers), a time-dependent thermal profile is applied to the interior of the die cavity and a heat convection boundary condition was applied to the die exterior to represent dissipation of heat into the air. The mesh was refined along the interior of the cavity to get a better picture of the thermal gradients and material behavior in this area. In this work the strain developed by applying a cyclic thermal profile along the interior of the die cavity is then applied to a localized model. The thermal profile in the casting process consists of four main process conditions:

1. Injection of the molten aluminum,
2. Solidification,
3. Ejection of the solidified aluminum, and
4. Lube of the die cavity.

The stresses and strains developed during the thermal cycles must be analyzed at high temperatures and low temperatures since the coating must be optimized for both conditions. In these initial results a strain profile was taken from a planar surface close to a corner and then applied to the local model (Figure 3).

3.2 Local Analysis

The total strain determined from the global analysis was used as part of one of the boundary conditions for the local analysis. A fixed thermal displacement was the product of the total strain found with the global model and the width of the local model. The temperature field used in the global model was also used in the local model but applied to all the nodes (Figure 4). At this point the deposition stress has not been applied to the local model and the pressure in the die cavity has been assumed to be negligible.

The local model is dependent on several material properties including CTE, Young's modulus, Poisson's ratio, yield stress, and strain hardening. The local model has been run for several coating systems (Table 1), but ultimately the modeling will be used in conjunction with wettability data used to determine a non-wetting outer layer. As can be seen with these preliminary results, both high temperature conditions and low temperature conditions will have to be considered to fully optimize a coating system for a specific application (Figure 5).

These initial results show the importance of optimizing the coating at high temperatures and low temperatures. At high temperatures, the Cr_3C_2 , TiN, and TiBCN/NiAl systems are in compression and the CrN, TiAlN, and Al_2O_3 systems are in tension but at low temperatures all the systems show tensile residual stresses. The TiBCN/NiAl coating has been developed

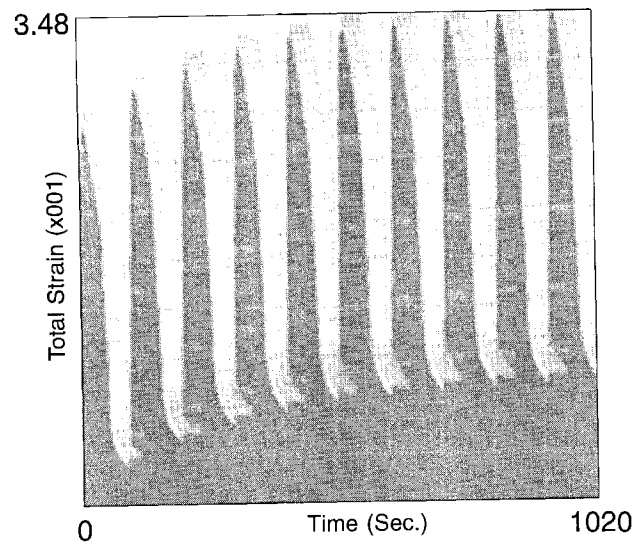


Fig. 3: Time-dependent total strain calculated by global FEM used to obtain initial results of residual stresses of various coatings with a localized model.

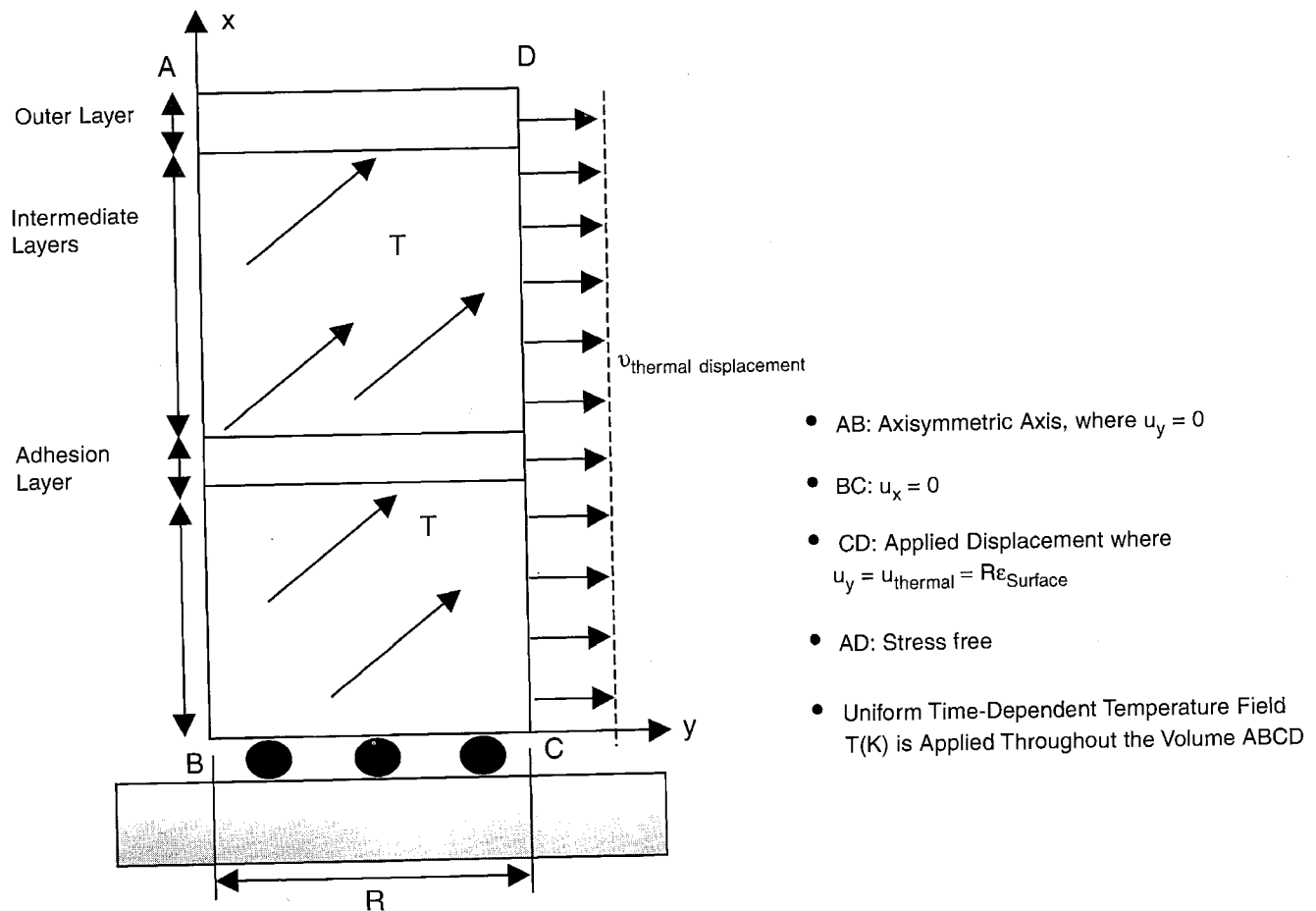


Fig. 4: Schematic of boundary conditions applied to local mesh including a fixed thermal displacement, time-dependent temperature profile, and rollers.

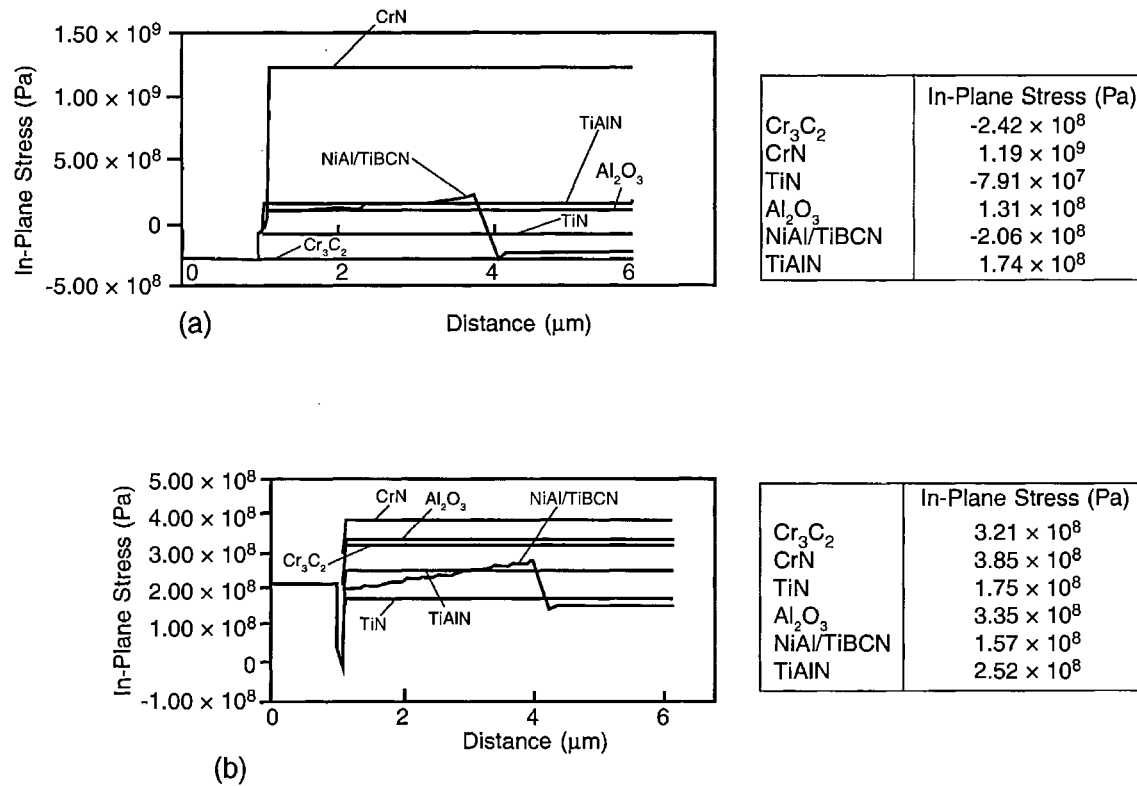


Fig. 5: In-plane residual stresses measured in the steady state with the local model at (a) high temperature and (b) low temperature with the global strain applied.

Table 1. Material Systems Used for Local Model

Bulk Die Material	Adhesion Layer	Outer Layer
AISI Type H13	Cr	CrN
AISI Type H13	Ti	TiN
AISI Type H13	Al	Al ₂ O ₃
AISI Type H13	Cr	Cr ₃ C ₂
AISI Type H13	Ti	TiBCN/NiAl
AISI Type H13	Ti	TiAlN

for the glass molding industry and is an example of grading a layer to accommodate the thermal stresses due to the CTE mismatch and the use of multiple layers to obtain optimal mechanical properties.³ It should be stated that the results are based on material properties from the literature and will be revised as actual material properties are experimentally measured.

4.0 Conclusions

This paper describes a two-step finite element analysis which includes a “global” nonlinear thermal-

mechanical analysis of an overall die to determine strain fields on the surface of the die cavity that are then applied to a “local” model used to determine the thermal stresses in the coating. The global model is necessary since the stress/strain state in a coating architecture is dependent on the position in the die cavity where the coating is analyzed. Preliminary results from the local model show how it will be used to determine an optimized coating structure with a gradual stress transition from the substrate (bulk H13 steel die material) to the outer layer. Finally, the results of these analyses will be combined with wettability data to engineer a multilayer or/and

graded coating system. With the addition of accurate experimentally determined failure criteria and thermal fatigue data for the die and coating materials, it is anticipated that this two-step FEM can predict the reliability and performance of a coating system and assist in the investigation of potential mechanisms for thermal fatigue.

5.0 Acknowledgments

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Synthesis of Superlow Friction Carbon Films from Hydrogen Rich Acetylene Plasmas

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Abstract

In this paper, we introduce a class of new diamondlike carbon films that can provide superlow friction and wear properties to sliding surfaces in dry nitrogen. The films were produced in a plasma-enhanced chemical-vapor deposition system on AISI M50 and H13 steel substrates by using hydrogen-rich acetylene (C_2H_2) plasmas at room temperature. The friction and wear testing of the films was performed in a pin-on-disk machine under a 10-N load at a velocity of 0.5 m/s.

Test results revealed a very close correlation between friction and wear coefficients and the hydrogen content of the gas discharge plasma from which the DLC films were derived. Specifically, the films derived from plasmas with higher hydrogen exhibited increasingly lower friction and wear coefficients than films grown in pure C_2H_2 . The lowest friction coefficient (0.003) was achieved with a film derived from a gas mixture of 90 vol.% H_2 + 10 vol.% C_2H_2 , whereas the friction coefficient of films derived from pure C_2H_2 was 0.35. Similar correlations were observed for wear rates. Specifically,

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films derived from C_2H_2 were worn out rather quickly and the substrate steel was exposed, whereas films of highly hydrogenated plasmas remained intact and wore at rates 2–3 orders of magnitude lower than those of films obtained from pure C_2H_2 . Based on surface studies and tribological test results, a mechanistic model is presented to elucidate the superlow friction coefficients of films grown in highly hydrogenated plasmas.

1.0 Introduction

In recent years, interest in diamondlike carbon (DLC) films has increased tremendously, mainly because, many attractive properties offered by these films can meet the very stringent and increasingly multifunctional application needs of advanced mechanical devices such as gears, bearings, biomedical implants, mechanical seals, computer hard disks, metal-and/or plastic-forming dies, etc.^{1–5} These films are structurally amorphous and can be deposited on a variety of substrates at room temperature. There are several physical and/or chemical-vapor deposition processes such as ion-beam deposition, DC and RF magnetron sputtering, arc physical-vapor deposition, plasma-enhanced chemical vapor deposition (PECVD), and laser ablation that can produce high-quality DLC films on a variety of substrates.^{6–13} In most of these processes, DLC is derived from a hydrocarbon source gas (e.g., methane, acetylene, ethylene, etc.), but it can also be derived from solid carbon materials such as graphite, glassy carbon, fullerenes, etc. The films derived from hydrocarbons contain hydrogen in their microstructures, and are often referred to as hydrogenated DLC films. In recent years, researchers have developed ways to incorporate several elemental species (e.g., nitrogen, fluorine, boron, silicon, tungsten, titanium, niobium) into DLC films to obtain better optical, electronic, or tribological properties.^{14, 15}

Most DLC films are mechanically hard and rigid and hence are able to provide high wear resistance to sliding contact interfaces. Because of their high chemical inertness, they can also provide low friction and resist chemical or corrosive attack in aggressive environments. Previous studies have shown that the extent of reduction in friction and wear is greatly influenced by several factors. It was found that hydrogen content of the DLC film as well as the ratio of sp^2 to sp^3 bonds can have significant effects on friction and wear. Test environment and ambient temperature were also found to influence friction and wear behavior of these films. With respect to hydrogen content, researchers have shown that hydrogen-free DLC films performed better in moist air than dry air or inert gases, whereas hydrogenated DLCs exhibit superior friction and wear properties in dry and inert test environments.^{16–20} Several other factors (e.g.,

counterface material, film thickness, substrate hardness and stiffness, etc.) were also found to influence the friction and wear performance of most DLC films.^{19, 21–23} Elevated temperatures were found to have a detrimental effect on the friction and wear behavior of DLC films.²⁴ In particular, hydrogenated DLC films undergo phase transformation at elevated temperatures and became graphitized. The doping of DLC films with certain elements (such as silicon, titanium, tungsten, boron) may retard graphitization and hence enhance the durability of DLC films at elevated temperatures.

Recent systematic studies in our research laboratory have led to the development of a new class of DLC films that afford superlow friction and wear properties to sliding ceramic and steel substrates.^{25, 26} These films were produced in a PECVD system that used methane as the source gas. The lowest friction coefficient, 0.001 was measured on a film deposited on a sapphire substrate.²⁶ In this paper, we report on the friction and wear performance of new films derived from pure acetylene (C_2H_2) and $C_2H_2 + H_2$ plasmas. Specifically, we demonstrate that films with superlow friction and wear properties can also be obtained from highly hydrogenated C_2H_2 plasmas. The major emphasis in this paper is placed on the elucidation of the friction and wear mechanisms of the DLC films grown in highly hydrogenated C_2H_2 plasmas.

2.0 Experimental Procedures

In this study, we used a PECVD method to produce the DLC films on highly polished surfaces of AISI M50 balls and H13 steel substrates. The surface finish of these steel samples was better than 0.02 μm , RMS. The films were 1–1.5 μm thick and were derived from pure C_2H_2 and $C_2H_2 +$ an increasing amounts of hydrogen (up to 90 vol.%). C_2H_2 is an excellent source gas for the deposition of pure and metal containing DLC films at very high rates. The procedure for forming DLC films on steel substrates by PECVD involved sputter-cleaning of the substrates in an argon plasma for 30 min by applying a 1200–1700 V bias. The substrates were then coated with a 50–70 nm thick silicon bond layer by switching to a sputtering mode and sputtering silicon from a target. In some cases, silane (SiH_4) gas was also used to form the bond layer on the steel substrates. Finally, C_2H_2 or $C_2H_2 + H_2$ gases were introduced into the chamber and the deposition of DLC on the substrates was started. The gas pressure ranged from 10 to 13 mtorr and the RF bias was maintained between 400 and 600 V. The deposition rates in highly-hydrogenated plasmas (e.g., 10% $C_2H_2 + 90\%$ $C_2H_2 + H_2$) was very low, i.e., 0.3 $\mu m/h$, while in a C_2H_2 plasma, the rate was more

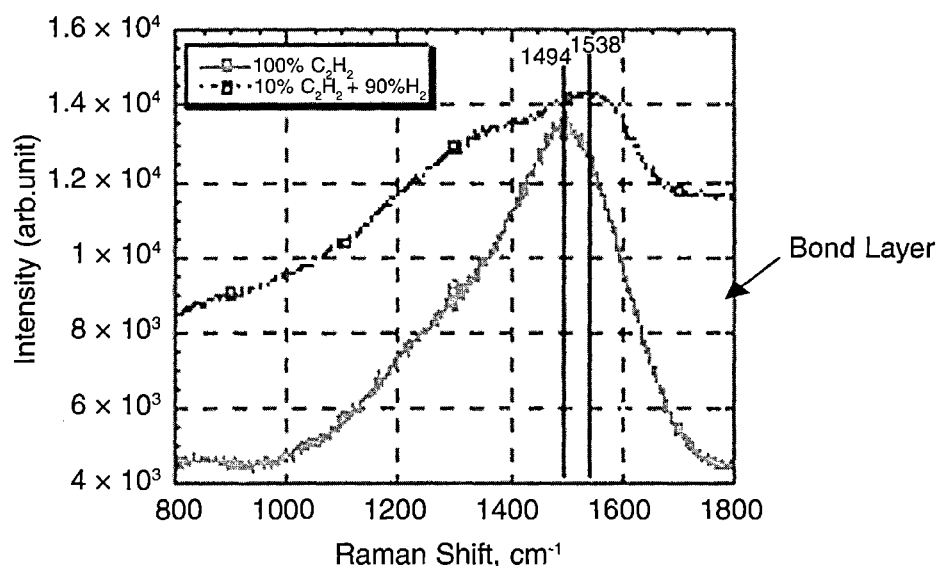


Fig. 1: Raman spectra of DLC films derived from pure C_2H_2 and 10% C_2H_2 + 90% H_2 .

than 3 $\mu\text{m}/\text{h}$. Further details of the deposition process can be found in Refs. 25-27.

The uncoated and DLC-coated samples were tested for friction and wear using a ball-on-disk tribometer in a dry nitrogen environment at room temperature. The contact load was 10 N (which created a peak Hertz pressure of ≈ 1 GPa between a 9.55 mm diameter M50 steel ball and steel disk). The sliding distance and velocity were 5 km and 0.5 m/s, respectively. To measure the friction coefficient of the DLC coating against itself, not against steel, AISI M50 steel balls used in the ball-on-disk experiments were also coated with DLC. The Vickers hardness of the substrates and balls was 8 GPa and their surface roughness was better than 0.05 μm RMS. Each coating was tested twice in dry nitrogen (0% humidity). The test chamber was purged with dry nitrogen for at least 2 hrs. after 0% humidity was attained on a hygrometer display unit. Wear volume (W_b) of the steel balls was determined with an optical microscope. Specifically, wear scar diameter and the diameter of the ball were used in the equation $W_b = 3.14d^4/64r$, where r is the ball radius, d is the diameter of the wear scar, and W_b is the wear volume. To simplify the calculations, we assumed that the wear scar was flat. Raman spectra of the films were measured with a Renishaw Raman microscope that uses a HeNe laser at 632.8 nm, with an output power of 25 mW. The focused spot size for the laser beam was 2 μm .

3.0 Results

The Raman spectra of the DLC films derived from pure C_2H_2 and $C_2H_2 + H_2$ source gases exhibited broad

peaks at ~ 1494 – 1538 cm^{-1} and shouldered peaks at 1320 – 1332 cm^{-1} . Figure 1 shows the Raman spectrum of a film derived from 100% C_2H_2 and that of a film derived from 10% C_2H_2 + 90% H_2 . The shouldered peaks were somewhat less pronounced on films derived from pure C_2H_2 than films derived from increasingly hydrogenated C_2H_2 plasmas. Overall, the DLC films tested in this study displayed Raman features typical of amorphous DLC films and were consistent with the Raman spectra presented elsewhere.^{28, 29} Figure 2 shows a scanning electron microscopy (SEM) cross-sectional photomicrograph of a film derived from a plasma containing 90% H_2 and 10% C_2H_2 . The film seems to have a featureless microstructure with no evidence of a columnar morphology, which is very typical of most PVD hard coatings.

Figure 3 summarizes the friction and wear performance of DLC films derived from various source gases. The friction and wear values in these graphs represent the average of two to three repeat tests. The friction coefficient decreases with increasing hydrogen in the plasma. In general, the higher the hydrogen, the lower the friction coefficient. Figure 4 shows the actual frictional traces of films derived from pure C_2H_2 and 90% H_2 + 10% C_2H_2 plasmas. As is clear, the friction coefficient of the films grown in pure C_2H_2 is the highest (fluctuating between 0.3 and 0.4). Furthermore, the frictional trace of this film is somewhat unsteady. After the sliding tests, we noticed that the film was totally worn out on the ball side of the sliding pair and that the steel substrate was clearly visible. In contrast, the DLC film grown in a gas discharge plasma that consisted of 10% C_2H_2 + 90% H_2 (see Figure 4) exhibited a smooth

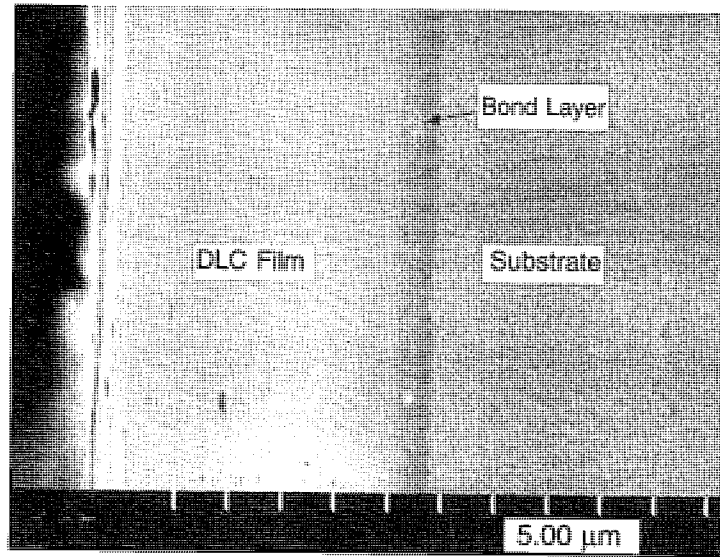


Fig. 2: Cross-sectional SEM photomicrograph of DLC film grown in 90% H_2 + 10% C_2H_2 .

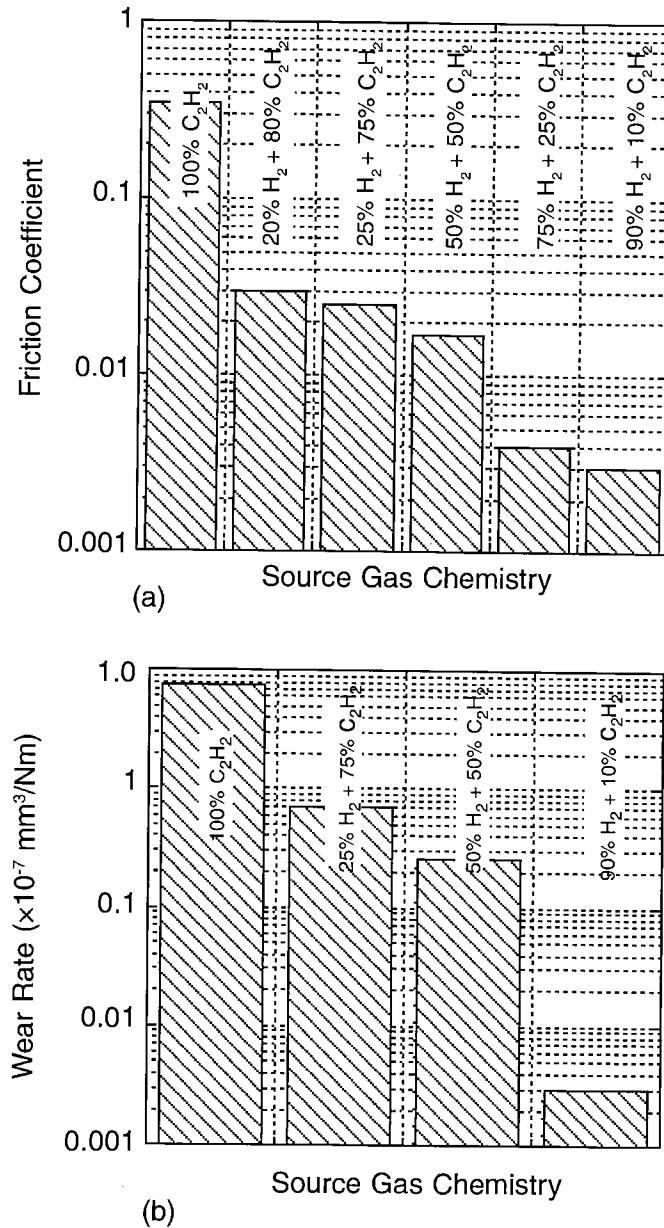


Fig. 3: (a) Friction and (b) wear performance of DLC films produced in various source gases.

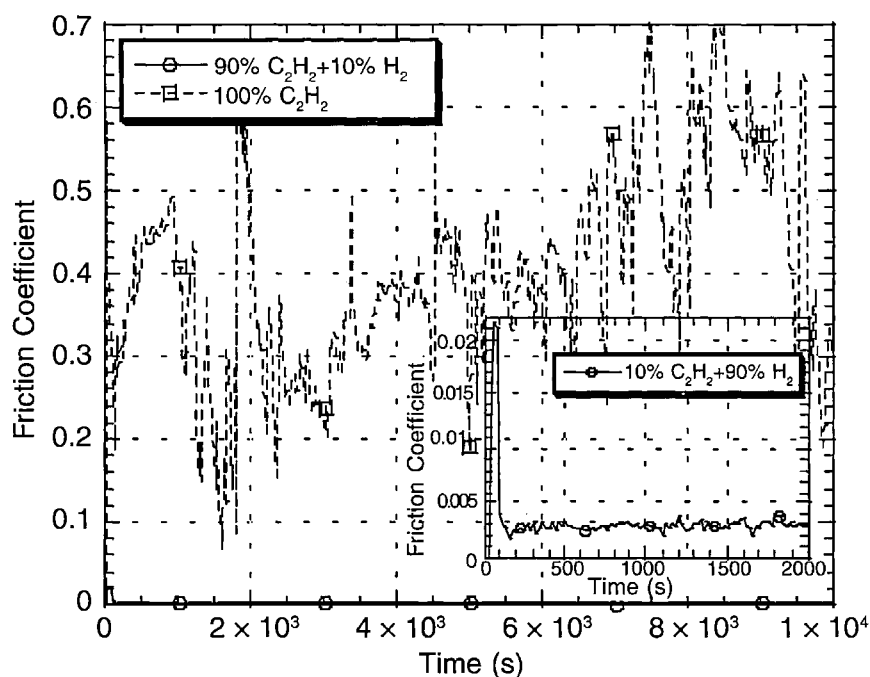


Fig. 4: Typical friction coefficient traces of DLC films derived from pure C_2H_2 and 10% C_2H_2 + 90% H_2 .

friction trace and provided the lowest friction coefficient among all the films tested in this study. When tested under the same conditions, the friction coefficient of an uncoated M50 ball against the H13 steel disk was 0.8.

The wear rates of all of the DLC-coated M50 balls during sliding against DLC-coated H13 disks in dry nitrogen are presented in Figure 3b. Note that these wear rates show a similar trend to that of the friction results presented in Figure 3a. Specifically, test data show that balls coated in pure C_2H_2 plasma suffer the most wear (i.e., $7.5 \times 10^{-7} \text{ mm}^3/\text{Nm}$), whereas balls coated with a film in increasingly hydrogenated C_2H_2 plasmas exhibit increasingly lower wear rates. The lowest wear, $2.8 \times 10^{-10} \text{ mm}^3/\text{N.m}$, was observed on a film that was derived from a plasma that consisted of 10% C_2H_2 + 90% H_2 . Figure 5 shows the size, shape, and condition of wear scars formed on two steel balls. The ball in Figure 5a was coated with DLC in a pure C_2H_2 plasma and this coating was worn out rather quickly. The ball in Figure 5b was coated with DLC in 10% C_2H_2 + 90% H_2 , and as can be seen, the coating is still intact. The wear rate of the ball in Figure 5a is 2500 times higher than that of the ball in Figure 5b. Note that the wear scar formed on the sliding contact spot of the ball in Figure 5b is rather clean and free of a transfer layer which is often encountered on balls slid against DLC films.³⁴⁻³⁷ When tested under the same conditions, the wear rate of an uncoated M50 ball against the uncoated H13 disk was $4.6 \times 10^{-6} \text{ mm}^3/\text{Nm}$.

4.0 Discussion

The results presented above suggest that the composition of the source gas plasma used during deposition of DLC films has a dramatic effect on the friction and wear behavior of the films. As is clear from Figures 3 and 4, the films grown in pure C_2H_2 plasmas wore quickly and exhibited very high friction. The films grown in a highly hydrogenated C_2H_2 plasma (containing 90% H_2) provided the best overall friction and wear performance. The exact mechanism(s) that control friction and wear behavior of DLC-coated surfaces are not yet fully understood, but several mechanisms have been proposed in past years. The generally accepted view is that the low friction of these films is mainly the result of the highly passive nature of their sliding surfaces.³¹⁻³³ Low friction due to bulk shear is very unlikely, because these films are amorphous, hence have no slip systems. High chemical inertness or passivity of sliding DLC surfaces apparently causes very little adhesion across their sliding contact interfaces and hence lowers friction. Micrographitization of sliding DLC surfaces and the formation of a transfer layer on mating surfaces can also significantly affect friction and wear behavior of DLC films.³⁴⁻³⁷ Furthermore, test parameters (such as ambient temperature, velocity, relative humidity, contact pressure, environment, etc.) can affect sliding friction and wear behavior of DLC films.^{16, 19, 20}

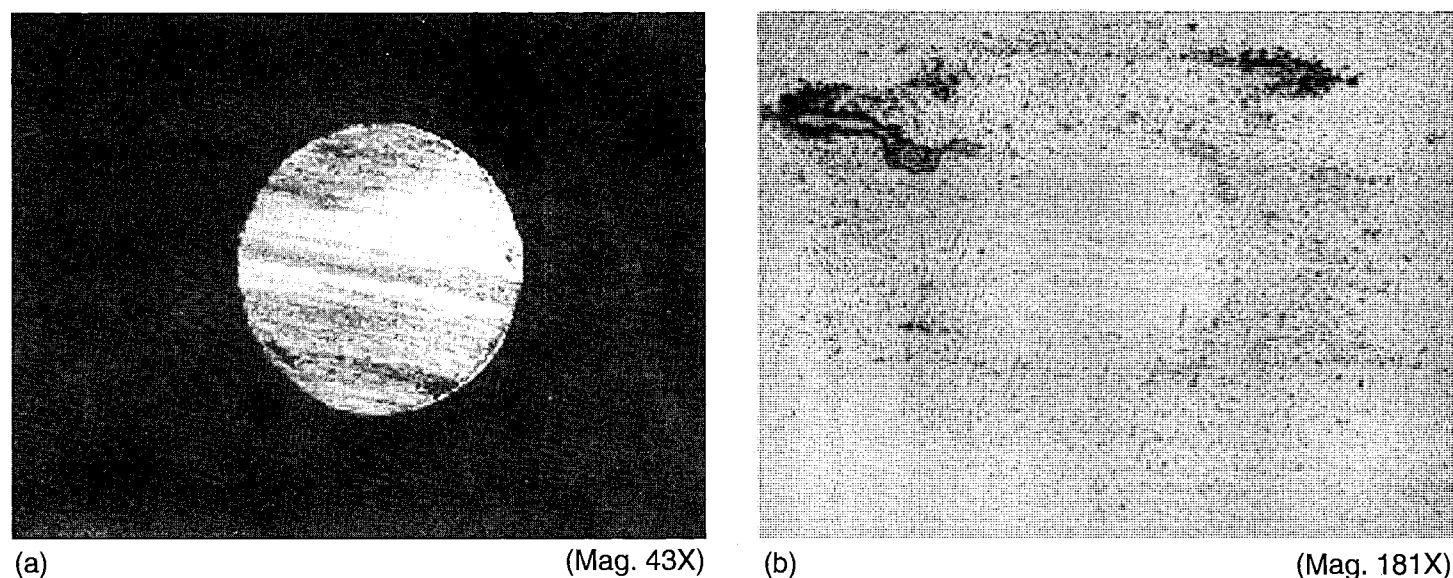


Fig. 5: Photomicrographs of wear scars formed on steel balls coated with DLC in (a) pure C_2H_2 and (b) 90% H_2 + 10% C_2H_2 .

It is well known that rubbing one rough surface against another generates large amounts of traction, and hence high friction, whereas rubbing one smooth surface against another often produces only low friction; this is particularly true for diamond and DLC films which provide low friction through an interface slip mechanism.^{2, 38, 39} In addition to testing parameters and physical roughness, the extent of chemical or adhesive interactions across a sliding interface can play a major role in friction. These bonds may result from a wide variety of short and long range chemical/physical interactions such as covalent, ionic, metallic, van der Waals, electrostatic, capillary forces, etc. Covalent bonding can occur between sliding diamond surfaces in ultrahigh vacuum and causes very high friction (i.e., friction coefficients >1).^{38, 40} However, when moisture or other chemically active gaseous species (such as oxygen, hydrogen, fluorine, etc.) are introduced into the test chamber, the friction coefficient of diamond drops precipitously to 0.05 or less. This is thought to be the result of chemical passivation of the free σ bonds on the surface and thus the elimination of strong covalent interactions across the sliding interface. This explanation is the most widely accepted for the self-lubrication mechanism of diamonds^{30-33, 40} High friction (0.8) between uncoated M50 steel and uncoated H13 tested in this study may have been largely due to the formation of strong metallic bonds across their sliding interface. Briefly, the making and breaking of bonds at the sliding interface largely controls the extent of friction between sliding DLC surfaces.

Besides very strong covalent bonding, some other forces (van der Waals, electrostatic, capillary, π - π^*

interactions) may also be present at the sliding contact interfaces of diamond or DLC films. The van der Waals attraction and π bonding are more relevant to graphite than to diamond or high-quality DLCs. When the sliding surfaces of diamond or DLC are graphitized under the influence of high thermal or mechanical loadings at high sliding velocities and/or temperatures, the extent of π bonds may become significant and can dominate the frictional performance of these materials.^{2, 34-37, 41} Furthermore, certain DLC films may contain high proportions of sp^2 -bonded or graphitic carbon precursors in their microstructures; hence the residual π bonding in these films may also be substantial. Finally, in open air, several mono-layers of water molecules and/or other gaseous species may have been present on the sliding surfaces of DLC films. These adsorbed layers may easily form a meniscus in and around the real contact spots that can in turn create residual capillary forces. In vacuum or well-controlled inert-gas environments, such forces are greatly reduced or are essentially absent.

In this study, the most striking observation was the existence of a close correlation between the source gas composition and the friction and wear performance of the resultant DLC films. Specifically, the DLC films produced in source gases with increasing amounts of hydrogen exhibited lower and lower friction and wear coefficients (see Figures 3 and 4), with the lowest friction coefficient, 0.003, provided by a DLC film grown in a 10% C_2H_2 + 90% H_2 plasma. The films grown in pure C_2H_2 plasmas exhibited the highest friction and wear. These observations suggest that the amount of hydrogen in the gas discharge plasma plays a critical role in the

friction and wear performance of the resultant DLC films. For the superlow-friction coefficients of DLC films produced in our study, we provide the following explanation.

As discussed earlier, hydrogen can chemically bond to and effectively passivate the free σ -bonds of carbon atoms in diamond and related materials and make these materials chemically very inert.³⁰⁻³³ It is important to remember that the C-H bonding is extremely strong (stronger than single C-C, C-O, or C-N bonds). We believe that when extra hydrogen is used during DLC deposition, several important events occur and control the structural chemistry of the resultant DLC films that ultimately govern the friction and wear performance. First, it is logical to claim that the amount of hydrogen in the bulk, as well as on the surface, of the DLC films will increase substantially. Most of the hydrogen atoms are expected to be paired with the σ bonds of carbon atoms, but some unbonded free hydrogen may also be present as interstitial species in the bulk. Increased hydrogen density in the bulk and on the surface should effectively diminish or even eliminate the possibility of any unoccupied σ bonds remaining and participating in adhesive interactions during sliding contact.

Second, hydrogen is known to effectively etch out or remove the sp^2 -bonded or graphitic carbon precursor from the film surface and thus prevent the formation of planar graphitic phases and/or cross linking that can give rise to π bonding.⁴² When DLC films are prepared in a highly hydrogenated plasma and under energetic hydrogen ion bombardment, strong C-H bonding rather than C=C double bonding should be favored. As explained above, the existence of residual π bonding that can be the result of C=C double bonds in DLC can give rise to high friction. Such a C=C double bonding may have been present in films derived from pure C_2H_2 .

Finally, we believe that perhaps some of the carbon atoms (at least the ones on the near surface) were dihydrated, that is that two hydrogen atoms were bonded to each carbon atom on the surface. This can occur on the unreconstructed (100) surfaces of diamond structures under some special or supercritical conditions⁴² that may have been created by the energetic hydrogen bombardment in a highly hydrogenated gas discharge plasma. The existence of dihydrated carbon atoms on the surfaces will increase the hydrogen density of these surfaces and provide better shielding or polarization of strong σ bonds and thus superlow friction.

As mentioned above, other influences such as van der Waals and capillary forces, as well as electrostatic attraction, can also be present and contribute to the friction between two sliding surfaces. In fact, when we repeated some of the tests in open air, the friction

coefficients of films grown in 10% C_2H_2 + 90% H_2 increased to values as high as 0.06 (depending on the relative humidity). Because we ran the friction tests in a clean, dry nitrogen environment, the extent of capillary forces due to moisture precipitation on or around the real contact spots should be minimal or essentially absent. As for the van der Waals forces, they will always be present at the sliding contact interfaces but their relative contributions to the overall frictional force should be rather insignificant, because we used very high contact loads in our experiments. As for the possibility of electrostatic attraction, we feel that because the DLC films are in generally dielectric, their sliding surfaces can certainly accumulate static electrical charges. The main question is whether these charges will cause attraction or repulsion. When the free electrons of hydrogen atoms pair with the dangling σ bonds of carbon atoms, the electrical charge density is permanently shifted to the other side of the nucleus of the hydrogen atom and away from the surface. Such a shift in charge density allows the positively charged hydrogen proton in its nucleus to be closer to the surface than the electron that is used up by the σ bond of the surface carbon atoms. We believe that the creation of such a dipole configuration at the sliding interface should give rise to electrostatic repulsion rather than attraction between the hydrogen terminated sliding surfaces of the DLC films.

Briefly, we believe that hydrogen plays an essential role in both the type and extent of chemical/physical interactions and hence in the friction of DLC films. Films grown in hydrogen-rich C_2H_2 plasmas are more likely to contain more hydrogen on their sliding surfaces and in their microstructures than the films grown in pure C_2H_2 so these films are chemically more inert, and their covalent σ bonds (which can cause adhesion/friction) are absent.

5.0 Conclusions

Based on the results of this experimental study, the following conclusions can be drawn.

1. DLC films grown in pure C_2H_2 plasmas exhibit very poor friction and wear properties when tested in a dry nitrogen environment.
2. DLC films grown in highly hydrogenated C_2H_2 plasmas provide superlow friction and wear properties.
3. The large differences in friction and wear of these DLC films can be attributed to the difference in hydrogen concentration of the source gases from which they were derived.
4. Mechanistically, overhydrogenation of DLC films provides a higher degree of surface passivation, which is essential for reduced adhesion and hence friction.

6.0 Acknowledgments

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Use of Advanced Soft-Metal Engineered Surfaces to Control Galling of Carbon Steel Bolts in Gasketed Joints at Elevated Temperatures

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Abstract

In 1992 TXU Electric began applying soft-metal engineered surfaces on various components used within its generating stations. These thin, highly adherent gold or silver surfaces significantly reduced the risk of galling for joints that are heavily loaded, operate at elevated temperature, and remain stagnant for long periods. Field experience has shown that engineered surfaces can be used to create “metallurgical contrast” that is more effective against galling than conventional lubricants.

Bolting materials with soft-metal engineered surfaces applied using the Plasma Bond process retain their qualifications as pressure boundary materials and may be used in nuclear-safety-related applications. Galling resistance has been previously demonstrated in joints assembled by tensioning such as the 1996 use of this technology to deposit soft-metal engineered surfaces on reactor vessel head studs. The work presented in this paper demonstrates that the galling resistance provided by soft-metal engineered surfaces is also effective on bolting materials assembled by the much more common practice of torquing. These tests involve multiple

successive assembly, heating and disassembly cycles for heavily loaded carbon steel bolting materials.

1.0 Introduction

Laboratory testing and field experience has shown soft-metal engineered surfaces (such as gold and silver) provide effective galling protection even in very harsh environments. These thin, highly adherent metallic films create a substantial “contrast” in the chemical composition and physical properties between the two contacting surfaces. This significantly reduces the risk of galling under harsh conditions where conventional lubricants are often not effective. Galling results in an unnecessary waste of time, money, and materials. In a nuclear facility, workers can also accumulate radiation dose in the course of repairing galling damage.

Understanding how threaded fasteners with soft-metal engineered surfaces respond in gasketed joints requires an interdisciplinary understanding of metallurgy, tribology, and the design requirements for a leak free gasketed joint. When joints are assembled by a tensioning process, tribological issues are relatively straightforward. However, when joints are assembled by torquing, tribology governs how applied torque is converted into fastener load. If galling occurs during assembly, applied torque no longer meaningfully correlates to fastener load.

A leaking joint caused by insufficient or excessive differences in fastener load is considered to be an assembly failure. A stuck fastener represents a disassembly failure. Apparatus and procedures used to simulate a gasketed joint must therefore address both assembly and disassembly issues. This paper describes equipment and procedures that were developed to assess the galling resistance of carbon steel bolting materials treated with Plasma Bond soft-metal engineered surfaces under harsh service conditions.

2.0 Friction, Wear, and Galling

Friction, wear, and galling are distinctly different phenomena but the circumstances under which they occur often seem similar. This discussion is based on clean, dry surfaces that would generally be considered smooth. When such surfaces touch, asperities (microscopic high spots) are the only locations where the objects actually make contact. The net surface area that is in *actual* contact is therefore only a small fraction of the *apparent* contact area.¹ Under load, the asperities flatten, either elastically or plastically, until there is sufficient contact area to carry the load with no further deformation.

When two solid surfaces are in contact and in relative motion, microscopic particles from the tips of the asperities can be dislodged from one or both surfaces. Heavier loads tend to dislodge more and larger particles, which can move about in the interface. If the wear particles are expelled from the interface and the concentration of particles remains low, the impact on friction is negligible. If wear particles remain trapped in the interface they may suffer further deformation and work harden which contributes to abrasion thereby accelerating wear. When wear particles reattach to the solid surface, this is “adhesive wear” which is the precursor to galling.

Galling is characterized by relatively large pieces of metal being torn from one surface and deposited on the other and friction at the interface can increase dramatically. If galling occurs during assembly, leak tightness of the joint assembled by torque can not be assured.

When an interface is under load, shear forces must exceed the friction force to cause the surfaces to slide across each other. Friction, wear, and galling can occur only while an interface is moving and carrying load. Under certain circumstances, it is possible to sustain relative motion at the loaded interface with virtually no wear. Hard surfaces and surfaces with substantial metallurgical contrast often tend to be quite resistant to wear. Soft-metal engineered surfaces create metallurgical contrast that helps friction remain reasonably consistent over a wider range of applied load.

2.1 Risk Factors for Galling

Evaluating risk involves considering the likelihood and the consequences of an occurrence. Consequences are assessed on a case by case basis but likelihood (probability of occurrence) can often be estimated through experience. Various investigators are likely to rank these galling risk factors somewhat differently but most investigators should agree that similar materials is the number one risk factor.

1. Similar chemical compositions and mechanical properties,
2. High load across the interface,
3. Elevated temperature,
4. Hard particles in the moving interface,
5. Extended stagnant time,
6. Metallurgically clean surfaces, and
7. Number of torqued assembly cycles.

Some materials, like aluminum and austenitic stainless steel, are very susceptible to galling even at moderate temperatures and loads. Metallic engineered surfaces have a unique risk associated with poor

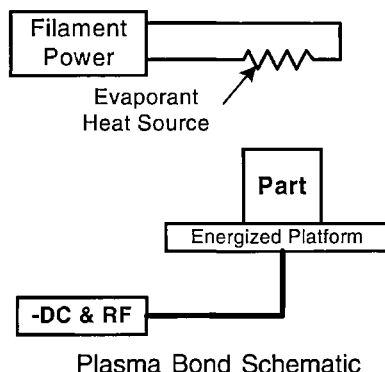
adhesion. If relatively large “sheets” of the metallic layer become dislodged “patches” of clean bare metal substrate are available to directly contact the opposing surface. Poor “wetting” would be the analogous behavior for a conventional lubricant.

3.0 The Plasma Bond™ Process

The patent pending Plasma Bond™ process is an enhanced vacuum coating process that is used to deposit very thin (less than 1 μm), strongly adherent metallic layers on a wide range of metal or nonmetal substrates. The item to be treated must be clean (reasonably free of volatiles) and is often glass bead blasted. Final cleaning may include back-sputtering that is conducted in vacuum immediately prior to depositing the metallic layer and is intended to produce an ultra clean surface. This high degree of surface cleanliness is considered essential to achieve the desired adhesion of the deposited surface.

The engineered surfaces are deposited from a low-pressure energetic vapor flux (mixture of ions, recombined neutrals, and vapor) that surrounds the item to be treated. The metal is introduced into the space surrounding the item using heated filaments. Deposited materials used in this process are very pure to ensure that potentially harmful trace contaminants are not present.

Mixed negative DC bias and RF energy contributes to creating the plasma, and attracts positive metal ions. The heated filament also contributes thermions. The most intense zone of potential gradient extends for 2 or 3 cm from the item. This strong potential gradient results in a “dark space” where ion concentrations are low because they are rapidly drawn to the charged object. Evaporant ions are accelerated toward the substrate and impact with kinetic energy on the order of 100 eV.



The recombined neutrals and the vapor are believed to impact the surface with kinetic energy in the approximate range of 0.01 to 10 eV. On average, the impact energy is high compared to vapor deposition and produces a strong bond with the substrate.

The metal vapor deposits predominately in a line-of-sight path from the evaporant source, but the metal ions that enter the dark space are able to coat the item three-dimensionally. The ions are also able to penetrate into relatively narrow cavities in the substrate. This occurs as a result of (1) evaporant ions experiencing scattering collisions in the plasma and (2) the applied charge.

During high-energy plasma deposition, metallurgical structures could be affected by the dramatic increase in substrate temperature. This may not be acceptable when the substrate is an ASME-qualified pressure-retaining bolt. The Plasma Bond process uses a low flux density, which limits the number of energetic impacts so temperature rise in the substrate material is negligible. Heat from the filament (transmitted as radiation) is responsible for temperature increase in the substrate. Metallographic examination has confirmed the Plasma Bond process does not alter metallurgical structures or produce a heat-affected zone.

4.0 Requirements for a Gall-Resistant Engineered Surface

Galling risk can be substantially reduced by engineered surfaces with the following characteristics:

1. Creates substantial metallurgical contrast between the opposing surfaces.
2. Does not introduce hard particles into the moving interface.

Engineered surfaces typically consist of two or possibly three layers. Each layer may be a pure element or an alloy. The galling resistant engineered surfaces used in this work consisted of a Ni base layer and a AgPd alloy working surface (Ni-AgPd). Unlike conventional lubricants the thin metallic layer is solid. Its inherent structural integrity and the fact that it is well supported by the substrate allows it to remain in place and structurally sound under heavy loads and at high temperatures for extended periods of time.

Testing and field experience suggest that about 1000 atom layers (200 nm) is sufficient to provide an effective soft metal barrier to galling. The overall thickness of the Plasma Bond engineered surface typically ranges between 300 and 1000 nm. A base layer, such as nickel, is intended to strongly bond to the substrate and aid in the adhesion of the working surface. The working surface, in one embodiment, may represent at least half of the total deposited thickness, and the balance of the deposit thickness is in the base and an optional transition layers. Bond strength for Plasma Bond-deposited engineered surfaces is expected to be 50 MPa (7 ksi) or higher.

Experience with other material layers such as chromium and titanium has shown they may detract from galling resistance. Chromium layers appear to contribute “hard debris” in the interface and contribute to galling risk. Preliminary work also suggests that nickel performs better than titanium as a base layer. Sometimes “active” metals, like titanium, are somewhat gall prone, and the soft-metal working surface may not effectively “screen” their gall prone nature.

Sometimes it is important to ensure a substrate’s properties are not altered. An example is materials qualified for use as an ASME-qualified pressure boundary. The Plasma Bond process does not alter substrate so its properties (and qualifications) are retained. The deposited layers are chosen to be chemically compatible with the working environment and metallurgically compatible with the substrate. Strict purity requirements are imposed on deposit materials to ensure potentially harmful concentrations of contaminants do not come into contact with the substrate material.

Soft-metal engineered surfaces need to be supported by and are mechanically influenced by the substrate because they are very thin, malleable, ductile, and have limited intrinsic strength on their own. On a microscopic scale, where galling initiates, there is a substantial contrast in chemical composition and physical properties. Applied loads induce stress fields that certainly will penetrate the very thin (typically 300 to 1000 nm) engineered surface layer, so the mechanical response of the engineered surface is strongly influenced by the mechanical properties of the substrate.

Iron-base or nickel-base substrates with yield strengths ranging between about 200 MPa (30 ksi) and 1000 MPa (150 ksi) appear to be mechanically compatible with the soft-metal engineered surfaces. The 50 MPa (7 ksi) bond strength appears to be adequate to keep the ductile and malleable Plasma Bond surface attached to the substrate in spite of local plastic deformation of the substrate material. This is based on visual assessments of engineered surfaces with gold working layers used in tensioned applications. Gold surfaces provide a color contrast that makes visual assessment possible.

Common non-destructive examination techniques (ultrasonic, magnetic particle, and dye penetrant) are unaffected by the deposited film. Glass bead blasting is often used to prepare the surface prior to depositing an engineered surface. Small surface-connected cracks may be “peened” shut by the action of the glass beads. However, this concern can be adequately addressed with an appropriate baseline inspection prior to surface preparation.

5.0 Comparison of the Galling Protection Provided by Engineered Surfaces and Conventional Lubricants

It is important to realize that the galling protection provided by engineered surfaces relies on “metallurgical contrast” while the galling protection provided by conventional lubricants relies on “avoiding contact” of the solid surfaces. These are very different mechanisms.

Engineered surfaces achieve maximum galling resistance when designed with a substantial “metallurgical contrast” (large differences in chemical composition and mechanical properties) between the contacting surfaces. Metallurgical contrast can be achieved by applying either hard or soft coatings. Testing has shown that hard surfaces provide less effective galling protection.² Local deformation is believed to cause hard surfaces to disbond and spall, which injects hard particles into the moving interface. Plasma Bond soft-metal engineered surfaces appear to be malleable, ductile, and remain attached to the substrate even when the substrate is plastically deformed.

When a low shear strength metal is deposited on one of the sliding surfaces that are in contact, the friction force during sliding will be reduced. Soft silver or gold films shear easily and prevent the hard substrate asperities from coming into frequent contact. This relatively easy shear at the contact points produces fewer damaging asperity/asperity interactions, which results in lower friction and reduced wear. Soft-metal engineered surfaces provide effective wear reduction when adhesive wear predominates.³ Particles preferentially dislodge from the soft-metal engineered surface so is it possible to largely avoid work hardening particles in the debris in the interface. Furthermore, if small quantities of small hard particles are introduced into the interface, these hard particles can get “buried” in the soft metal surface, which immobilizes them so they will do no harm.

5.1 Conventional Lubricants

Lubricants are very sophisticated materials. Their viscosity, thermal stability, and chemical affinity (ability to wet) for metallic surfaces, can be altered (within limits) to satisfy a given set of interface friction, load, and temperature requirements. Even the most viscous conventional lubricants with a strong tendency to wet metal surfaces have negligible shear strength compared to a solid, making them vulnerable to being “squeezed out” of the interface. In a static joint, gaps may form in

the previously continuous lubricant film allowing asperities to make metal to metal contact. The time needed to develop these “gaps” depends on load, temperature, and the lubricant properties and can range between a few hours and several months. Conventional lubricants can also “collect” hard particles that can contribute to galling risk during disassembly. Gaps in the lubricant film and hard particles are factors that contribute to galling risk.

Changes in the lubricant itself can also affect joint disassembly. Elevated temperature can selectively remove a lubricant’s more volatile components causing it to become stiff and hard. If the lubricant hardens yet retains its chemical affinity for the interface surfaces, this can effectively “glue” the interface together. The time needed for heat to alter a lubricant’s chemical structure and physical properties can range between months and years. While technically, this is not galling, the joint still can’t be dismantled.

It is interesting to notice that risk factors for galling and lubricant failure are actually quite similar. Risk factors for lubricant failure include:

1. High load across the interface,
2. Elevated temperature,
3. Hard particles in the moving interface, and
4. Extended stagnant time.

A laboratory can easily distinguish between galling and lubricant failure, but when a fastener sticks in the field the distinction can be quite subtle. In an industrial situation the difference between galling and lubricant failure is probably seldom recognized.

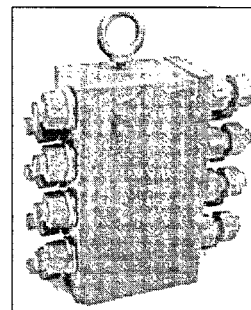
6.0 Measuring Fastener Performance and Galling Resistance Using a Simulated Gasketed Joint

A means of consistently reproducing representative mechanical and environmental conditions was needed to assess the galling resistance provided by Plasma Bond soft-metal engineered surfaces. The mechanical conditions included simulating the “soft” nature of a gasketed joint during torqued assembly, consistently applying a substantial fastener load, and maintaining that load in a stagnant condition through a heated cycle. The environmental conditions include exposing the fasteners to temperatures near the maximum expected operating temperature in the plant for appropriate lengths of time.

Under special conditions Plasma Bond surfaces are self-lubricating² so fastener performance (conversion of applied torque to fastener load) is maintained over several assembly cycles. This self-lubrication is believed to come from WD-40 (used to “preserve” the Plasma Bond surface) as it permeates the deposited metal surface.

Subsequent testing showed fastener performance noticeably declined (increased friction) when load-bearing surfaces were wiped between successive assembly cycles.⁴ Some of the preliminary tests done in conjunction with this work confirmed that fastener performance declined very rapidly on successive assembly cycles when they were heated for as little as 3 days. This experience clearly shows a suitable assembly lubricant is needed to maintain fastener loads in an acceptable range. It necessary to maintain fastener load in a narrow (about $\pm 10\%$) range to make a meaningful assessment of galling risk.

Test blocks that mimicked gasketed joints were designed and built, while test procedures that reflect field techniques for assembling gasketed joints by torquing were developed. Belleville washers were used to simulate the 0.5 to 0.8 mm (20 to 30 mils) “crush” or “compliance” (deformation in response to an applied load) in the sealing element in a gasketed joint. The compliance for the load cell used to determine fastener assembly performance was measured and also found to be reasonably similar to the expected “crush” in a sealing element.



Heated Test Block Assembly

For practical reasons, there was a desire to “accelerate” the test but there was no reason to expect the commonly used Arrhenius approach (raising the temperature to simulate longer exposure times) would affect the behavior of the contrasting metal surfaces. It did however, seem likely that an increased load would have a detrimental effect on the galling resistance of the soft-metal engineered surfaces. Based on engineering judgment it was decided to “accelerate” the tests by using increased fastener load rather than by raising the temperature.

6.1 Equipment

Preliminary tests were conducted to identify critical details in the main test, ensure suitability of the test procedures, and to assess the overall severity of the test. These tests exposed the fasteners to 325°C (616°F) for periods of about 70 hours (as shown in Table 1).

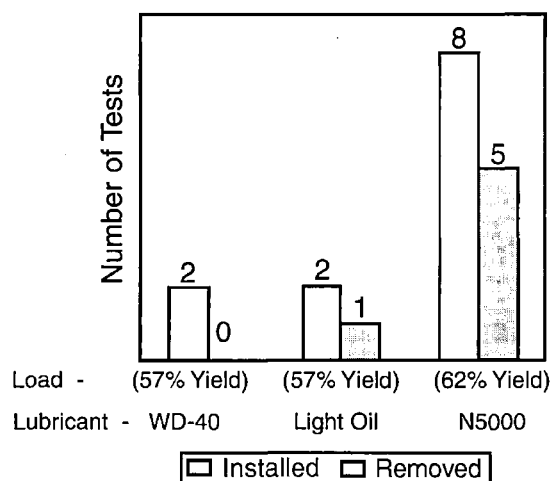


Fig. 1: Baseline galling evaluations on as-received carbon steel studs.

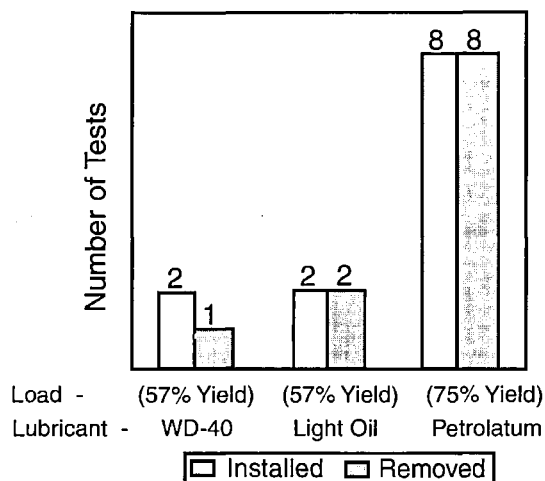


Fig. 2: Preliminary galling evaluations on Ni-AgPd carbon steel studs.

The main test was again conducted at 325°C (616°F) but the duration of the operating cycles ranged between 70 and 2040 hrs. This large variation in exposure time was intended to assess how longer exposure times (50,000 hrs.) might affect galling risk. The target value for fastener load was set at about 111 kN (25,000 pounds) which corresponds to about 75% of specified minimum yield strength for this material. The test was planned for up to 12 assembly-heat-disassembly cycles, but if more than 5% galling occurred during disassembly, the test would be terminated.

6.2 Test Results

Baseline tests were conducted to evaluate various candidate assembly lubricants and to assess the overall severity of the test equipment, procedures, and environment. Figure 1 presents results from twelve untreated carbon steel fasteners that were cleaned, degreased then assembled using various lubricants. Loads were moderate (57 - 62% of yield), the temperature was 325°C (616°F) and the duration was three days.

Eight of these untreated studs were assembled using LocTite N-5000, loaded to 62% yield, and exposed to 325°C (616°F) for 3-days. LocTite N-5000 is commonly used in the nuclear industry and is widely considered to be an effective lubricant. Three of the eight studs galled during disassembly even though the loads and temperatures seem quite typical. The 38% failure rate suggests that N-5000 provides less-than-adequate galling protection during disassembly. These results confirmed that the equipment, assembly procedures, and conditions of the test produce significant galling risk.

Twelve studs with Ni-AgPd Plasma Bond surfaces with an overall thickness of about 500 nm on the inclined thread surface were exposed to one 325°C (616°F) heated cycle. The “light” lubricants (WD-40 and mineral oil) proved to be unsatisfactory assembly lubricants because fastener preloads could not be maintained in the desired range. These “light” lubricants were not included in the main test. Petrolatum appeared to be an effective assembly lubricant. Friction within the joint (expressed as nut factor) was reasonably comparable for Petrolatum and LocTite N-5000. Petrolatum is the preferred lubricant for use in conjunction with a Plasma Bond surface. Its simple chemical structure breaks down under heat so metallurgical contrast governs disassembly. Furthermore, it is unlikely to be converted into “glue” during service.

The studs were loaded to about 75% of the material’s specified yield strength, which is a very high stress under TXU design philosophy. The results in Figure 2 confirm that the soft-metal engineered surfaces virtually eliminated galling under conditions that caused 38% galling failures on untreated fasteners in the baseline test.

The objective of the main test (Figures 3 and 4) was to determine practical operational limits for Plasma Bond-treated fasteners installed using torque. Thirty-two fasteners with 500 nm Ni-AgPd Plasma Bond surfaces were exposed to 325°C (616°F) and loaded to about 75% yield. Petrolatum was the assembly lubricant.

Mechanical damage accumulated during assembly-disassembly cycles and length of stagnant time at elevated temperature are thought to contribute to galling risk. Figure 3 shows the duration of each heated cycle. The test was terminated after the eighth cycle because

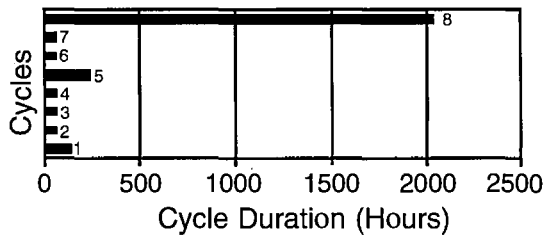


Fig. 3: Duration of successive assembly cycles.

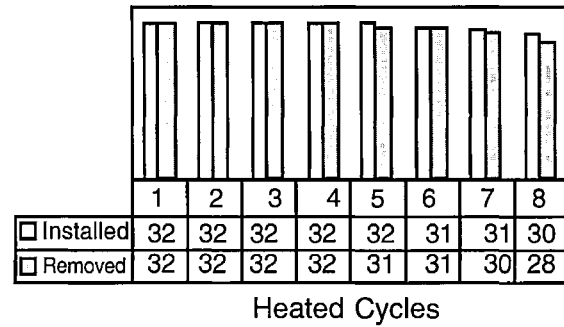


Fig. 4: Galling evaluation for carbon steel studs exposed to successive heated cycles.

Table 1

Qty	Part	Material	Notes
56	Studs	A-193 B7; ¾" (19 mm)-10 Minimum Yield - 720 MPa (105 ksi)	(12) Clean and Degreased (Fig. 1) (44) Ni-AgPd 500 nm Thick (Figs. 2 and 3)
56	Nuts	A-194 2H; ¾" (19 mm) -10 Heavy Hex	Clean and Degreased
56	Hardened Washers	Carbon Steel; 1/8" (3.2 mm) Thick, Flat	Clean and Degreased
56	Belleville Washers	Inconel; 1/8" (3.2 mm) Thick	20 mils Deflection at 7000 Pounds Load (0.5 mm Deflection at 30 kN Load)
4	Test Block	Carbon Steel; 11 × 8 × 23 cm (4.5 × 3 × 9")	(8) ¾" × 4-1/2" Through-Holes.
4	Lower Plate	Carbon Steel; 1.3 × 8 × 23 cm (½ × 3 × 9")	Drill and Tap (8) ¾" Through Holes

two of thirty (more than 5%) fasteners galled during disassembly. Exposure times for the first seven cycles was relatively short ranging between about 70 and 240 hrs. Plasma Bond surfaces with mechanical damage accumulated over seven cycles were used in the long duration (2040 hrs.) exposure. Combining long exposure and surfaces that accumulated damage over seven cycles were used to "conservatively" assess the galling risk. The total time-at-temperature was nearly 2800 hrs.

Figure 4 shows one fastener galled during cycle five, another during cycle seven and two fasteners during the eighth cycle. The two galling events in cycle eighth are believed to have occurred due to the combined effect of damage that had accumulated over eight assembly-operating-disassembly cycles and the relatively long duration of cycle eight. After breakaway, nearly all (over 90%) of the fasteners could be easily dismantled by hand. This was true after each of the eight heated cycles. The free span of the studs had "stretched" by about 2% after cycle eight. (Clear evidence of the high stress imposed on the fasteners).

As was expected, the galling risk appears to increase with successive assembly cycles. The time-dependent component of galling risk appears to accumulate more quickly early in the cycle. This data (very approximately) suggests that about half of the time-dependent galling risk in a 100,000 hours operating cycle, might accumulate during the first 1000 hours.

7.0 Field Experience

Sixteen Plasma Bond-treated Steam Generator primary manway studs were installed (using tensioning) with no conventional lubricant. After they were exposed to 330°C for 17 months they were easily removed by hand. Visual examination revealed no flaking or disbondment.

Fifty-two reactor vessel head closure studs with engineered surfaces were installed (using Tensioning) with LocTite N-5000 lubricant then exposed to 315°C for 17 months. The studs were easily removed and visual examination revealed the engineered surfaces showed no signs of flaking or disbondment even after they were

subjected to "IceSolv" blast cleaning with CO₂ pellets propelled by air at 0.8 MPa (120 psi) to remove the old lubricant.

Stainless steel trunnion bolts used to seal the lids on radioactive filter canisters routinely galled making it necessary for maintenance workers to enter the radiation field near the filter canister and remove the damaged trunnion bolts. TXU has experimented with an earlier version (Ni-AgPd) engineered surface on these trunnion bolts and to date, no further galling has been reported.

The striker plate and latch mechanism on the control room door needed to be replaced on an almost weekly basis due to galling degradation that caused the door to "hang" open. Failure of the door to close resulted in nuisance security alarms. Following application, on the striker plate only, of an experimental (Ni-AgPd) engineered surface around 1995 the door has functioned without incident. *This example shows that soft-metal engineered surfaces effectively eliminated wear under certain conditions.*

8.0 Conclusions

1. Plasma Bond engineered surfaces provide effective gall resistance without altering an item's bulk properties. Only one of the surfaces needs to be treated to create the desired metallurgical contrast.
2. The galling protection provided by soft-metal engineered surfaces deposited using the Plasma Bond process is superior to the galling protection provided by conventional lubricants. As conditions become more harsh (high loads, elevated temperature, long stagnant times) this disparity in galling protection becomes more pronounced.
3. When the fastener loads are limited to about 60%

of yield, galling resistance of the Plasma Bond surface remains effective for an economically useful, but limited, number of torqued assembly-operation-disassembly cycles.

4. The time-dependent part of galling risk for torqued fasteners with soft-metal Plasma Bond engineered surfaces, accumulates early (first 1000 hrs.) in the operating cycle and may remain nearly constant thereafter. (This assumes conventional assembly lubricants are not used).
5. Appropriate use of engineered surfaces can result in operation and maintenance cost savings through greater operational reliability, less frequent maintenance, easier disassembly, fewer repairs of galling-related damage, and extension of component life.

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Fabrication and Characterization of TiB₂/TiC and Tungsten Co-Sputtered Wear Resistant Coatings

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Abstract

Co-deposited thin films of titanium carbide (TiC)/titanium diboride (TiB₂) and tungsten (W) were deposited on 52100 bearing steel substrates using magnetron sputtering, under conditions of varied working gas pressures and with different W metal concentrations. Coatings were characterized using scratch adhesion, indentation, and sliding wear tests. Films exhibited very good adhesion with critical scratch adhesion values from 50-70 N, with slightly higher values measured for W-containing films. Observations from Rockwell

C indentations to compare relative toughness, suggest that adding a moderate amount (from 16 to 22 at.%) of W to the TiC/TiB₂ coatings reduced the damage diameter around the indentations, and resulted in a less-severe cracking mode (fine radial cracking observed for W-containing films). This suggests that TiC/TiB₂/W coatings have higher coating/substrate interfacial toughness than pure TiC/TiB₂ coatings. Nanoindentation of the TiC/TiB₂/W coatings resulted in hardness values in the range of 20-30 GPa, with higher values for coatings with higher W content. Reciprocating sliding wear tests were performed on the coatings using a tungsten carbide-

cobalt (WC-Co) ball counterface. At a lower initial stress of 1.33 GPa, addition of W to the TiC/TiB₂ matrix resulted in higher wear factors, whereas at a higher initial stress of 1.91 GPa, W-containing TiC/TiB₂ films had lower wear factors than for the pure TiC/TiB₂ coating. This behavior suggests a load (or stress) sensitive wear performance.

1.0 Introduction

Carbide ceramic materials (e.g., boron carbide (B₄C), titanium carbide (TiC), and silicon carbide) offer extremely high hardness,¹ but suffer from low ductility and toughness, which has restricted their application. These materials, even when deposited in thin-film form with mechanical support from the underlying substrate, still suffer from low durability.

Addition of metals, as toughening agents, is a method that has been developed by the cutting tool industry, where Co, Ni, and other metals act as “binders” that are incorporated with tungsten carbide (WC)² and TiC, resulting in higher-toughness ceramic-metal (cermet) bulk components. Similar approaches have been applied to fabrication of *ceramic-metal* (cermet) coatings. An early study of radio frequency (r.f.) magnetron sputtered W-Co-C coatings examined effects of Co content and bias on the formation of transfer films and wear of coated disc and steel counterface pins.³ Recent studies by the present authors⁴⁻⁶ have demonstrated exceptional hardness and improved toughness for cermet coatings (e.g., B₄C & Mo, TiC & W), compared to their pure carbide coatings.

Other investigations of co-deposition of various combinations of materials can be found in the literature. For example, co-sputtering has been used to fabricate metal-metal alloy coatings, such as niobium (Nb)-chromium (Cr),⁷ Nb-tantalum (Ta),⁷ and aluminum (Al)-molybdenum (Mo).⁸ Other examples of co-sputtered systems include nitride (Al nitride (AlN))-metal (Al),⁹ sulfide (MoS₂)-metal (gold (Au)),¹⁰ and nitride (TiN) – MoS₂.¹¹

In this investigation, the authors prepared and characterized cermet films consisting of TiB₂/TiC with W additions, in order to determine the effects of working gas pressure and W-concentration on the tribological performance of the cermet films.

2.0 Experimental Details

Hardened and tempered (Rockwell C hardness > 60) bearing steel (52100) substrate disks were polished using 5 and 1 μm alumina paste on an automatic polisher. Prior to coating deposition, specimens were washed in a degreaser solution, washed in acetone, then isopropyl alcohol, and then blown dry with hot air. Disks were

mounted on a stainless steel specimen plate and then inserted into the vacuum system which was pumped down to a base pressure less than $6-7 \times 10^{-6}$ torr. Immediately prior to bond layer coating, specimens were subjected to a dc plasma etch to further remove surface contamination. Typical etch conditions included a working gas (99.95% pure Argon (Ar)) pressure of about 37.5 mtorr, an initial applied voltage > 735 V, and an etch duration of 5 minutes.

A titanium bond layer, of approximate thickness 150 nm, was deposited immediately after the plasma etch using DC sputtering with an unbalanced magnetron configured to a maximum-deposition-rate type II configuration.¹² This configuration has been shown, through experiments, to have higher ion flux and electron density at a substrate holder probe station.¹²

A sputter target of 60 wt.% TiC and 40 wt.% TiB₂, fabricated using self propagating high temperature synthesis (SHS) was provided by the Colorado School of Mines Advanced Coating and Surface Engineering Laboratory, for coating depositions. Overcoatings consisting of TiC/TiB₂ or TiC/TiB₂/W were deposited, also using unbalanced magnetron sputtering, with the parameters listed in Table 1. Different working gas pressure was initially investigated to determine its importance in the fabrication of high quality thin films. Tungsten metal was co-deposited with the TiC/TiB₂ material by attaching W wires on the carbide target with a clamping ring.⁴

Coating composition was established using x-ray Photoelectron Spectroscopy (XPS) after sputter etching the surface to remove about 100 Å of material. Coating hardness was determined using a Nanoindenter which provided hardness and elastic properties. Scratch adhesion was measured (average of at least three measurements) using a TEER computerized scratch tester, using a 5 mm dia. diamond ball. Coating hardness was measured using a Nanoindenter with three measurements taken and averaged. Relative coating-substrate interfacial toughness was measured from the damage induced by indentation with a Rockwell C indenter at an applied load of 150 kg. Wear testing of the coatings was performed by reciprocating sliding of a 5 mm diameter WC-Co ball against the coated substrates for 50 cycles. The initial loads that were applied were 5 and 15 N, which corresponds to initial contact stresses of 1.33 GPa (192 ksi) and 1.91 GPa (277 ksi), respectively. Profilometry was performed across the wear scars in three areas to enable calculation of wear volume from the integrated cross-section of the wear scar and the total length of travel of the WC-Co ball. Wear factors, expressed in mm³/N-m, were subsequently calculated. Optical, light metallography

Table 1. Coating Matrix for TiB₂/TiC/W Coatings

Run #	Number of Tungsten Wires	at.% W	Processing Details ¹ ; DC Plasma Etch Voltage, Ar Working Gas Pressure	Coating Thickness, μm
155	None	0	> 814 V etch, 2.6 mtorr	1.24
157	None	0	> 735 V etch, 1.75 mtorr	1.61
180	2 wires (1 mm dia.)	16%	> 1010 V etch, 1.75 mtorr	2.14
163	3 wires (1 mm dia.)	22%	> 1053 V etch, 1.75 mtorr	2.17

¹All coatings deposited with -40 V DC bias**Table 2. Summary of Scratch Adhesion, Hardness, Indent Damage, and Wear Factors for TiB₂/TiC/W Co-Sputtered Films on 52100 Steel**

Run #	Coating Composition	Scratch Adhesion, N	Nano-Hardness, GPa	Indent Damage Diameter, mm (Type of Damage)	Wear Factor Stress (GPa)
155	TiB ₂ /TiC	NM ¹	NM ¹	1.095 $\pm$ 0.031 (Large Flakes)	NM ¹
157	TiB ₂ /TiC	61.7 $\pm$ 3.5 (Cracks @ 20-30 N)	19.3 $\pm$ 0.59	0.864 $\pm$ 0.031 (Radial Cracks & Flaking)	Not Measurable ² (1.33) 7.73 $\times 10^{-6}$ (1.91)
180	TiB ₂ /TiC/ 16% W	61.7 $\pm$ 2.1	24.69 $\pm$ 3.61	0.670 $\pm$ 0.028 (Cracks & Flaking)	1.08 $\times 10^{-6}$ (1.33) 1.5 $\times 10^{-6}$ (1.91)
163	TiB ₂ /TiC/ 22% W	71.3 $\pm$ 12.7	29.47 $\pm$ 0.68	0.622 $\pm$ 0.008 (Very Fine Rad. Cracks)	1.51 $\times 10^{-6}$ (1.33) 1.5 $\times 10^{-6}$ (1.91)

¹Not measured due to coating failure during test²Wear could not be measured across scar using profilometry

was performed on the indentations and wear scars to characterize the cracking behavior and wear mechanisms.

3.0 Results

Table 2 lists a summary of all of the measured coating properties, which are discussed below in more detail.

3.1 Scratch Adhesion

Examining the scratch adhesion data shown in Table 2, suggests there is not a strong correlation of adhesion with coating composition. Coating #157 without any W addition, exhibited an average scratch adhesion value similar to coating #180, which had about 16 % W, although visual observation of coating cracking within the wear scar at loads between 20 and 30 N was

noted. The higher (e.g., 22%) W-containing film #163 did have a higher average adhesion value than the other films, however its large range in values precludes a correlation of adhesion with composition.

3.2 Relative Coating Toughness

Spall diameters (or diameter of crack extension) in the coatings from indentation with a Rockwell C-indentor were measured for comparison. Indentation induces compressive stresses immediately under the indent, but tensile stresses at the lip of the indentation. The subsequently induced damage or cracking has been referred to as a relative measure of the coating-substrate interfacial toughness.¹³ From the data in Table 2 and the corresponding indent photographs in Figure 1, it appears that working gas pressure is an important variable. For example, TiC/TiB₂ coating #157, fabricated at a lower

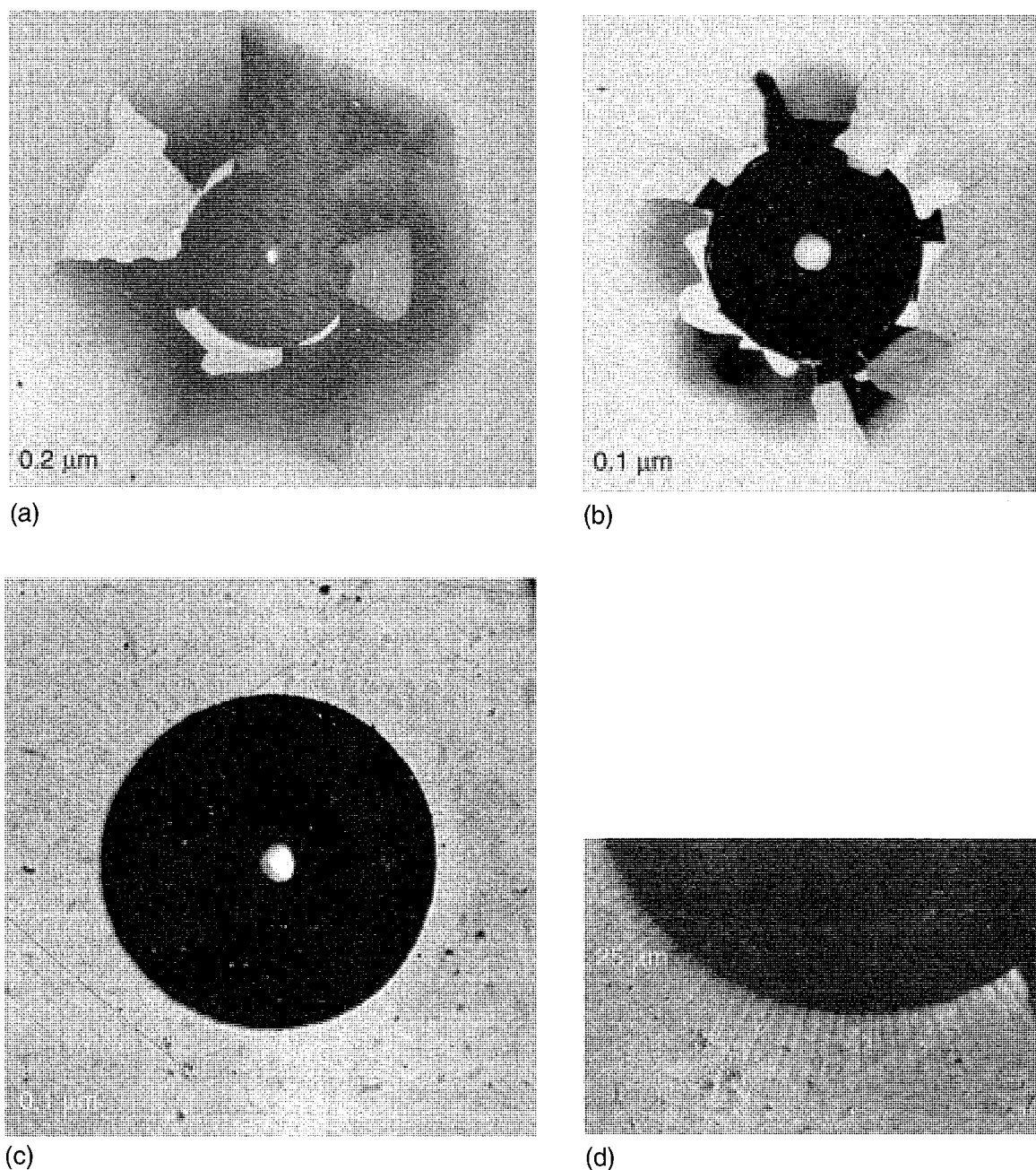


Fig. 1: Micrographs of coating cracking and flaking from indentations with Rockwell C- Indentor: (a) drastic cracking/flaking behavior for TiC/TiB₂ coating #155 deposited at higher (2.6 mtorr) working gas pressure, (b) reduced cracking/flaking damage for TiC/TiB₂ coating #157 deposited at lower (1.75 mtorr) gas pressure, (c) significantly reduced cracking and no flaking for TiC/TiB₂/22% W coating #163 deposited at lower (1.75 mtorr) gas pressure, and (d) higher magnification image of minor radial cracking for TiC/TiB₂/22% W coating #163.

working gas pressure of ~1.75 mtorr Ar exhibits a smaller crack diameter and less drastic flaking (Figure 1b) compared to TiC/TiB₂ coating #155 (Figure 1a), which was fabricated at a higher Ar gas pressure of 2.6 mtorr. Addition of W to the TiC/TiB₂ coatings (#180 - 16% W and #163 - 22% W) further reduces the diameter of

cracking and extent of flaking compared to the non-W containing coatings #155 and 157. Comparing the indent damage results in Table 2, coating #163 with the highest percentage (22%) of W exhibits the least amount of damage from the indentation, with only minor radial flaking and no evidence of flaking (Figures 1c and d).

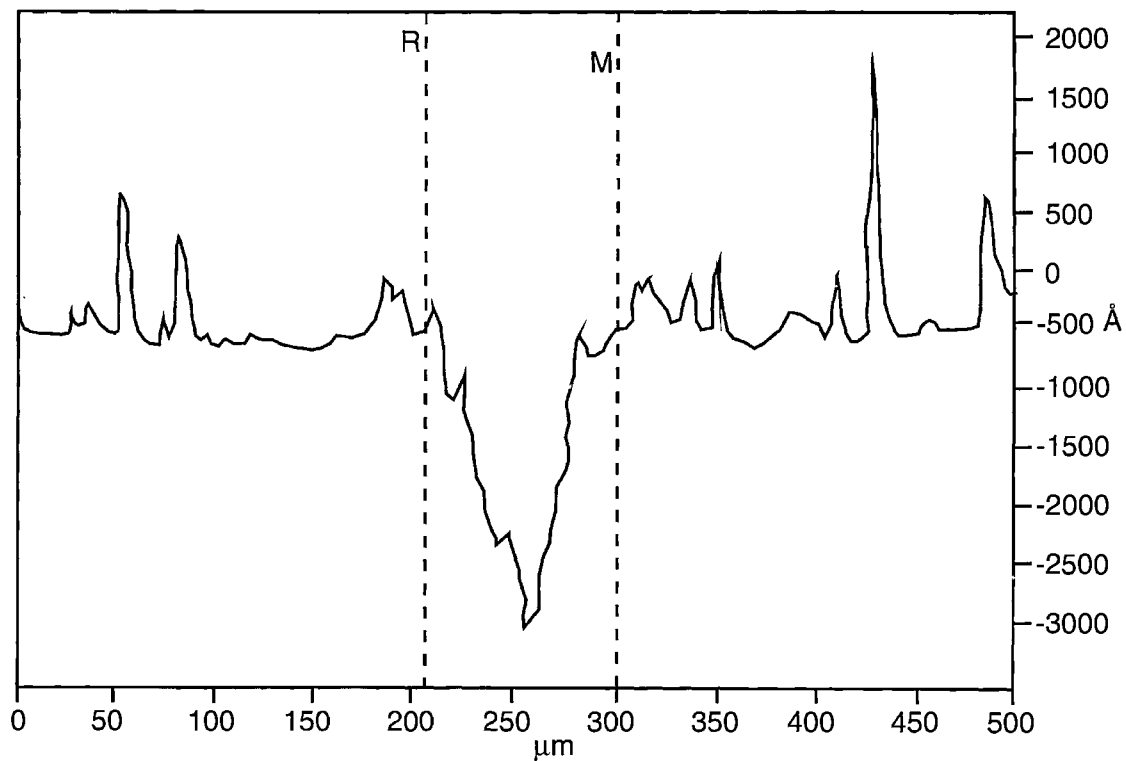


Fig. 2: Profile of wear scar from TiC/TiB_2 coating #157 after test at initial stress of 1.91 GPa, showing well defined scar depth which was less than the coating thickness (1.61 μm).

3.3 Nanohardness Measurements

Hardness values for the coatings, measured using a nanoindenter, are listed in Table 2. For coating TiC/TiB_2 #155 processed at the higher gas pressure, the coating failed/flaked during the hardness measurements and no reliable data could be obtained. Reducing the gas pressure during sputtering of TiC/TiB_2 coating #157, resulted in an adherent coating with a hardness of 19.3 GPa.

Adding W to the coatings resulted in a measurable increase in hardness. For example, adding 16 at.% W (coating #180) increased the average hardness by about 28% to 24.7 GPa, although this coating also had an increase in data scatter. Increasing the W content to 22 at.% (coating #163) further increased the hardness to nearly 29.5 GPa. The addition of the W to the TiC/TiB_2 matrix may result in the formation of W-containing ceramic compounds, such as WC and W_2B_5 , although these ceramics have lower hardnesses than either TiC or TiB_2 , thus their formation does not appear to be responsible for the increased hardness for the W-containing coatings. Other possible scenarios for the increase in hardness include: 1) formation of complex Ti, W-boride/carbide compounds or 2) incorporation of the W atoms in the lattice of smaller B and C atoms. The latter effect,

incorporating large atoms with small atoms in a coating structure has been reported to result in increased coating density (from reduced shadowing during coating deposition) and improved thermal shock properties.⁷

3.4 Sliding Wear Resistance

Wear test results, reported as wear factors, are listed in Table 2 for TiC/TiB_2 and $\text{TiC}/\text{TiB}_2/\text{W}$ coatings, as a function of different applied loads (or different initial stress values). For TiC/TiB_2 coating #155, deposited at higher working gas pressure, the film could not withstand loading from the diamond pin and immediately failed. In contrast, reducing the working gas pressure during deposition for TiC/TiB_2 coating #157, resulted in an adherent film which exhibited non-measurable wear (measured by contact stylus profilometry) for the lower initial stress of 1.33 GPa. However, increasing the initial contact stress by 44% to 1.91 GPa, resulted in measurable wear, with a calculated wear factor of $7.7 \times 10^{-6} \text{ mm}^3/\text{Nm}$. Profilometry across the wear scar at the higher load (Figure 2) indicated an average maximum wear depth (MWD) of $\sim 220.3 \text{ nm}$. This MWD is however less than the total coating thickness of 1.61 μm , suggesting the coating was not worn through.

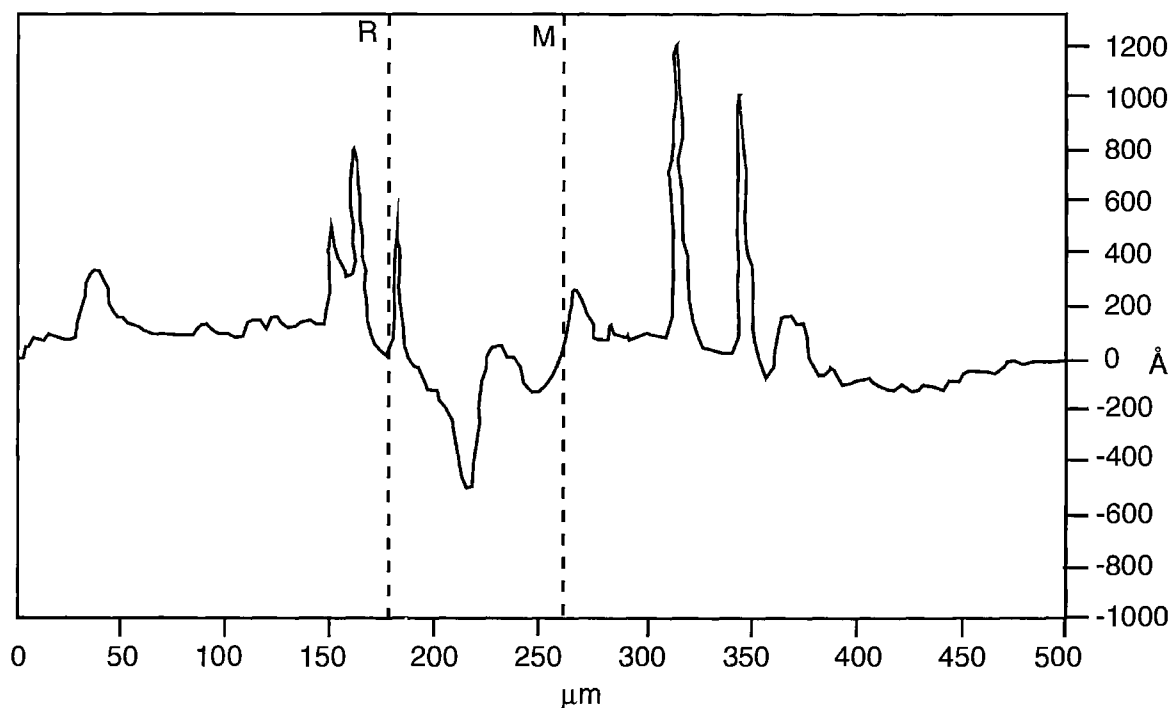


Fig. 3: Profile of wear scar from TiC/TiB₂/W coating #163 after test at initial stress of 1.91 GPa, showing significantly reduced MWD compared to coating #157.

Adding W to the TiC/TiB₂ matrix also resulted in coatings with very good wear resistance, e.g., in the range of low 10^{-6} mm³/Nm. Examining the calculated wear factors, listed in Table 2 for the W-containing TiC/TiB₂ coatings (#180 and 163), suggests there may be slightly higher wear resistance for the lower W-containing film #180 (specifically for the lower load test). At the lower load test conditions (e.g., 5 N = 1.33 GPa initial stress), wear factor data suggests adding W reduces the wear resistance for the composite films, compared to the pure TiC/TiB₂ coating. Conversely, at the higher test load of 15 N (1.91 GPa initial stress), the wear factor data suggests the addition of W may be beneficial to improve wear resistance, although there does not appear to be a correlation of percent W loading with wear resistance. For example, at the higher test load of 15 N, a reduction in wear factor by about 80% was calculated for the W-containing coatings compared to the pure TiC/TiB₂ film. This behavior suggests a load (or initial stress) sensitive wear behavior for the TiC/TiB₂/W coating system in contact with a WC-Co counterface.

Maximum wear depths for the W-containing TiC/TiB₂/W coatings were much lower than for the pure TiC/TiB₂ coating (MWD of 220.3 nm at 15 N load). For example, average MWDs of 70.8 nm (5 N) and 71.4 nm (15 N) were measured for coating #180 (16 at.% W), while MWDs of ~10.5 nm (5 N) and 53.7 nm (15 N)

(scan shown in Figure 3), were measured for coating #163 (22 at.% W). Visual examination of the wear scars revealed only faint indications of wear debris, presumably either from the mating WC-Co pin or from the coating itself.

4.0 Discussion

The overall conclusion from this study of multicomponent wear films was that the addition of W metal to TiC/TiB₂ is beneficial for improving the tribological properties of this candidate wear coating. Specifically, improvements in relative coating/substrate interfacial toughness, increased hardness, and increased wear resistance (under high test load (or initial stress) conditions) were observed for W-containing films. Improved toughness for the higher-W (i.e., 22 at.%, #163) film appeared as complete elimination of flaking from indentation, and only minor radial cracking. Both of the W-containing films exhibited increased nanohardness, with over a 50% increase measured for the higher W film #163. Finally, increased wear resistance was calculated for W-containing films, compared to pure TiC/TiB₂, but only at the higher initial stress of 1.91 GPa. At the lower initial stress of 1.33 GPa, addition of W to TiC/TiB₂ resulted in higher wear factors, and higher W films had the highest wear

factor. This behavior suggests a load (or stress) sensitive wear performance.

The observations of higher relative coating-substrate interfacial toughness, higher hardness, and lower wear factors (at the higher test stress) for TiC/TiB₂/W coatings may be due to the fabrication of higher density coatings with low porosity from the addition of W and the application of bias during deposition. It has been suggested,⁷ that co-deposition of metals with a large difference in atomic radii (e.g., Nb & Cr) may disturb self-shadowing during deposition, resulting in a microstructure consisting of fine columns with no voids between the grains. In contrast, the microstructure for co-deposited metals of similar atomic radii (e.g., Nb & Ta), was coarse columnar with open grain boundaries.⁷ For the TiC/TiB₂/W coatings studied here, B and C are very small atoms (e.g., B: 0.97Å; C: 0.77Å), whereas both Ti and W are much larger (i.e., Ti: 1.47Å; W: 1.37Å). Therefore the difference in sputtered specie atomic sizes for the elements in the TiC/TiB₂/W system may have promoted dense microstructures which would result in the improved mechanical properties.

The wear resistance trend for the TiC/TiB₂/W coatings of increased wear factors for films with higher % W (at the lower initial stress of 1.33 GPa), supports previously reported results for W-Co-C films where increasing the percentage of Co in the films, from 18 at.% to 26-30 at.%, resulted in increased wear coefficients.³ In addition, the value of the wear factors for the W-Co-C film and the TiC/TiB₂/W film, with nearly equivalent percent metal concentrations (i.e., 18 at.% Co³ and 16 at.% W, this study) were nearly equivalent. For example, the wear coefficient for the W-18 at.% Co-C film was $9.8 \times 10^{-7} \text{ mm}^3/\text{Nm}$,³ whereas the wear factor calculated from this study for the TiC/TiB₂/16 at.% W film was $1.08 \times 10^{-6} \text{ mm}^3/\text{Nm}$. This very consistent wear data was in spite of different counterfaces for the two studies (e.g., 1045 mild steel pin in ref. 3 vs. WC-Co ball in this study), although the initial stress was nearly equivalent (e.g., 1 GPa for ref. 3 vs. 1.33 GPa in this study).

In this study, it was also observed that increasing the initial stress for the wear test to 1.91 GPa (44% increase from 1.33 GPa) changed the wear trend, with reduced wear factors for TiC/TiB₂ films containing W, although no absolute trend with percent W addition was observed.

The observation of lower wear factors (for the higher initial wear stress) and higher relative toughness for coatings containing W, suggests a possible correlation of coating toughness with wear resistance. This supports previous work performed by the authors on the B₄C – Mo system⁵ and published literature that improved fracture

toughness for bulk ceramics results in greater wear resistance.¹⁴ For bulk ceramics, wear is predominately controlled by microfracturing, and therefore processing to increase fracture toughness will reduce the extent of microfracturing.¹⁴

5.0 Summary

Co-sputtered thin films of TiC/TiB₂/W exhibited good adhesion to 52100 steel substrates, increased nanohardness, improved coating/substrate toughness, and improved wear resistance (at higher initial stress) for films containing W. Higher nanohardness of the TiC/TiB₂/W coatings was observed for coatings with higher W contents. Addition of a moderate amount (from 16 to 22 at.%) of W to the TiC/TiB₂ coatings reduced the damage diameter around indentations, and resulted in a less-severe cracking mode. Reciprocating sliding wear tests at a lower initial stress of 1.33 GPa, indicated addition of W to the TiC/TiB₂ matrix resulted in higher wear factors, whereas at a higher initial stress of 1.91 GPa, W-containing TiC/TiB₂ films had lower wear factors than for the pure TiC/TiB₂ coating. This behavior suggests a load (or stress) sensitive wear behavior for these films.

Addition of W to TiC/TiB₂ coatings favorably improves the tribological properties of this coating system, with the suspected reason being the incorporation of a larger size atom (e.g., W) into the coating structure, resulting in a higher density film with higher hardness.

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Structure and Mechanical Properties of Magnetron Sputtered Coatings in the Ni-Al-N Ternary System

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Abstract

NiAl and NiAl-AlN coatings were deposited using RF magnetron sputtering in different argon-nitrogen atmospheres from a NiAl compound target. In this paper, the NiAl and Ni-Al-N film structures and mechanical properties, including nanohardness, Young's modulus, film adhesion and residual stress, are presented together with their tribological behavior. The best properties and performance were achieved by

depositing the film with a 50 nm thick titanium interlayer and using a substrate bias of 50 volts. With increasing the nitrogen content in the sputtering atmosphere, the AlN content in the Ni-Al-N coatings increases, the film hardness, Young's modulus, friction coefficients, and wear resistance increase, but the film adhesion becomes worse and the compressive residual stress becomes larger. Overall, the film deposited in an argon-nitrogen atmosphere with 10% nitrogen exhibited the best mechanical performance.

Table 1. Process Parameters for Deposition of Ni-Al-N Coatings

Parameters	Range of Values
Base Pressure	$<1 \times 10^{-3}$ Pa
Pressure of the Ar-N ₂ Sputtering Atmosphere	0.4 Pa
Amount of N ₂ in the Sputtering Atmosphere	0, 5%, 10%, or 20%
RF Power Density	4.67 to 18.67 W $\times$ cm ⁻²
Substrate-to-Target Distance	70 mm
Substrate Bias	0 or -50 volts
Substrate Preheating	No
Substrate Temperature (Estimated)	From 310 to 420 K

1.0 Introduction

Coatings in the Ni-Al-N ternary system have been developed as non-sticking (by molten glass), oxidation resistant, and wear resistant coatings for glass molding dies and forming tools.¹ In this work, NiAl and NiAl-AlN coatings have been deposited using RF magnetron sputtering in different argon-nitrogen atmospheres from a NiAl compound target synthesized by a one step SHS-consolidation technique.^{2,3} The NiAl coating has been identified as a promising “working layer” since it has excellent oxidation resistance and non-wettability to molten glass.⁴ The purpose of this paper is to report results on mechanical properties and tribological performance of magnetron sputtered NiAl and NiAl-AlN thin films, and discuss the relationships among deposition parameters, film structure and these properties.

2.0 Methods

Table 1 lists the typical sputtering parameters applied to the film deposition process. Various substrates, including H13 tool steel, AISI 304 stainless steel, glass, and Si<100> wafers, were used in this work. Before being placed into the chamber for deposition, all substrates were ultrasonically cleaned consecutively in acetone, ethanol, and deionized water for 30, 15, and 10 minutes, respectively. Before deposition of Ni-Al-N coatings with substrate bias, the PVD chamber was back-filled with argon to 0.67 Pa and the substrate bias was set to -500 volts, producing a glow discharge sputter etching of the substrate. Sputter etching of the substrates was not conducted for the set of coatings deposited without substrate bias. When a titanium adhesion layer was produced prior to the deposition of Ni-Al-N coatings, a 50 nm thick titanium thin film was sputtered

from a titanium target using 1.5 kW (3.1 W $\times$ cm⁻²) power from a 40 kHz AC plasma source. The films used for the characterizations described in this paper (a general film thickness of about 2 μ m) were deposited using a RF power density of 11.2 W $\times$ cm⁻², otherwise, the power density will be noted separately in this paper.

A Siemens D-500 KRISTALLOFLEX-810 (Karlsruhe, Baden-Württemberg, Germany) X-ray diffraction (XRD) with CuK α radiation was used to characterize the film's crystal structure. Both scanning electron microscopy (SEM) (JOEL JXA-840) and scanning transmission electron microscopy (STEM) (PHILIPS CM200) were used to capture photomicrographs and study the film's microstructure.

A MTS (MTS Systems Corporation, Eden Prairie, Minnesota, U.S.A) Nano Indenter XPiI was used to perform depth sensing nanoindentation testing on the coatings and to obtain values of nanohardness and Young's modulus. The nanoindenter was run in a continuous stiffness mode (CSM) with a dynamic contact module (DCM). In order to obtain statistical results, all coatings used for nanoindentation testing were deposited on the same AISI 304 stainless steel substrates, and at least ten indentations were made for each coating. The maximum indentation depth for each coating was at the level of 10% of the film thickness.

Adhesion scratch tests were conducted on each coating using a Teer Coatings, Ltd. (Hartlebury, Worcestershire, U.K), model ST-2200 scratch tester,⁵ with a Rockwell C diamond stylus (200 μ m radius and 120° apex angle). The film adhesion to the substrate was assessed by determining the critical load of failure, L_c , which was the average value recorded over a minimum of five runs for each film. Wear testing was conducted by means of multi-pass scratch testing using a 5 mm diameter WC-Co ball with the Teer Coatings ST-2200 scratch tester. Five and ten Newtons were

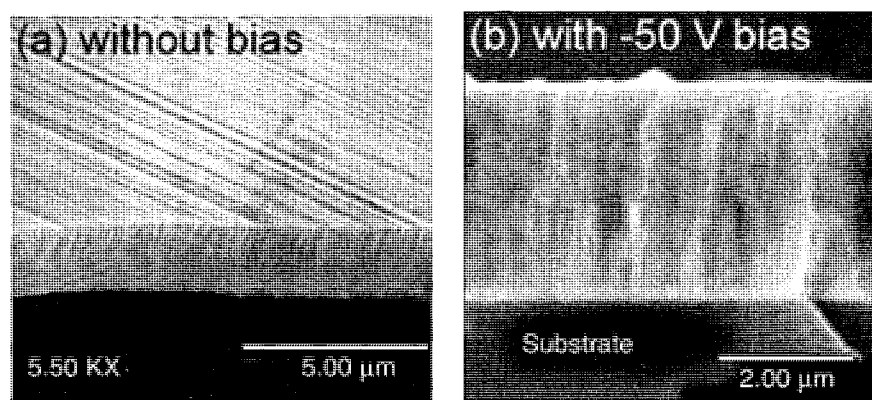


Fig. 1: Comparison of fractured cross-sectional SEM photomicrographs of NiAl thin films deposited on AISI 304 stainless steel substrates using (a) $18.67 \text{ W} \times \text{cm}^2$ target power and no substrate bias and (b) $11.2 \text{ W} \times \text{cm}^2$ target power and -50 volts substrate bias, respectively.

chosen for the loads to test the coatings deposited without and with substrate bias, respectively. All other test conditions were maintained the same for all runs. At least five runs were made for each coating to obtain statistically valid results. To determine the wear volume, samples were analyzed using a Veeco/Wyko optical profilometer (Tucson, Arizona, U.S.A). The friction coefficients of the WC-Co ball on the coatings were determined from the friction data taken from the wear tests.

The residual stresses in the coatings were determined using XRD methods,⁶ namely, $\sin^2\chi$ X-ray analysis for NiAl films and $\sin^2\psi$ X-ray analysis of the {110} NiAl planes for NiAl-AlN thin films.

3.0 Results

3.1 Film Structure

The film stoichiometry and the chemical states of elements in the films were investigated using x-ray photoelectron spectroscopy (XPS).³ Equiatomic NiAl films were deposited by magnetron sputtering of a NiAl target in a pure (99.9999%) argon atmosphere. When the nitrogen content in the argon-nitrogen sputtering gas was increased from 5 to 20%, the relative atomic concentration of nitrogen in the films varied from about 9 to 30%. Introducing nitrogen into the sputtering gas resulted in the formation of AlN in the Ni-Al-N films.

The texture and microstructure of NiAl and NiAl-AlN thin films deposited without substrate bias were characterized by XRD, SEM and TEM, and presented in previous papers.^{2,3} The unbiased NiAl and Ni-Al-N

thin films showed (110) NiAl to be the dominant XRD peak. The average crystallite size was estimated by the Scherrer equation from the broadening of the x-ray diffraction lines.⁷ The NiAl particle size was approximately 12 nm in the NiAl films. Introducing nitrogen significantly reduced the NiAl grain sizes in the NiAl-AlN films, ranging from about 5 to 1.3 nm as nitrogen content varied from 5 to 20%. The typical microstructure of unbiased NiAl films was determined to be a fibrous columnar zone T crystalline microstructure with a thin featureless quasi-amorphous layer beneath, whereas the unbiased NiAl-AlN films contained a homogeneous microstructure with very fine nano scale NiAl (110) grains distributed in an amorphous matrix.

When a -50 V substrate bias was applied during sputtering, the NiAl film exhibited the same crystallographic phases as those for unbiased NiAl films, but had larger grains (~15 nm) than did the unbiased film. Figure 1 compares the fractured cross-sectional SEM photomicrographs of the NiAl thin film deposited with -50 volts substrate bias to that of the unbiased film. The biased NiAl film exhibited a typical columnar zone T microstructure with denser fibrous grains than that of the unbiased film.

There is no peak other than NiAl (110) exhibited in the XRD patterns of NiAl-AlN coatings deposited without substrate bias. However, very different XRD patterns were observed for Ni-Al-N thin films deposited with -50 volts substrate bias. Upon increasing the nitrogen content from 5 to 20% in the sputtering atmosphere weakened the NiAl(110) peak, while AlN peaks became stronger and observable as either cubic

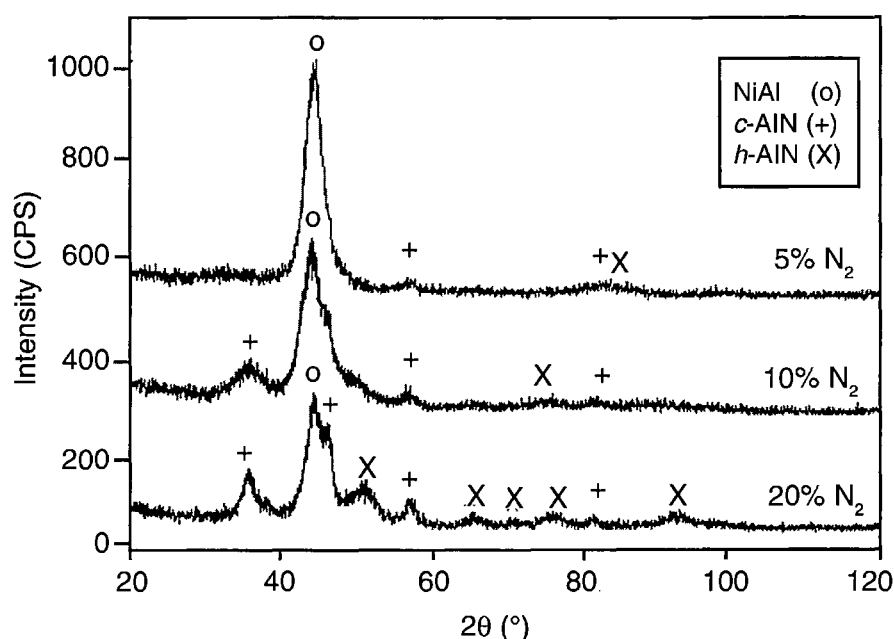


Fig. 2: XRD patterns of NiAl-AlN thin films on Si<100> wafers deposited with -50 volts substrate bias in different (Ar + N₂) atmospheres: 5, 10, and 20% nitrogen, respectively. An incident glancing angle of 2° was used in the XRD analysis.

or hexagonal phases (see Figure 2). As indicated in the fractured cross-sectional SEM photomicrographs, the biased NiAl-AlN films exhibited a dense and featureless microstructure.

3.2 Nanohardness and Young's Modulus

Figure 3 shows the nanohardness and Young's modulus of Ni-Al-N films as a function of substrate bias and sputtering atmosphere. The values of nanohardness and Young's modulus of both unbiased and biased NiAl thin films were approximately 14 and 205 GPa, respectively. The Young's moduli of the NiAl films are higher than those of the NiAl target, which was determined to be 169 GPa by resonant ultrasonic spectroscopy (RUS). The Ni-Al-N thin films showed increased nanohardness and Young's moduli when a -50 V substrate bias was applied. When nitrogen was introduced into the sputtering atmosphere, the Young's moduli decreased initially, then increased from 180 to 211 GPa as the nitrogen content in the sputtering atmosphere increased from 5 to 20%. The nanohardness of Ni-Al-N coatings increased with the nitrogen content in the sputtering gas. Values for nanohardness ranged from 15 GPa for films deposited at 5% nitrogen to 18 GPa for films deposited at 20% nitrogen.

3.3 Film Adhesion to Substrate

As listed in Table 2, the average critical loads of coatings deposited with -50 V substrate bias were in the range of 20-30 N for films deposited onto AISI 304 stainless steel substrates and on the order of 28-35 N for films deposited onto H13 tool steel substrates. Compared to the coatings deposited without substrate bias, the adhesion of Ni-Al-N coatings to AISI 304 stainless steel substrates was improved by approximately 15 Newtons when a substrate bias was applied. As expected, the deposition of a 50 nm thick titanium adhesion layer prior to the deposition of Ni-Al-N coatings further improved the adhesion by a magnitude of approximately 7 N.

3.4 Tribological Behavior

The volumetric wear factors and friction coefficients of the Ni-Al-N coatings against a WC-Co ball counter surface are shown in Figures 4 and 5, respectively.

The volumetric wear factors of the films deposited without substrate bias decreased with increasing nitrogen content in the coating. The improvement in wear resistance is thought to be due to the relative concentration of the AlN component in the coatings

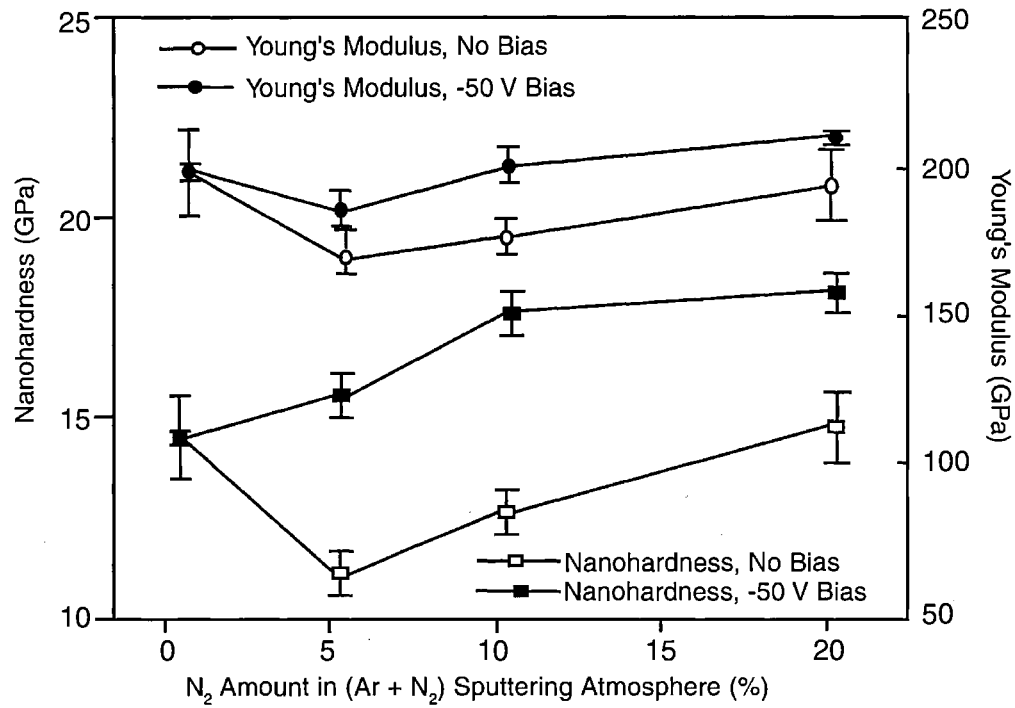


Fig. 3: Nanohardness and Young's modulus of the Ni-Al-N thin films as a function of the nitrogen content in the argon-nitrogen sputtering atmosphere. Comparison is also made between the coatings deposited with substrate bias of -50 volts and those deposited without substrate bias. Error bars are shown for all data points. Largest standard deviation occurred for the NiAl film deposited without substrate bias, namely, ± 1.15 GPa for nanohardness, and ± 10.66 GPa for Young's modulus.

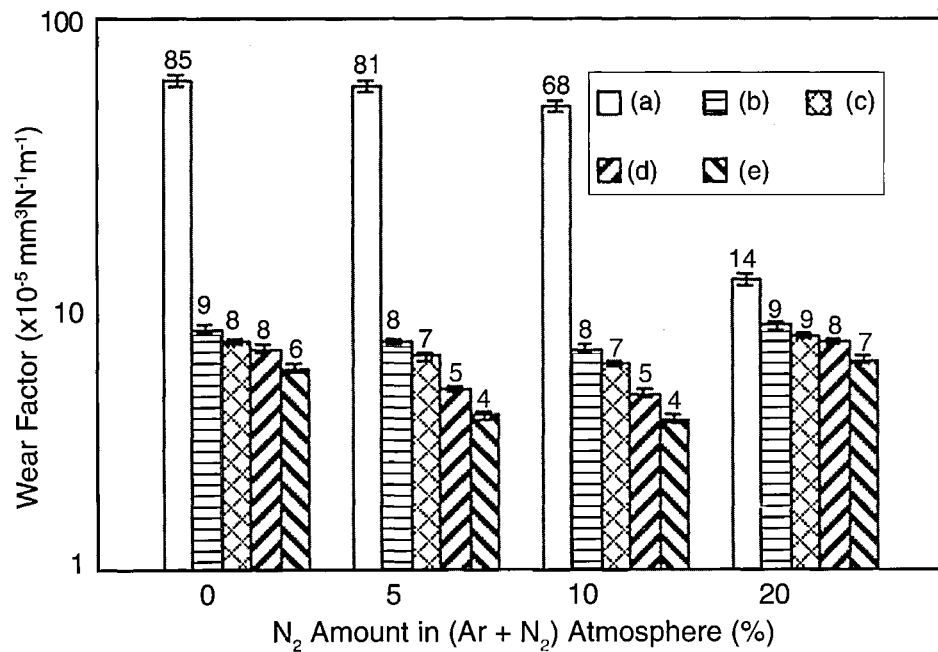


Fig. 4: Volumetric wear factors of the NiAl and NiAl-AlN coatings against WC-Co ball. The coatings were deposited under different conditions: (a) without substrate bias, on AISI 304 stainless steel, (b) with -50 V substrate bias, on AISI 304 stainless steel, (c) with -50 V bias and 50 nm thick titanium interlayer, on AISI 304 stainless steel, (d) with -50 V substrate bias, on H13 tool steel, and (e) with -50 V bias and 50 nm thick titanium interlayer, on H13 tool steel. Error bars are shown at the top of the columns. NiAl film deposited without bias on AISI 304 stainless steel showed the largest standard deviation of $\pm 4.2 \times 10^{-5} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$.

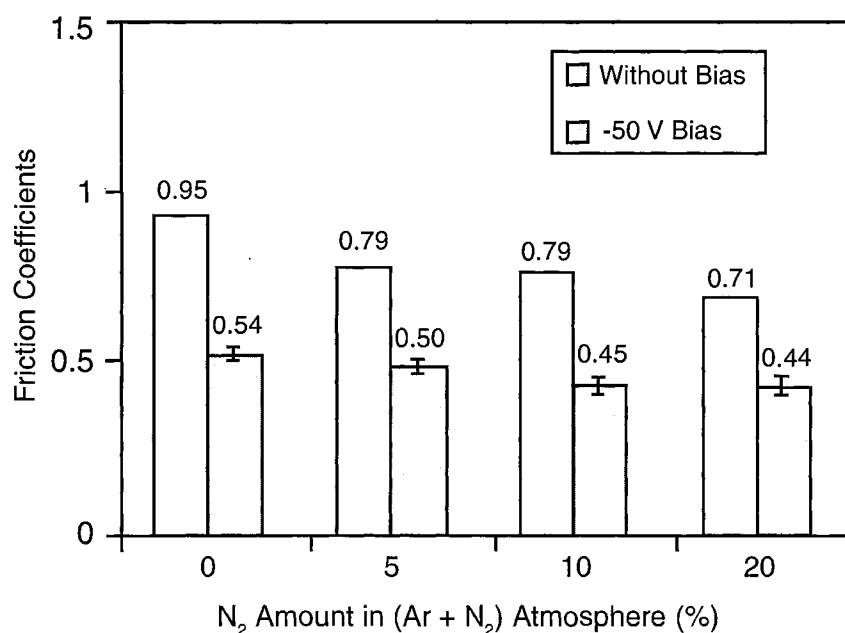


Fig. 5: Friction coefficients of the NiAl and NiAl-AlN thin films as a function of nitrogen content in the (Ar + N₂) sputtering atmosphere. Error bars are shown at the top of the columns. The largest standard deviation is of ± 0.076 .

Table 2. Average Critical Loads of Failure (in Newtons) of Ni-Al-N Films Deposited Under Different Conditions

Deposition Conditions			NiAl (N)	NiAl-AlN (N)		
Substrate	Bias (V)	Interlayer		5%	10%	20%
AISI 304 Stainless Steel	0	No	16.7	10.5	11	9.9
	-50	No	30	26	27	20
	-50	50 nm Ti	37	34	34	30
H13 Tool Steel	-50	No	35	32	31	28
	-50	50 nm Ti	40	37	38	34

Note: Data errors of critical loads are within 1.6 Newtons.

sputtered in nitrogen, since AlN is more wear-resistant than NiAl. Compared to the unbiased films, the wear factors of the coatings deposited with a -50 V substrate bias were reduced substantially. Only a slight difference was observed for wear factors among biased coatings deposited in different amounts of nitrogen. These results together with the critical loads as shown in Table 2 indicate that the AlN or nitrogen content in the Ni-Al-N

coatings has less effect on the wear resistance, as long as the film adhesion to the substrate is substantially improved. However, improved wear resistance due to the presence of AlN is still noticeable in Figure 4. On the other hand, as expected, depositing a 50 nm thick titanium adhesion interlayer further improved the wear resistance. The biased coatings deposited on H13 tool steel substrates exhibited better wear performance than

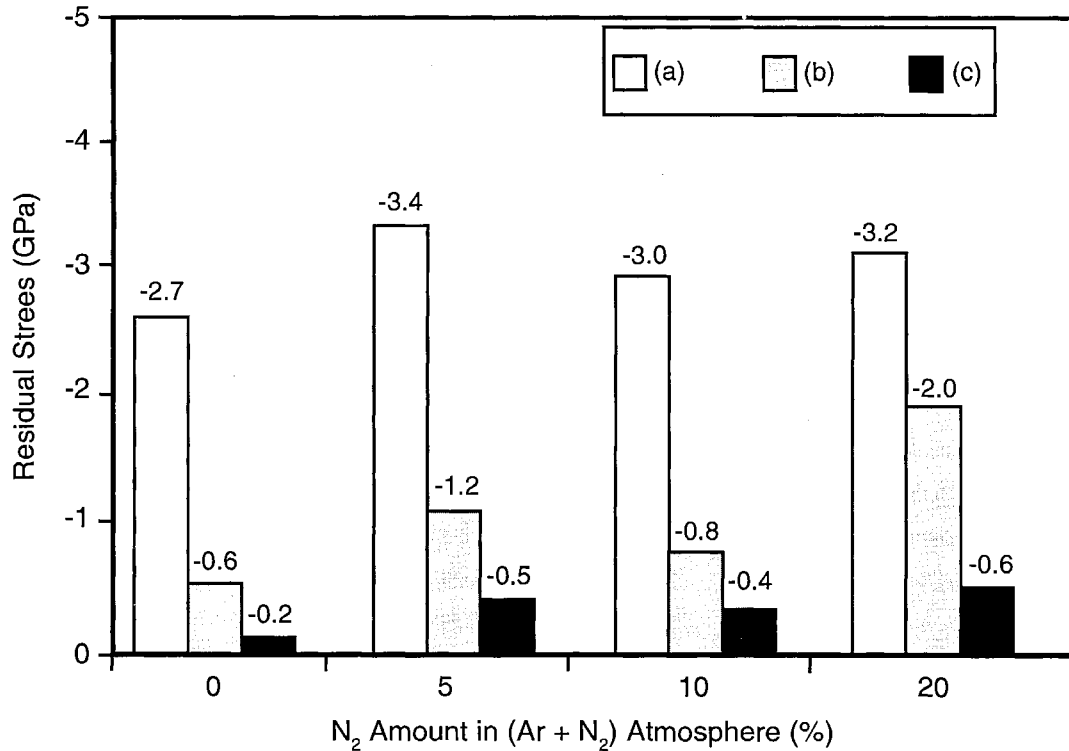


Fig. 6: Average residual stress values for thin films on AISI 304 stainless steel substrates in the Ni-Al-N system deposited under different conditions: (a) without substrate bias or Ti interlayer, (b) with -50 volts substrate bias, but without Ti interlayer, and (c) with -50 volts substrate bias and Ti interlayer. Data errors are within 15%.

those on AISI 304 steel substrates. In summary, the biased coating deposited in 10% nitrogen with a titanium adhesion layer performed best and exhibited a wear factor of $6.6 \times 10^{-5} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$ on AISI 304 stainless steel substrate, and $4 \times 10^{-5} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$ on H13 tool steel substrate.

The friction coefficients of both unbiased coatings and biased coatings exhibited the same trend, i.e., decreasing with increasing nitrogen content, as shown in Figure 5. This trend indicates that the friction coefficient of Ni-Al-N thin films is a function of the AlN or nitrogen content in the coating. However, the differences in friction coefficient among biased coatings are smaller than those among unbiased coatings. The average friction coefficient of Ni-Al-N coatings deposited with -50 volts substrate bias is 0.48.

3.5 Residual Stress

Figure 6 shows the estimated average residual stress values for thin films on AISI 304 stainless steel substrates in the Ni-Al-N system. It is important to note that a large scatter in the data was observed while constructing the lattice parameter vs. $\sin^2\psi$ or $\sin^2\chi$ plots. Nevertheless,

some general trends could be observed, and qualitative comparisons among different coatings are still valid since they were all measured using the same instrument with the same experimental conditions. The films deposited without substrate bias exhibited high compressive residual stresses on the order of 3-4 GPa. Using a -50 V negative bias voltage reduced the magnitude of compressive residual stresses significantly. The addition of a 50 nm thick titanium interlayer also reduced the magnitude of compressive residual stresses.

The residual stresses were found to be substrate dependent. For instance, the unbiased NiAl films were determined to have lower compressive residual stresses on Si (-0.99 GPa) and on glass (-0.25 GPa), in comparison to those on AISI 304 stainless steel. Thus, it seemed that sputtered coatings exhibited larger compressive residual stresses on softer substrates and smaller residual stresses on stiffer substrates.

4.0 Discussion

Sputtering gas composition was an important variable in the sputter deposition of coatings in the Ni-Al-N system. The nitrogen amount incorporated into

the Ni-Al-N thin films was in proportion to the nitrogen content in the sputtering atmosphere. Sputtering gas composition affects the film stoichiometry and defect concentration, and thus the film structure, properties and performance. Introducing nitrogen into the sputtering atmosphere changed the film from a typical columnar zone-T microstructure of NiAl films to quasi-amorphous nano-composite NiAl-AlN films, since the adsorbed nitrogen atoms reduced adatom mobility and the subsequent grain growth.⁸ Consequently, the film properties and performance were affected by the film stoichiometry. Introducing nitrogen into the deposited Ni-Al-N films, the critical loads reduced slightly, residual compressive stresses increased slightly, but wear resistance improved slightly. The nanohardness, Young's modulus, and friction coefficient are more composition dependent than other properties. Increasing the nitrogen content in the Ni-Al-N films caused the nanohardness and Young's modulus to increase and the friction coefficients to decrease. These changes in mechanical properties can be related to the AlN content in the Ni-Al-N films.

Substrate bias played an important role in the deposition of Ni-Al-N thin films using RF magnetron sputtering. A negative substrate bias of 50 V increases the energy and momentum of impinging particles, and acts to densify the film by accelerating plasma ions across the plasma sheath and thus energetic particle bombardment to the substrate during deposition. Consequently, substrate bias has a significant effect on the film microstructure, and thus film properties such as density/porosity, residual stress, adhesion of film to substrate, and wear resistance. Compared to unbiased films, applying a substrate bias of -50 volts during deposition of Ni-Al-N thin films resulted in larger NiAl grains and crystallization of AlN particles. This significantly reduced the compressive residual stresses and improved the film adhesion to substrate and the wear resistance of the film.

Substrate temperature during the deposition of thin films in the Ni-Al-N system was not an independent variable, but was affected by other deposition process parameters such as target power and substrate bias. The increase of substrate temperature observed in this work resulted from sputter etching of the substrate prior to the film deposition process and substrate bias during the film deposition process. Substrate temperature plays an important role in atomistic film growth by controlling surface motion and bulk diffusion, and thus has a significant effect on the film structure and properties.

Comparing the various results presented above provides the following summary of relationships among film properties. The adhesion of the film to the substrate

is inversely related to the compressive residual stress. Compressive residual stresses in the coatings were observed to have a detrimental effect on the film adhesion. The wear resistance is positively related to the film adhesion. In general, the better the adhesion, and the smaller the compressive residual stress, the better the wear resistance.

5.0 Conclusion

This work investigated structure, mechanical properties and tribological performance of the Ni-Al-N thin films deposited using RF magnetron sputtering from a NiAl compound target.

Applying a substrate bias of -50 volts during the deposition process of Ni-Al-N coatings resulted in denser and more completely crystallized films, and improved the film properties and performance significantly. The addition of a 50 nm thick titanium adhesion interlayer also improved the film properties and performance. On the other hand, the Ni-Al-N thin films exhibited an apparent difference in mechanical properties due to the difference in composition of thin films deposited in different argon-nitrogen atmospheres. Overall, the NiAl-AlN film deposited in 10% nitrogen possessed the best mechanical properties and tribological performance.

6.0 Acknowledgments

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Correlation of Nitrogen Gas Processing Level to Structural and Tribological Properties of MoS₂/Ti/N Solid Lubricated Coatings

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Abstract

There has been much interest recently in PVD deposited solid lubricants consisting of MoS₂ doped with a metal such as Ti. Coatings have been deposited for this study by unbalanced magnetron co-sputtering of MoS₂ and Ti targets in Ar and Ar/N₂ low pressure plasmas. This study examines the effect of nitrogen gas processing level on compositional and structural properties of the coatings and on tribological behavior of coatings during extensive wear testing. It is shown

that the presence of nitrogen resulted in microstructural densification, amorphization, and hardening (up to 40% harder), but at the cost of poorer adhesion and increased friction during wear testing. Physical testing methods used included: scratch testing, multi-pass wear testing, and environmental (elevated humidity) pin-on-disc testing. A Hiden EQP quadrupole mass spectrometer was also used to analyze plasma species and energies of ions present during deposition to determine the effect of the nitrogen gas processing level on plasma conditions. These probe data

indicate that molecular nitrogen incorporation could be a significant cause of coating embrittlement for high nitrogen gas processing levels. Finally, wear rates of the coatings are compared to Teer Coatings' commercially available MoST®.

1.0 Introduction

The use of sputter deposited MoS₂-based coatings for wear applications is increasing in popularity. The low shear strength of MoS₂ layers makes it an ideal low friction coating candidate. The addition of a metal such as titanium densifies the structure, making it harder and resistant to oxidation, a weakness of this class of coatings. The resulting coating is typically amorphous but has excellent wear properties under a variety of testing conditions and is solid lubricated. The formation of a transfer layer between coating and counterface keeps friction forces to a minimum; friction is limited to sliding between the easily shearing basal planes of the strained MoS₂ structure.^{1,2} Coefficients of friction are often close to zero, in cases of low to moderate loading.³

Many studies have suggested that re-orientation of the basal plane parallel to the substrate occurs as the result of sliding.² The use of AFM in the wear track shows evidence that after wear the sliding surface can be composed of a mosaic of atomically clean basal plane oriented grains with disorder around the *c* axis.⁴ When the coating is examined as a whole, the wear mechanism will develop two distinct regions within the coating. The bulk of the coating is relatively unaffected by the wear process, while the buffer layer and transfer film are responsible for the lubrication properties. The buffer layer typically has a reduced grain size in the *c* direction and has a turbulent pattern of basal plane orientations.^{5,6} The wear of the coating involves two simultaneous processes:

1. Materials transfer from the coating to the buffer layer, and
2. From the buffer layer to the counterface.

Friction coefficients of sputter deposited MoS_x coatings have been shown to exhibit a minimum in the substoichiometric range. The microstructure of coatings with $1.4 < S/Mo < 1.8$ exhibit the molybdenite hexagonal structure while coatings with lower sulfur content are amorphous.⁷

A primary method for reducing oxidation and improving friction characteristics is densification of the microstructure. Densification can be accomplished in-situ during deposition through ion beam assisted deposition (IBAD)⁸ or via a high ion bombardment sputtering method such as closed-field unbalanced magnetron sputtering.⁹ Densification reduces the surface area of the coating available for oxidation.¹⁰ Another

method of densification is the process of doping MoS₂ with a metal such as titanium.^{9,11} This study begins with a MoS₂ structure already densified by the addition of titanium, and examines the possibility of improving the resistance of a MoS₂/Ti coating to moisture and oxidation by introducing nitrogen gas during sputter deposition.

2.0 Methods

2.1 Deposition Techniques

All coatings in this study were deposited by closed-field unbalanced magnetron sputtering onto hardened and polished M4 tool steel substrates. Unbalanced water-cooled magnetrons of opposite polarity were used to simultaneously power two sputtering targets: Ti and compound MoS₂. The targets were oriented in a 90° co-sputtering arrangement, as shown in Figure 1. In this way, a high sputter rate could be achieved and a mass spectrometer could be substituted for the substrate holder for plasma diagnostic analysis. To produce a homogenous coating, the substrate holder was arranged within the plasma flux, in this way the surface of the substrate was situated to each target at the same angle.

Three Advanced Energy MDX-L DC power supplies were used during the sputtering process. One was connected to the substrate holder to provide the substrate with a negative bias voltage. The titanium target was powered by a magnetron connected to one of the DC power supplies, while the DC supply powering the magnetron for the MoS₂ target was also connected to an AE Sparc-le unit, which transforms the DC signal to a pulsed square wave signal. The Sparc-le was used in "Active Arc" mode, meaning that during arcing the power supply would pulse the DC signal to minimize coating damage.

The first 5 minutes of the sputtering process were identical for every run. While a substrate bias of -300 V was applied, the Ti magnetron was operated at 0.12 kW in order to sputter clean the substrate surface. The second step was the deposition of a titanium interlayer. In this stage, the substrate bias was reduced to -50 V, while the Ti magnetron power was turned up to 1.2 kW. This power level was used for another 5 minutes. The third stage of the coating was a 25 minutes co-deposition of MoS₂ and titanium. While the Ti magnetron power was reduced, the power of the MoS₂ magnetron was increased from zero to a specified level, which was maintained during the entire deposition. The original intent was to keep the sum of the magnetron power levels at approximately 2.0 kW so that the substrate heating would be equal between coatings and also that the thickness of the coatings would be comparable. Nitrogen gas was added

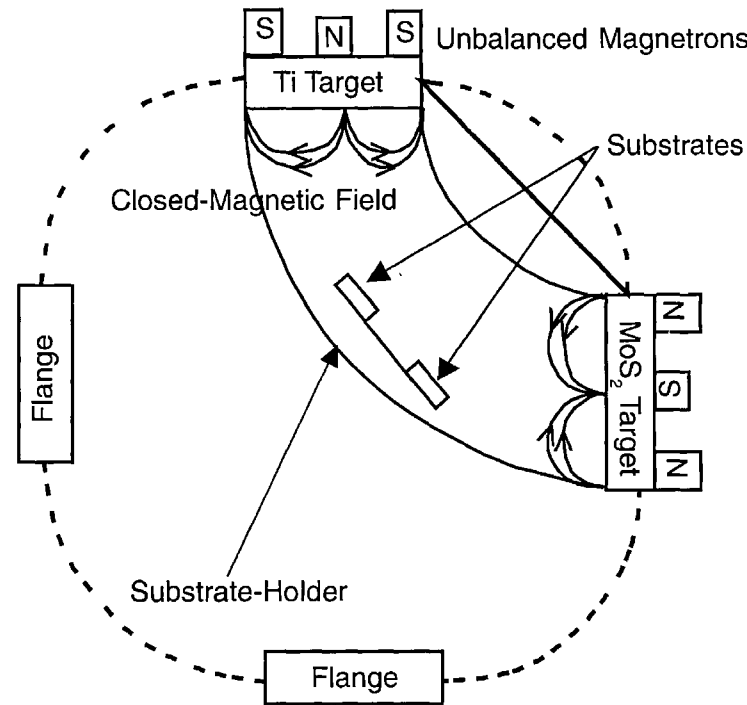


Fig. 1: Top view of the 90° co-sputtering arrangement.

Table 1. Process Parameters for Select MoS₂/Ti and MoS₂/Ti/N Coatings

Coating Name	Total Pressure (mT)	N ₂ Gas Processing Level (%)	Ti Power (kW)	MoS ₂ Power (kW)	Substrate Bias (V)	Coating Thickness (μm)
MoS ₂ /Ti-2	3.0	0	0.30	1.70	-50	1.66
MoS ₂ /Ti/N-1	3.0	10	0.21	1.20	-50	1.24
MoS ₂ /Ti/N-2	3.0	20	0.21	1.20	-50	0.91
MoS ₂ /Ti/N-3	3.0	30	0.21	1.20	-50	0.84
MoS ₂ /Ti/N-6	3.0	60	0.60	1.20	-50	1.30

during deposition after interlayer deposition. The nitrogen gas processing level is defined as the ratio of nitrogen gas partial pressure to the total working gas pressure (both nitrogen and argon). The specific deposition parameters of each coating are shown in Table 1.

2.2 Coating Analysis and Mechanical Evaluation

All coatings were analyzed and tested using the same methods. All coatings were analyzed using x-ray

diffraction in standard $\theta/2\theta$ mode with 2θ varying between 5 and 80°. Cross-sectional Transmission Electron Microscopy (XTEM) was used to analyze the microstructure of the two best performing coatings, MoS₂/Ti-2 and MoS₂/Ti/N-1.

Initial performance evaluation consisted of Knoop microhardness testing and scratch testing. Knoop testing was performed using loads of 10, 25, and 50 gm-f. Generally, hardness decreased as a linear function with increased applied load. The measured hardnesses were plotted as a function of the applied load and the maximum hardness of the coating was determined at

the zero point of the applied load. Scratch testing was performed using a Teer ST-2200. The standard rate of increasing the load for hard coatings is 100 N/min; this standard was used to test these coatings. The scratching speed used was 10 mm/min. The scratch tester was also used for multi-pass wear testing, using a 5 mm diameter WC-Co ball moving at 150 mm/min with a period of 2 s (2 mm track length). In order to analyze the lifetime of the coating, a load of 30 N was applied for a maximum duration of 3000 cycles. Wear rates were calculated by dividing the average cross-sectional wear area by the duration of the test. Wear rates reported at varying humidity levels were calculated for samples that were tested in an environmental pin-on-disc apparatus because they could not easily be tested at elevated humidity using the linear multi-pass apparatus.

2.3 Evaluation of Plasma Conditions

A Hiden Electrostatic Quadrupole Probe (EQP) mass spectrometer was used in the course of the research work to determine neutral and positive ion distributions in the plasma. The EQP uses an electrostatic sector field analyzer for ion energy analysis. Ions are detected using a pulse counting ion detector. The EQP has two primary modes of operation: residual gas analysis (RGA) or secondary ion mass spectrometry (SIMS) mode to detect positive or negative ions. The former utilizes an ionization source within the front end of the EQP in order to ionize atoms immediately after entering the probe orifice. In this study an orifice of 100 μm diameter was used. The EQP is differentially pumped using a (60 l/s) turbomolecular pump along with a rotary pump in order to achieve base probe internal pressures of 1×10^{-9} Torr. When typical gas pressures (several mT) are used in the chamber, the internal pressure increases to a value of 1×10^{-7} Torr.

The probe was mounted to a flange and positioned so that the sampling orifice would be located in approximately the same position and the same angle as the substrates. Deposition conditions were repeated without the substrates present, and data was collected in both RGA and positive ion SIMS modes. In addition to repeating deposition conditions, additional process levels were analyzed to provide a greater range of data. For example, nitrogen gas processing levels were varied between 0 and 70%. Only data collected in RGA mode will be presented for the sake of brevity.

2.4 Teer Coatings' MoST[®] Coating

Teer Coatings Ltd. is the commercial leader in the sputter deposition of solid-lubricant coatings, and uses

the trade name of MoST[®] for their MoS₂-based coatings. For this study, Teer Coatings Ltd. provided three samples each of three varieties of coatings: MoS₂, MoST[®] (low titanium content), and MoST[®] (high titanium content). In this paper, the coatings will be referred to as: TC-MoS₂, TC-MoST(l), and TC-MoST(h), respectively. All samples were deposited on hardened M2 high-speed tool steel, which had been ground to 600 grit (and unpolished) before deposition. All TC coatings were deposited using closed-field magnetron sputtering of multiple targets without the presence of nitrogen gas.

3.0 Results

3.1 Structure and Composition Analysis

The range of coatings deposited using a MoS₂ target using varying N₂/Ar pressure ratios has been tested. EDS detected the presence of molybdenum and sulfur; nitrogen is not detectable by that system. In accordance with previous studies, the sub-stoichiometric limit of MoS_{2-x} was detected, with x varying from 0.18 to 0.74 with increasing nitrogen (up to 60%), as shown in Figure 2. Only nitrogen was present in addition to argon. Figure 3 is a ternary phase diagram of the composition (in atomic percent) showing a sampling of the compositions produced before and after adding nitrogen during processing. The compositions became increasingly sulfur deficient as a result of the addition of nitrogen, although the ratio of Mo:Ti remained constant.

X-ray diffraction traces of MoS₂/Ti coatings produced with the nitrogen processing levels of 10, 20, and 30% are shown in Figure 4. The XRD traces of the MoS₂/Ti/N coatings show a very small to negligible MoS₂ (002) basal plane peak. Small Ti (010) and TiN (111) peaks are visible in all three nitrogen-processed coatings (substrate peaks are indicated by an "S"). Figure 4 supports the possibility of a nano-crystalline microstructure: amorphous MoS₂ with fine interspersed titanium and titanium nitride crystals.

Cross-sectional Transmission Electron Microscopy (XTEM) analysis was made of two coatings with the best overall tribological performance: MoS₂/Ti-2 and MoS₂/Ti/N-1. The specimens used for XTEM analysis were MoS₂/Ti-2 and MoS₂/Ti/N-1 coatings on silicon wafer substrates. In Figure 5, a photo-micrograph of MoS₂/Ti-2 shows three regions: silicon substrate, titanium interlayer and amorphous MoS₂/Ti composite. Although predominately amorphous, it appears that there is a complex pattern most likely resulting from the angular sputtering expected for this co-sputtering configuration (Figure 1). The photo-micrograph of MoS₂/Ti/N shows only two regions: silicon substrate and amorphous

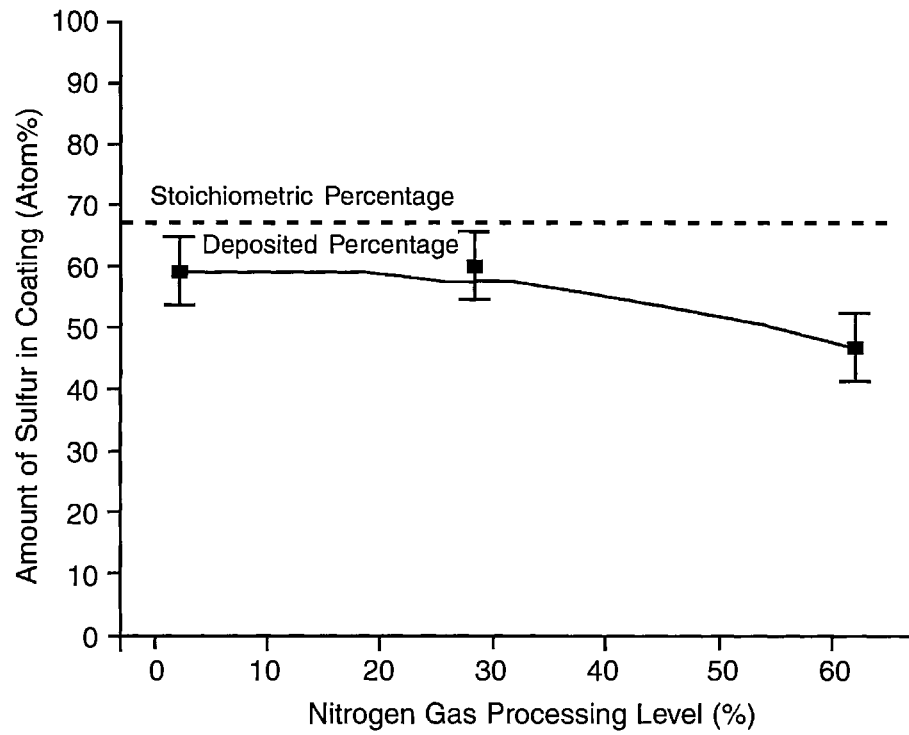


Fig. 2: Variation of sulfur content in $\text{MoS}_2/\text{Ti}/\text{N}$ coatings as determined by EDS.

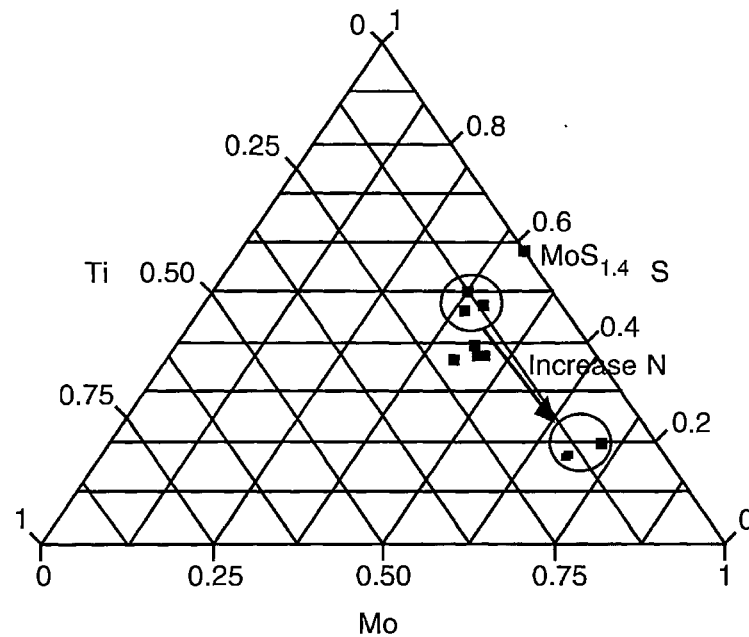


Fig. 3: Ternary phase diagram showing the stoichiometric effect of increasing nitrogen gas level during the deposition of MoS_2/Ti coatings.

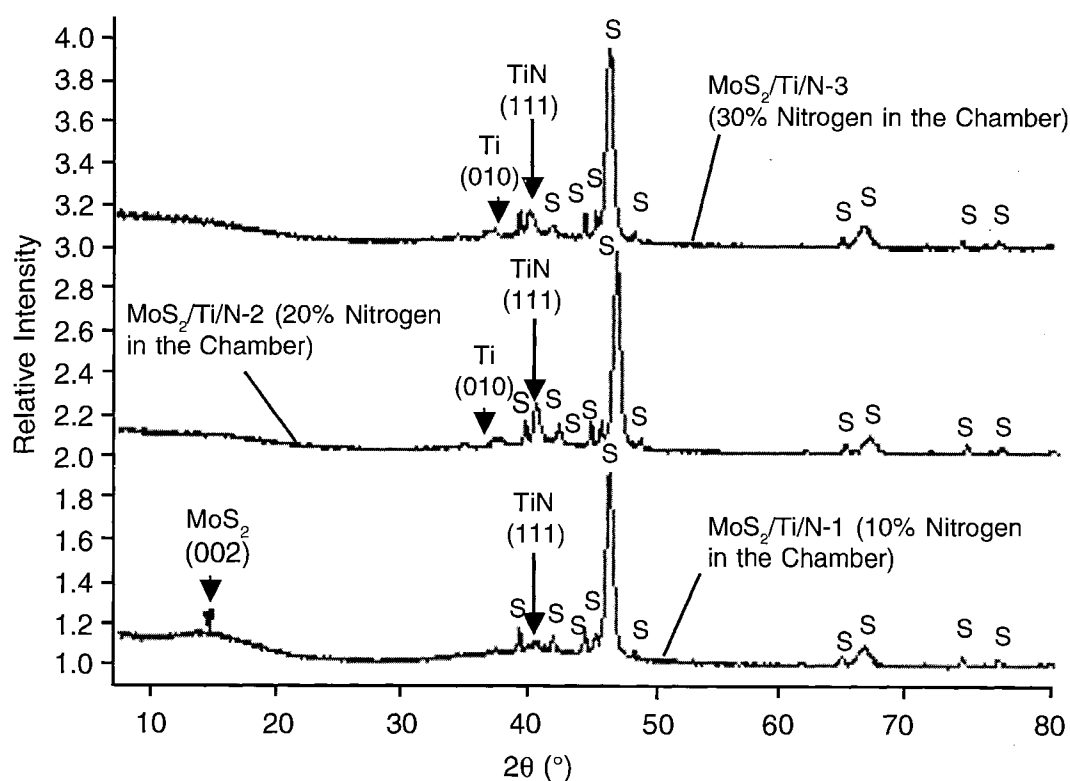


Fig. 4: XRD traces of the MoS₂/Ti/N coatings.

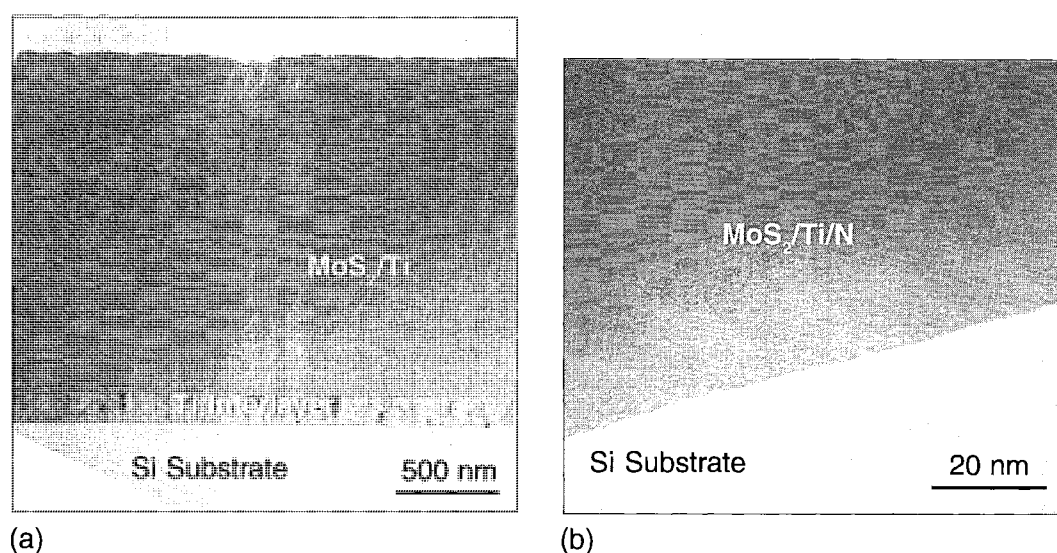


Fig. 5: XTEM photo-micrographs of (a) MoS₂/Ti-2 and (b) MoS₂/Ti-N1.

MoS₂/Ti/N composite. No titanium interlayer was visible in the coating although it was deposited as a discrete layer, suggesting that the presence of nitrogen made it more favorable for the titanium to become incorporated

in the bulk of the coating. It remains undetermined whether a composition gradient exists in the amorphous MoS₂/Ti/N coating, although the coating microstructure appears homogeneous.

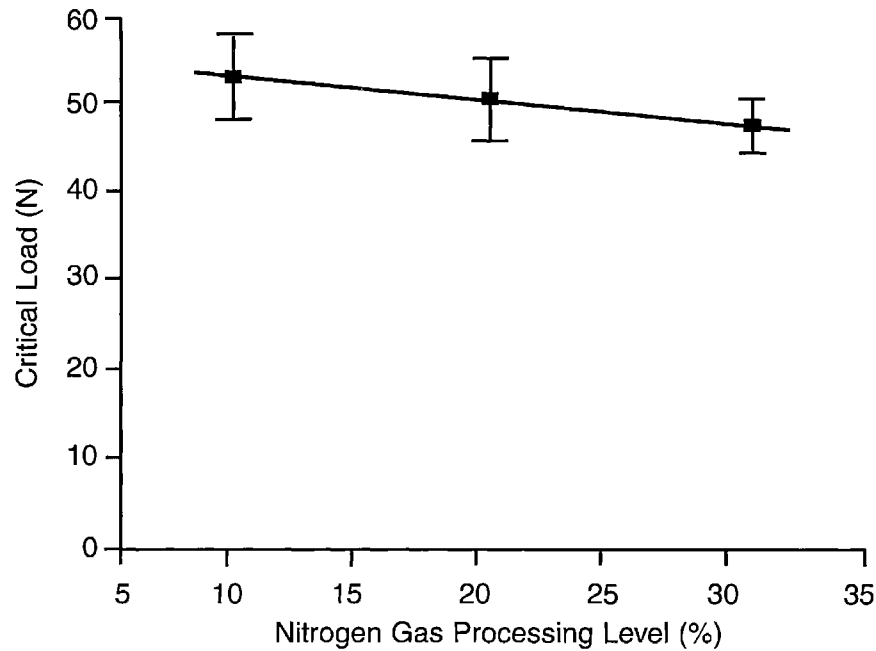


Fig. 6: Critical loads of the $\text{MoS}_2/\text{Ti/N}$ coatings compared to the nitrogen processing level.

3.2 Mechanical Properties

The effect of adding nitrogen during processing decreased the average critical loads of the coatings as shown in Figure 6. The presence of nitrogen made the coatings more brittle, as evidenced by cracking failure modes present during scratch testing (as opposed to shearing failure modes seen in MoS_2/Ti coatings). The average microhardness values increased slightly as shown in Figure 7. The average hardness value of 700 kgmm^{-2} was approximately 40% greater than the average value for MoS_2/Ti coatings.

3.3 Performance Evaluation and Comparison

The friction force response shown in Figure 8 more readily illustrates the wear behavior of the $\text{MoS}_2/\text{Ti/N}$ coatings. The steady state friction coefficient of the MoS_2/Ti -2 coating was 0.0245, while the friction coefficients of the nitrogen coatings were higher. The steady state friction coefficient of $\text{MoS}_2/\text{Ti/N}$ -1 was 0.037 and increased to 0.090 for $\text{MoS}_2/\text{Ti/N}$ -3. Even though the coefficients of friction were higher for nitrogen processed coatings, the wear rates for the $\text{MoS}_2/\text{Ti/N}$ coatings were lower than the best performing MoS_2/Ti coating, as shown in Figure 9. A reason for this improvement can be seen by comparing the effect of the

nitrogen processing level (over a wider range, from 0 to 60%) with the average coating hardness and average cross-sectional wear area. Figure 10 shows clearly that the hardest coating exhibited the least wear in an aggressive multi-pass wear test.

Two coatings were also tested under higher humidity levels in order to determine the effect of nitrogen on the wear behavior in a humid environment. MoS_2/Ti -2 and $\text{MoS}_2/\text{Ti/N}$ -1 were tested at three levels of humidity: 0% RH, 45% RH, and 75% RH ($\pm 5\%$ RH). Figure 11 shows that $\text{MoS}_2/\text{Ti/N}$ -1 consistently outperformed MoS_2/Ti -2, suggesting that low levels of nitrogen processing increased the ability of the structure to resist oxidation during wear processes. The lowest wear rate was exhibited by $\text{MoS}_2/\text{Ti/N}$ -1 at 45% RH. The wear rate of MoS_2/Ti -2 increased slightly with increasing relative humidity.

Figure 12 compares the wear rates of coatings produced for this study with those commercially available from Teer Coatings Ltd. The wear rates of the TC coatings were generally lower than the wear rates of the MoS_2/Ti coatings produced for this study, although $\text{MoS}_2/\text{Ti/N}$ -1 outperformed the commercially available TC-MoST(h) coating. For the 30 N multi-pass tests, the wear tracks of the TC-MoST and the TC-MoST(l) coatings were not measurable (NM) with the profilometers available for this study. The TC coatings were not tested using the environmental wear test apparatus.

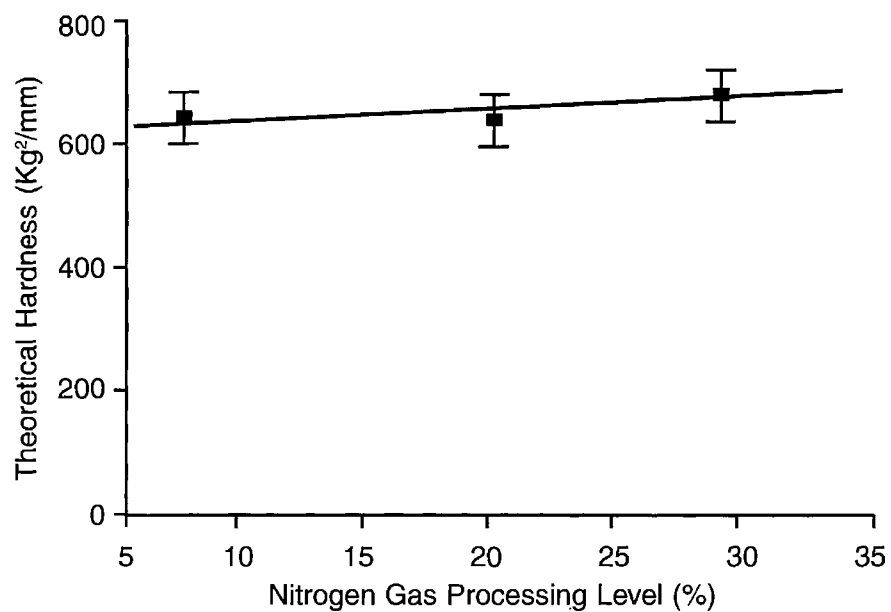


Fig. 7: Microhardness of the MoS₂/Ti/N coatings compared to the nitrogen processing level.

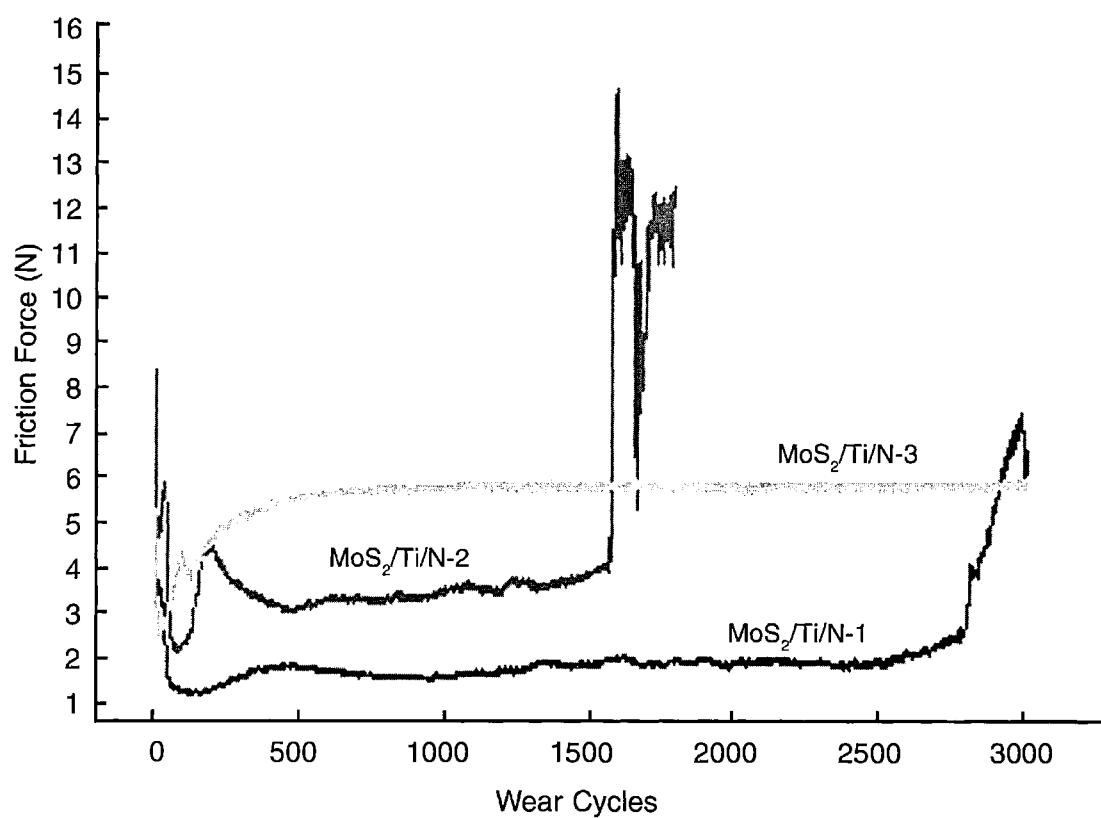


Fig. 8: Friction force response during multi-pass wear tests at 60 N of the MoS₂/Ti/N coatings.

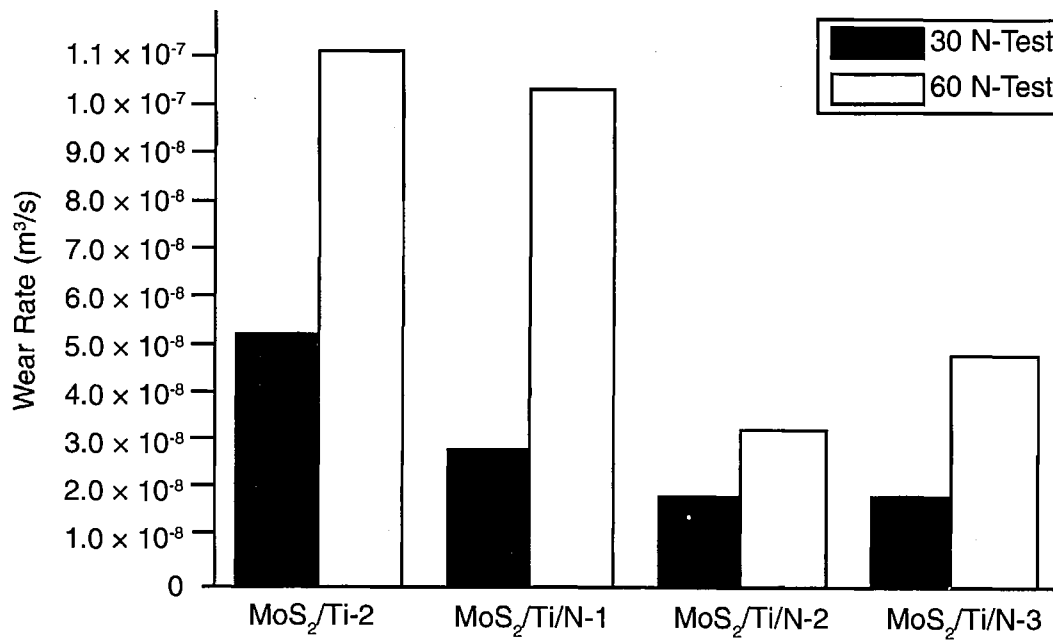


Fig. 9: Wear rates resulting from the 30 N and 60 N multi-pass tests performed on the $\text{MoS}_2/\text{Ti}/\text{N}$ coatings.

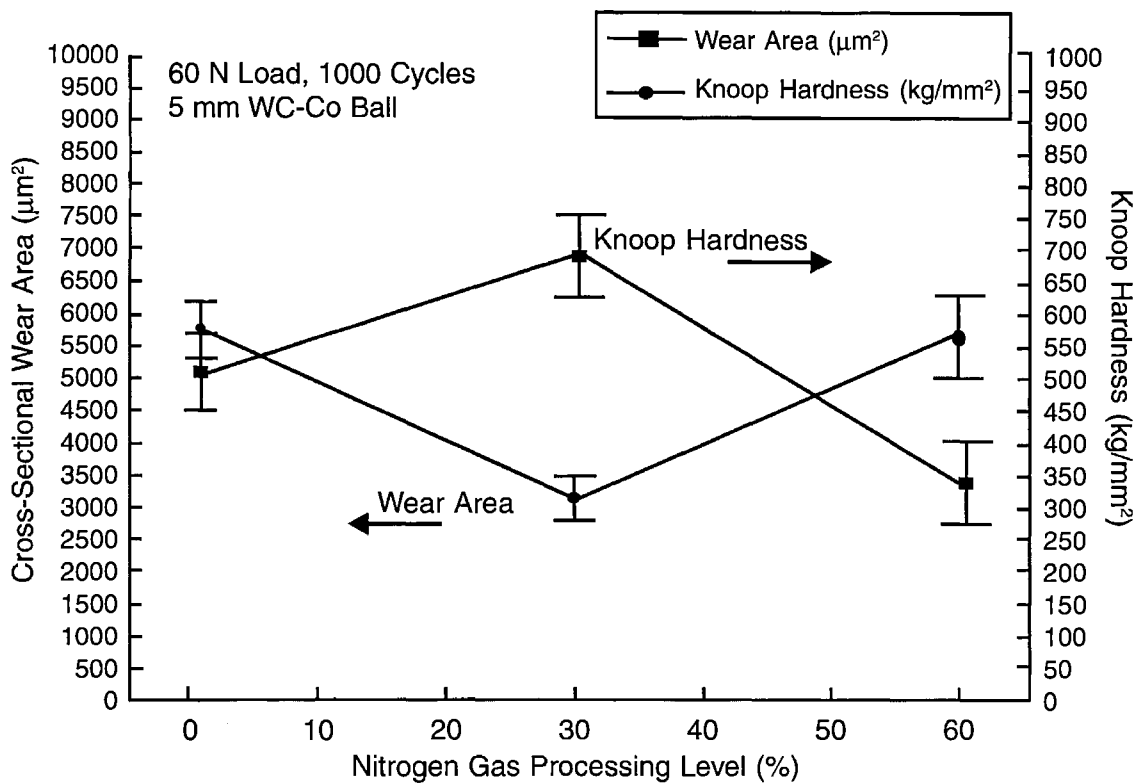


Fig. 10: Effect of nitrogen processing level on wear area and microhardness.

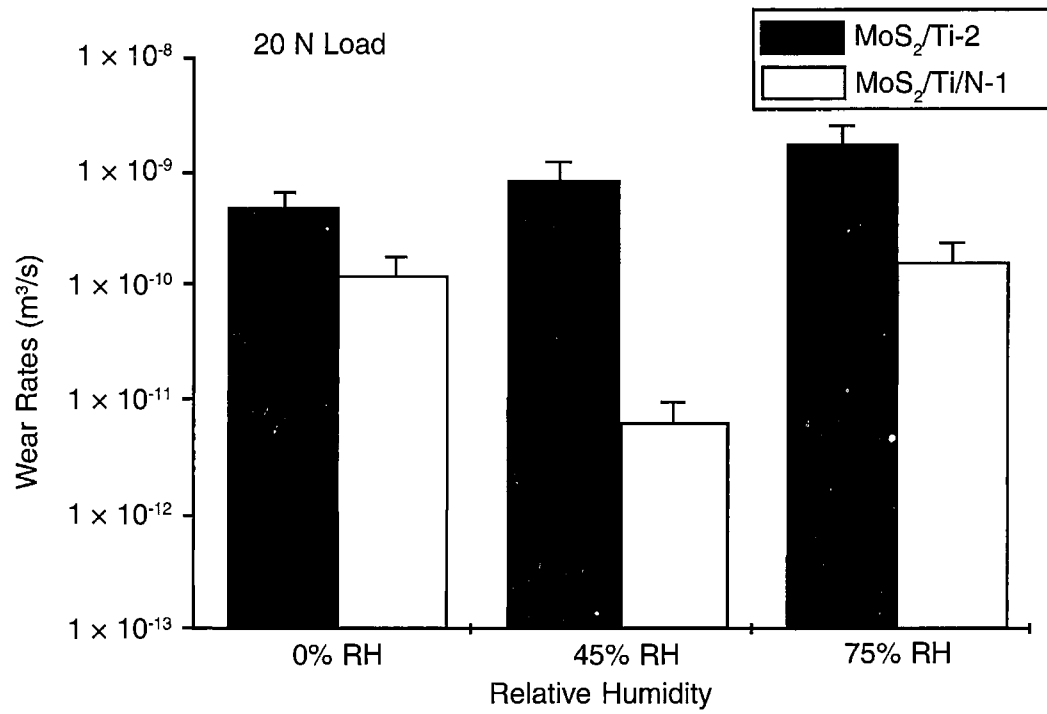


Fig. 11: Wear rates of $\text{MoS}_2/\text{Ti}-2$ and $\text{MoS}_2/\text{Ti}/\text{N}-1$ coatings as the result of environmental pin-on-disc wear tests.

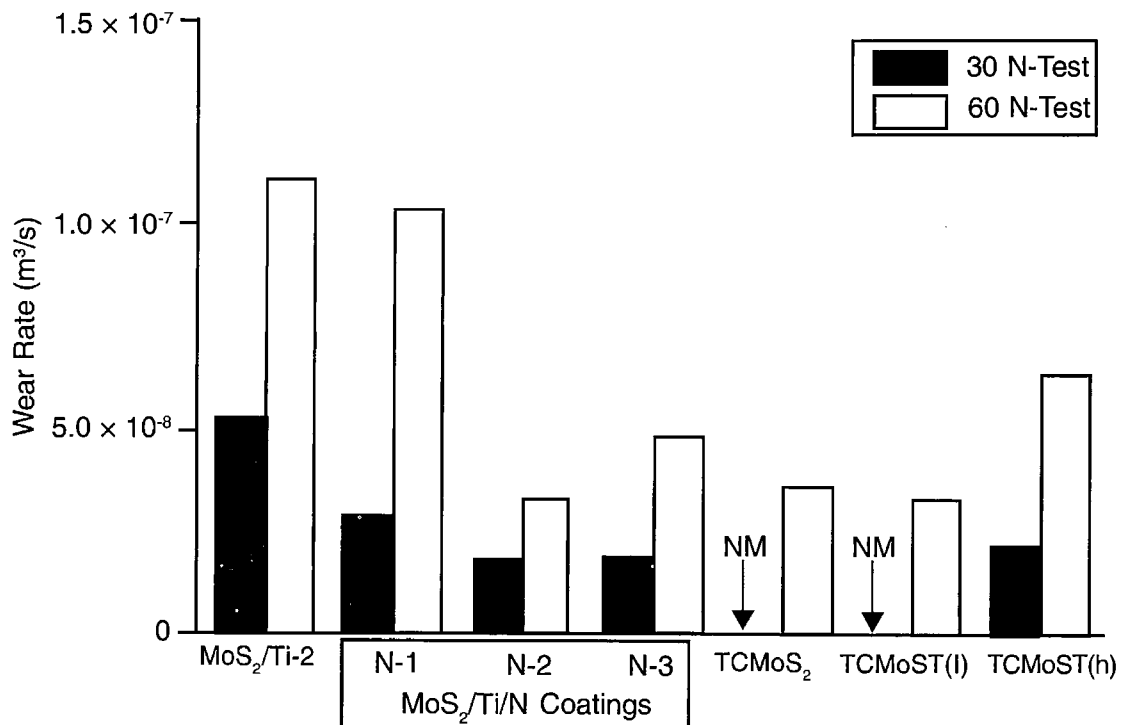


Fig. 12: Wear rates of $\text{MoS}_2/\text{Ti}/\text{N}$ coatings in comparison to Teer Coatings' MoS_2 and $\text{MoST}^{\text{®}}$ coatings as the result of multi-pass wear tests (NM: Not Measurable).

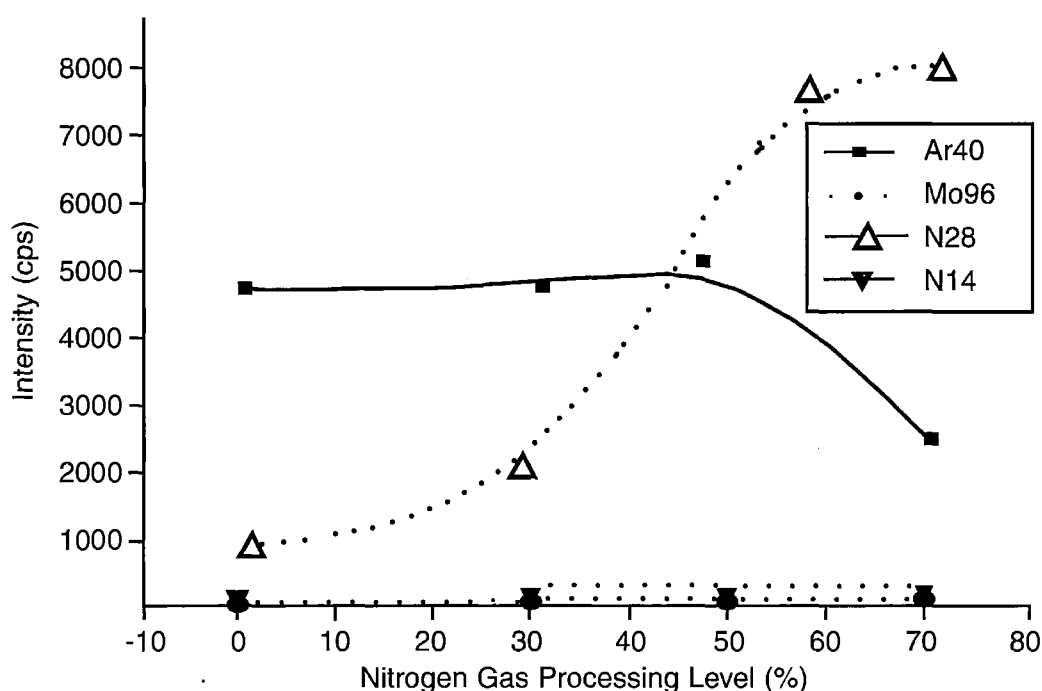


Fig. 13: Effect of nitrogen gas processing level on mass distributions of neutral species.

3.4 Evaluation of Plasma Conditions

As a result of analysis of the plasma conditions present during the reactive sputtering processes to deposit $\text{MoS}_2/\text{Ti}/\text{N}$, the most notable effect is seen in the analysis of neutrals as shown in Figure 13. The addition of nitrogen during processing was only beneficial to tribological performance at levels less than 30% of the total chamber pressure. The ideal deposition regime was found before the large increase in N_2 (N28). Incorporation of molecular nitrogen in the coating could be significantly detrimental to the coating structure and be a possible cause of brittleness. Atomic and singly ionized nitrogen has the benefit of densifying the coating structure while molecular nitrogen is more likely to disrupt film growth and remain in the structure as entrapped gas.

4.0 Discussion

4.1 Influence of Microstructure on Performance

The addition of titanium to the MoS_2 coatings produced for this study resulted in coatings which had better adhesion and improved tribological characteristics

in comparison to pure MoS_2 coatings. An additional improvement was made by adding a reactive gas, nitrogen, as 10% of the working gas while co-depositing MoS_2 and titanium. Most of the MoS_2/Ti coatings deposited by CFUBMS were dense columnar structures, with only slight parallel basal plane orientation, as indicated by a broad MoS_2 (002) XRD peak. Small titanium and TiN peaks were evident in several coatings, indicating some crystalline phases. The MoS_2 structure can be significantly distorted in the c -direction, but not in the a and b directions of the lattice. For this reason, the structure can accommodate large numbers of titanium and/or nitrogen atoms in the c -direction creating a new type of structure that is not necessarily a proper nanocrystalline or amorphous structure.¹¹ TEM analysis showed a complex structure, mostly amorphous but with small regions of strained MoS_2 layers and a larger scale angled pattern in the structure, perhaps the result of the co-sputtering angle.

The best performing $\text{MoS}_2/\text{Ti}/\text{N}$ coating was entirely amorphous. The addition of nitrogen increased the hardness of the coatings, which improved the friction and wear characteristics of the coatings. Higher levels of nitrogen used during processing embrittled the coating, causing the coatings to crack and blister during testing. The poor tribological properties of $\text{MoS}_2/\text{Ti}/\text{N}$

coatings with high nitrogen processing levels corresponded to the inclusion of nitrogen gas in the structure. The best MoS₂/Ti and MoS₂/Ti/N coatings were tested at elevated levels of humidity. The coating containing nitrogen and titanium was shown to outperform the coating containing added titanium but no nitrogen.

4.2 Influence of Plasma Conditions on Microstructure

As the result of the initial work with the mass spectrometer, optimum coatings were deposited at 3 mT total pressure. The addition of nitrogen during processing visibly produced additional species, most notably S⁺ and S₂⁺. A large increase in the N₂ neutrals was found at nitrogen gas processing levels higher than 30%, and it is believed that the significant embrittlement of MoS₂/Ti/N coatings at high nitrogen levels is due to the microstructural incorporation of molecular nitrogen gas. An increase in magnetron power typically resulted in higher total metal ion counts, but only in slightly higher energies, due to the collision energy losses between the cathode surface and the substrate surface. Substrate bias produces a higher stressed coating, even to the point of spallation at levels less than -100 V, but the effect of lower substrate bias on energies of ions has not yet been determined.

5.0 Conclusion

The coatings in this study were deposited by co-sputtering two targets: pure titanium and compound molybdenum disulfide. Analysis of the coatings suggests that the microstructures are complex, consisting of both layered MoS₂ and amorphous MoS₂/Ti composite. Coatings with the best tribological performance were compared to commercially available benchmark coatings of similar composition and structure. After optimizing the MoS₂/Ti coating, the optimum parameter settings were used to deposit MoS₂/Ti/N coatings reactively. An increase in the nitrogen gas processing level acted to further densify the coatings, resulting in slightly harder and more brittle structures. The presence of nitrogen during processing reduced the relative ratio of sulfur to molybdenum (S:Mo) in the coating, while the titanium percentage of the composition remained relatively constant. The optimum nitrogen processing level was determined to equal 10%. The addition of this level of nitrogen resulted in coatings that exhibited a 30% decrease in the wear rate.

A quadrupole mass spectrometer was used as a plasma diagnostic tool to determine the plasma

conditions during the optimized coating process. An increase in the magnetron power resulted in increased numbers of positive metal ions of the powered target and increased the numbers of argon ions. An increase in the nitrogen gas processing level increased the numbers of non-ionized N₂ molecules by 30%. Above this level coatings were extremely brittle, suggesting that nitrogen molecules may have been incorporated in the microstructure.

6.0 Acknowledgments

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Characterization of Industrial Surfaces with Scanning Probe-Based Techniques

Analysis of Composite Surfaces with the Atomic Force Microscope: A Problem Solving Approach

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Abstract

This paper gives an overview of AFM techniques commonly used for surface analysis in industry. We briefly describe the principle of operation for each technique and then discuss specific examples, giving the practical context or problem, the investigative approach, the results and the response (where appropriate).

1.0 Introduction

Composite surfaces of industrial interest may be created either deliberately (by joining two materials) or accidentally (contaminants and defects). The mapping and identification of different material regions on composite surfaces can help greatly in process

development, process control and troubleshooting. The Atomic Force Microscope (AFM) is a powerful tool for this purpose.¹ The AFM makes three-dimensional images of surfaces. In addition to showing the topography, AFM can distinguish different regions in an image based on mechanical characteristics, such as adhesion and stiffness, as well as electrical and magnetic properties. In this paper we review several important AFM techniques: contact mode height and friction imaging, tapping mode height and phase images, and nano-indentation.^{2,3} We use examples from our own work as well as from the literature.

2.0 General Aspects of AFM Imaging

In all scanning probe microscopes, a sharp needle (probe) is brought into proximity with the surface to be examined. It either touches the surface or is very close to the surface. A precision scanner (usually a piezoelectric device) moves the probe relative to the surface in the X, Y, and Z directions, while a sensor records the interaction with the surface. In a scan of surface topography, control electronics adjust the Z position to maintain a constant interaction level while the probe is scanned in the XY plane in a raster pattern. A computer keeps track of the Z position of the probe and displays this as a map of the surface topography (Z as a function of X,Y position). The XY scan sizes that can be used range from a few nm (to show individual atoms) to more than 100 μm (to show structures that can also be seen easily in an optical microscope). For most samples of industrial interest, the useful XY scan sizes range from 0.2 to 100 μm . This excludes atomic resolution imaging (which is not usually of practical interest), but it does include imaging of single polymer molecules and crystal structures (facets, lamellae and defects) down to a few nm resolution. The Z axis range of the scanner is typically 5 μm . Images can be displayed with a Z scale ranging from 1 nm or less (to show crystal steps that are 1 atom high, i.e. < 0.2 nm high) to more than 5 μm (to show moderately rough ground or etched surfaces).

3.0 Contact Mode

In contact mode imaging, the probe tip is attached to a soft, flexible cantilever. During scanning, the probe is in continuous, sliding contact with the surface. As the probe rides up and down the hills and valleys on the sample surface, the cantilever deflects up and down. This deflection is sensed using a light beam reflected from the back side of the cantilever and directed onto a target

photodiode. The servo electronics regulate the Z position of the scanner to keep the *deflection* at a set value.

3.1 Topography of Rolled Aluminum – a Case Study

An aluminum mill produced aluminum coil to be used as a visible, class A surface of a motor vehicle. The customer complained that portions of the coil appeared to be stained, with variation in appearance across the width of the web. Three types of regions were examined by AFM: the “unstained” middle of the web, the “stained” outer portion and the boundary between those regions. Contact mode height imaging found little difference between the stained and unstained regions. Both had a topography similar to the shiny surface of ordinary aluminum foil, which consists of rugged ridges (up to 1 μm high) separated by flat, smooth “land” regions. See Figure 1. The lands have fine structure consisting of tiny ridges less than 10 nm high and many small bumps 10-20 nm high. The bumps lie on top of the tiny ridges, indicating that they are formed on the surface after the foil emerges from the rollers. These bumps are believed to be the residue of the rolling oil, after the coil has been baked out. Returning now to the stained coil, the AFM images of the *boundary* region showed a distinct topography, in which the tiny ridges on the land were completely hidden under an amorphous layer. This layer was a nearly-continuous coating of residue bumps similar to the isolated bumps found on ordinary foil. This correlated with optical microscopy, in which we noticed that optical interference fringes were seen only in the boundary region. Such fringes indicate a coating thickness of 100 nm or more. Surface chemical analysis indicated that the residue was a varnish probably produced by pyrolysis of the rolling oil. As a result of this work, the process engineers adjusted the air knife after the last set of rollers so that it removed more of the oil.

4.0 Tapping Mode

In tapping mode imaging, stiffer cantilevers are used. The base of the cantilever is vibrated at a frequency equal to or near the natural resonant frequency of the cantilever. When the probe is well away from the sample surface, the tip vibrates up and down with a ‘large’ amplitude (tens of nm). This oscillation amplitude is detected using the same light beam arrangement that is used in contact mode. As the probe is brought closer to the sample surface, the amplitude suddenly decreases when the tip is first able to touch the surface at the

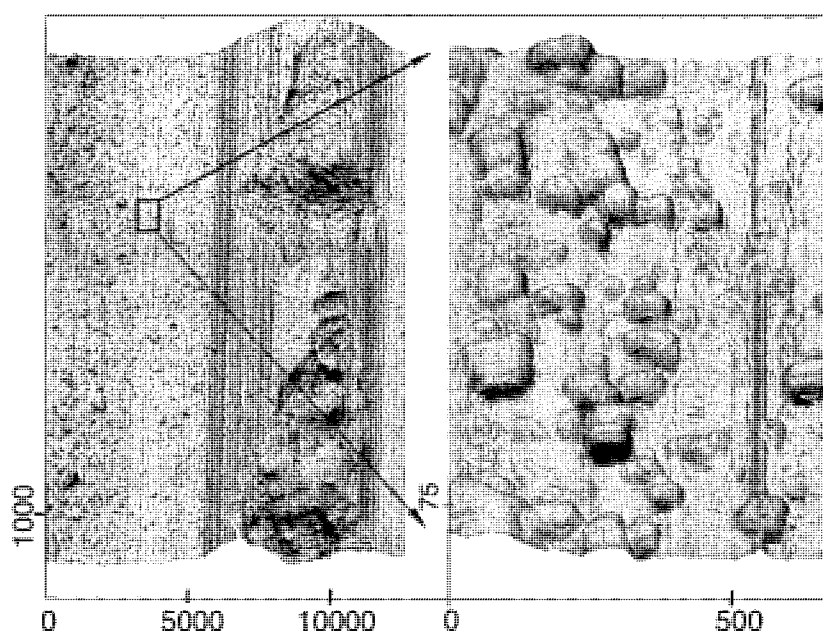


Fig. 1: Contact mode AFM images of the shiny side of ordinary aluminum foil. 3D views rendered in slope mode. Horizontal and vertical scales are given in nm. Image courtesy of Advanced Surface Microscopy, Inc.

downward extreme of its oscillation. The servo electronics regulate the Z position of the scanner to keep the *amplitude* at a set value. During normal scanning, the probe makes intermittent contact with the sample surface. This provides high image resolution (due to a strong tip-surface interaction), while minimizing lateral forces. As a result, scanning is more gentle, both for the sample and the probe tip.

4.1 Phase Imaging

In addition to sensing the amplitude of the tip's oscillation, it is possible to sense the phase of the tip response relative to the driver that vibrates the base of the cantilever. On many surfaces, the phase delay varies systematically from spot to spot within an image. See Figure 2. Any interaction between probe and specimen which causes a loss of mechanical energy can increase the damping of the oscillating probe, which in turn causes its phase to lag further behind the driver; this is registered as lower phase.⁴ Two important interactions are stiffness and adhesion. When the drive frequency is lower than the cantilever resonance, stiffer regions are imaged with higher phase and stickier regions are imaged with lower phase.

Phase images are useful because they often show extraordinary contrast for many composite surfaces. These include contamination deposits, discontinuous

(i.e. defective) thin films, devices built of composite materials (e.g. magnetic recording heads) and cross-sectional specimens of composite materials. Both inorganic and organic materials can be examined.⁵

In our laboratory, we prepared a contaminant specimen by first applying skin oils to a glass slide and then removing most of the deposit by wiping with a paper tissue. Figure 3 shows height and phase images of the residual material. The height image shows a slightly rough background consisting of tiny, rounded bumps (about 10–30 nm wide). Superimposed on this are a couple rounded blobs (about 100–300 nm wide) and many needle-like features (about 200–300 nm long, 10–20 nm wide and 2–3 nm high). In the phase image, the large blobs were dark and the needles were bright relative to the background. In contact mode images (not shown), only the substrate and aggregates of needles on the substrate were visible in the height image, whereas the friction image showed that regions corresponding to substrate, blobs and aggregates of needles had medium, high and low lateral force, respectively. Based on the foregoing observations, we identify the blobs as oil nanodroplets and the needles as crystallites. In tapping mode, the force was small enough so that the tip could track the liquid-air interface of the nanodroplets, even imaging the crystallites floating on the oil, whereas in contact mode the probe could not image the droplets, because it slides on the glass substrate.

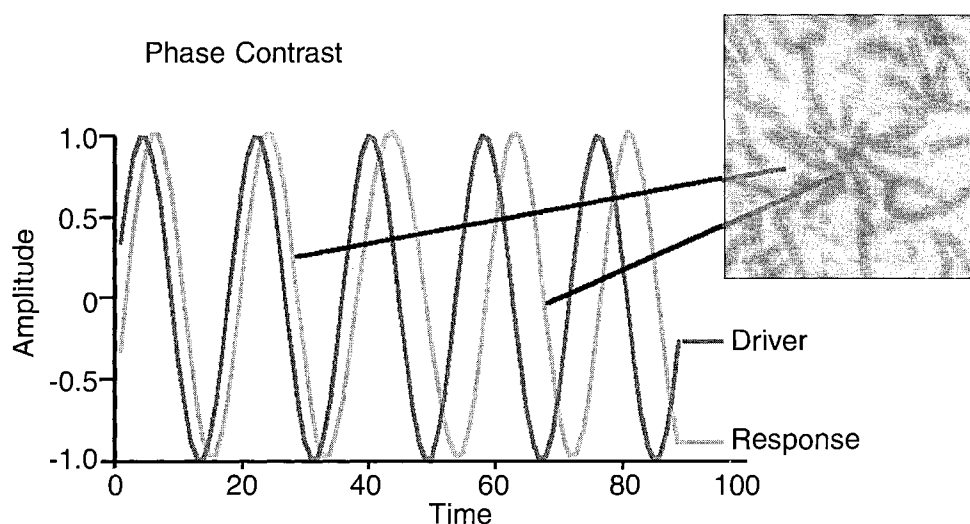


Fig. 2: Graph showing time lag (phase shift) between driver and tip response as a function of position on a specimen surface and an image mapping the phase lag. Dark areas correspond to larger phase lag of the cantilever response relative to the driver that shakes the cantilever base. The narrowest features are about 10 nm wide. Image courtesy of Advanced Surface Microscopy, Inc.

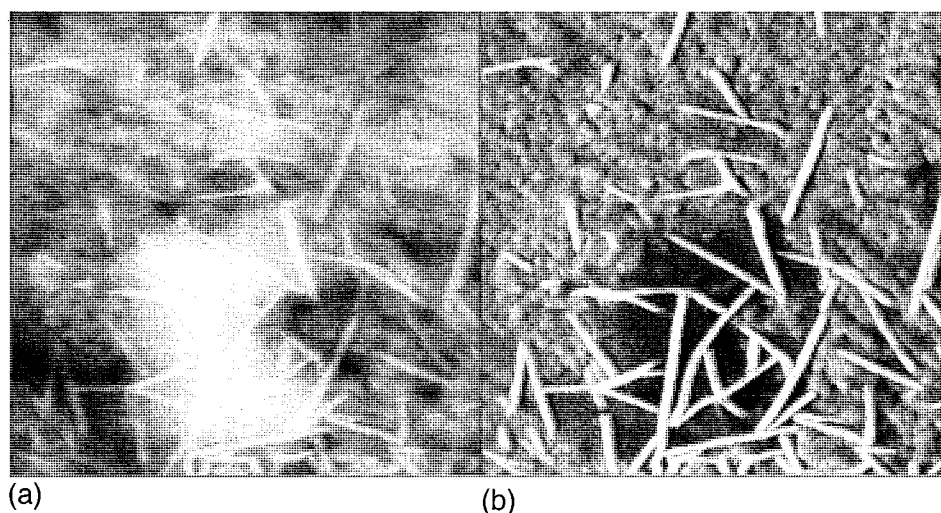


Fig. 3: (a) Tapping mode height and (b) phase dual image of skin oil nanodroplets and crystallites on a glass substrate. 1 x 1 μm image. Image courtesy of Advanced Surface Microscopy, Inc.

4.2 Corrosion Film Growth

Corrosion of industrial process equipment has a major impact on cost of ownership factors such as efficiency and reliability. In an experimental test of corrosion growth mechanisms, test coupons of mild steel were placed in a dry steam environment for different

lengths of time. Height and phase images of a specimen exposed for a short time are shown in Figure 4. The height image is difficult to interpret because of the large rolling hills and valleys of the original surface. However the phase image shows distinct regions of bright contrast. These correspond to deposits in the form of rounded bumps and thin films seen in the height image. With

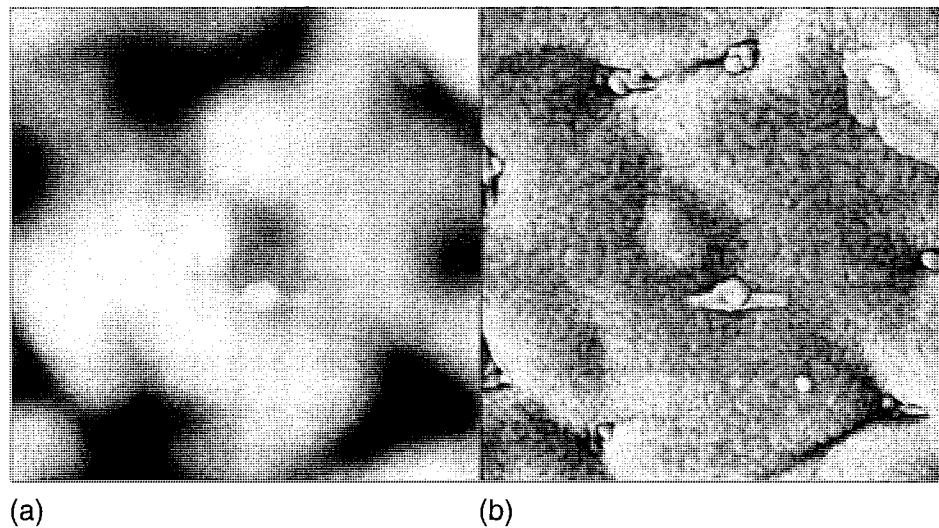


Fig. 4: (a) Tapping mode height and (b) phase dual image of mild steel after short exposure to dry steam. $1 \times 1 \mu\text{m}$ image. Image courtesy of Advanced Surface Microscopy, Inc.

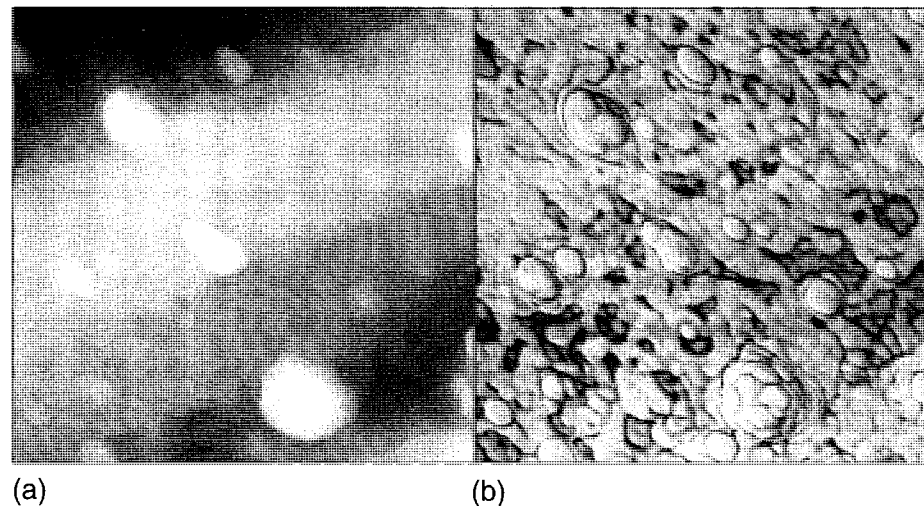


Fig. 5: (a) Tapping mode height and (b) phase dual image of mild steel after longer exposure to dry steam. $1 \times 1 \mu\text{m}$ image. Image courtesy of Advanced Surface Microscopy, Inc.

longer exposure (see Figure 5), there are more bumps and the thin film deposit nearly covers the surface. Gaps in the film reveal the substrate, which stands out in dark phase contrast. These results indicate that the corrosion deposit grew by a complex mechanism involving both island-like growth (leading to bump formation) and layer-by-layer growth (leading to broad coverage).

4.3 Particle Identification in Sliding Wear

Like corrosion, wear has great practical importance. Magnetic recording heads can suffer sliding wear during normal operation of a hard disk drive. A composite head consists of two ferrite regions (the pole pieces) separated by a diamagnetic gap material, and these regions are

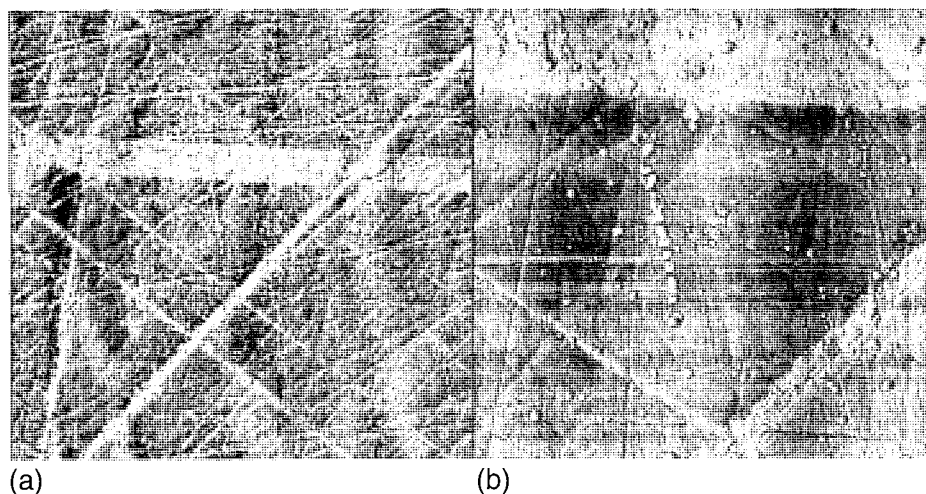


Fig. 6: Phase images of a mini-composite magnetic recording head. The ferrite is dark and the gap is bright. (a) 10 μm and (b) 3 μm scans. Image courtesy of Advanced Surface Microscopy, Inc.

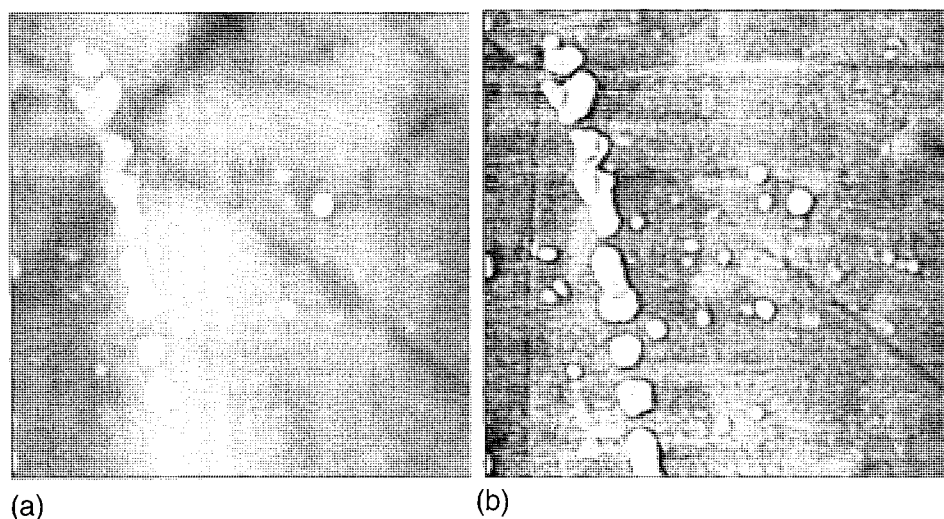


Fig. 7: (a) Height and (b) phase dual image of a recording head. 1 μm scan. Image courtesy of Advanced Surface Microscopy, Inc.

clearly contrasted in a phase image where the ferrite is dark and the gap is bright. See Figure 6. In a 3 μm image, a string of particles was seen on the ferrite material (Figure 6). A 1 μm height image shows that the particles are bumps about 4 nm high, and the corresponding phase level matches that of the gap (see Figure 7). This suggests that the particles are fragments of gap material contaminating the ferrite surface.

5.0 Nano-Indentation

Stiffness and hardness are important mechanical properties. AFM affords the possibility of measuring these properties with very high spatial resolution. For nano-indentation work, the standard Si probe used in tapping mode is replaced by a probe consisting of a stainless steel cantilever with an attached diamond tip.

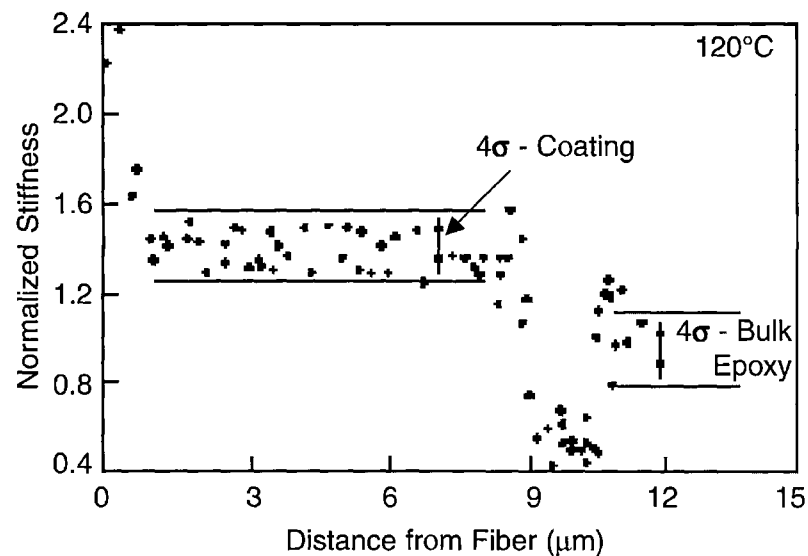


Fig. 8: Stiffness variation across a three layer polymer structure at 120°C. (Reproduced with permission from Ref. 6).

In a nanoindentation experiment, the AFM horizontal scan is halted and the scanner extends, pressing the probe into the specimen surface until a set load is achieved. This load is measured using the deflection of the cantilever. The scanner then retracts. From the deflection vs. Z-travel data, one can estimate the stiffness. For hardness measurements, one can image the indented spot and measure the size of the permanent mark. The spatial resolution of the technique depends on the probe tip size and the applied load. Generally, tip widths are in the range 10-30 nm and loads are in the range 100 nN to 100 μN. At the lowest loads, the contact area can be as little as a few 10s of nm² and the penetration depth as little as 1-3 nm. Useful information can be obtained for ultrathin films that are as little as a few nm thick (albeit with some effect due to the substrate) and horizontal spatial resolution can be much better than 100 nm.

5.1 Stiffness Variations Across an Interface

In composite structures, interfacial properties are critical factors limiting strength. In one common process for making a metal fiber-polymer composite, the metal fibers are first coated with a liquid solution containing epoxy pre-polymers.⁶ After drying, there is a solid, uncured epoxy layer on the metal fibers, this 'sizing' layer may be 1-10 μm thick. The sized fibers are then placed in a bulk mixture of a second type of epoxy containing a stoichiometric amount of amine curing

agent and heated to cure the bulk. During this process, the curing agent diffuses into and fully cures the sizing layer. The metal fibers are now embedded in a strong epoxy matrix. AFM specimens can be made by cross-section polishing. VanLandingham and co-workers⁶ investigated stiffness variations across the coating-bulk interface in such a system. The stiffness of the coating and the stiffness variation across the interface was evaluated by making a linear sequence of indents at 0.3 μm intervals along a path extending about 12 μm from the fiber surface out into the bulk epoxy. Several parallel rows of indents were made with small longitudinal offsets so that the effective spatial resolution perpendicular to the interface was about 50 nm. A special feature of this work was a temperature study. In a graph (Figure 8) of relative stiffness as a function of position, 4 regions were noted in the data captured at 120°C:

1. The region immediately adjacent to the metal fiber had high stiffness due to a proximity effect,
2. The coating (extending to 8 μm from the metal surface) was about 50% stiffer than the bulk epoxy,
3. A transition region about 1.5 μm thick between the coating and the bulk epoxy layers had reduced stiffness (about 60% of the bulk), and
4. The bulk epoxy. The existence of this transition region or interphase and its reduced stiffness at elevated temperature were unexpected and indicated that the interphase has a glass transition temperature of about 100-120°C, as compared with 150 and 160°C for the coating and bulk epoxies.⁷

6.0 Conclusions

Atomic Force Microscopy is a well-established technique for solving practical problems in industry. Height imaging is valuable for issues relating to appearance and surface finish. Tapping mode height and phase imaging adds the capability of mapping material regions of a surface with spatial resolution down to 10 nm with sensitivity to ultrathin coatings (even a single molecular layer can be detected). Applications include investigations of contamination, corrosion and wear. Nano-indentation with a diamond-tipped cantilever reveals stiffness variations across material interfaces, where mixing may create surprises.

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Characterization of Industrial Coatings with Atomic Force Microscopy

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Abstract

Coatings are part of everyday life. Anywhere we go, we see coatings. Highly diverse science and technology supports the development, production, application, and characterization of coatings. For these reasons, coating scientists, engineers and technologists are very much interested in developing deeper understanding of coatings. We have been utilizing atomic force microscopy (AFM) to solve a wide array of industrial problems in paints and coatings during the last three years.

The AFM results related to industrial paints and coatings are presented in this paper. We have carried out studies using AFM to profile surface morphology, and surface compositional mapping of coatings. We are applying AFM to examine accelerated and naturally weathered coatings. Film formation studies of various emulsion polymer systems used in the paint industry have been carried out. The AFM has been shown to be an excellent tool for assessing paint film formation. We are also using AFM for nanoindentation and nanoscratching studies to measure mechanical properties of coatings.

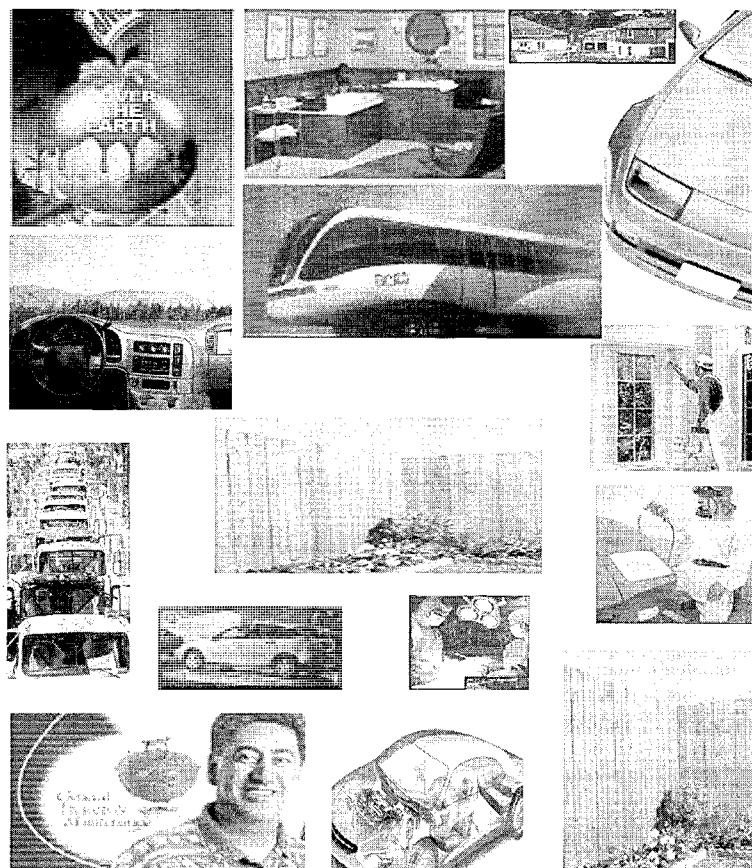


Fig. 1: Coatings everywhere.

1.0 Introduction

Industrial coatings are formed from complex formulations of polymers, pigments, metallics, additives, solvents, organic and/or inorganic chemicals. Understanding the science and technology affecting coatings' composition, structure, property, application, performance, structure-property relationships, environment, and how all of these aspects interact is key to successful coatings development. Coating science and technology involves various aspects of polymer, physical, analytical, organic and inorganic chemistries, materials science, engineering, physics, and statistics etc.¹⁻²

There are coatings everywhere in our life (Figure 1). The most common ones are: house paints, stains & varnish for wood furniture, powder coating for appliances, coatings for food cans, traffic paints, automotive paints, aircraft coatings, marine paints, floor coatings, inorganic coatings for aerospace, coatings for contact lenses, paper coatings, textile coatings, coatings for non-sticky pots and pans, coatings for computers, coatings for lawn & garden, etc.

Applied paint and coating scientists including Sherwin-Williams have been using a wide array of spectroscopic, chromatographic, thermal, physical,

chemical and microscopic techniques to solve industrial problems for many years. Recently, there have been reports of utilizing advanced analytical techniques such as SEM, TEM, and SPM (Scanning Probe Microscopy) in the research of emulsions, and coatings.³⁻⁷ In our microscopic laboratory, we have been using optical microscopy, SEM/EDX, FT-IR microscopy, and AFM to

- Improve quality and consistency of coatings,
- Provide customer service & problem solving, and
- In new product development.

This paper deals with studies related to characterization of various coatings using atomic force microscopy.

2.0 Methods

The Dimension 3100 AFM (Nanoscope III a Scanning Probe Microscope with Extender) of Digital Instruments, Inc., Santa Barbara, CA was utilized for these investigations. It is mounted with a 90 μm scanner. The microscope was placed on an integrated vibration isolation table and acoustic hood (Figure 2). Olympus tapping mode etched silicon probes (OTESPA-70) were used for height, phase and amplitude AFM imaging. Nanoindenting and nanoscratching was done with a diamond tip mounted on a metal foil cantilever (spring

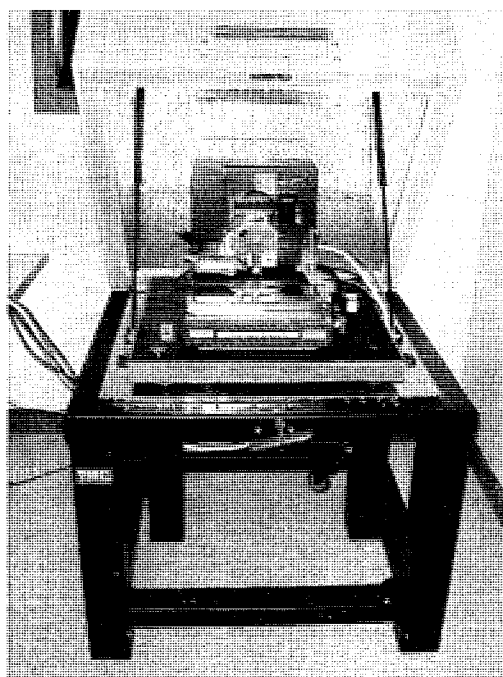


Fig. 2: Atomic Force Microscope on an integrated vibration isolation table and acoustic hood for large sample scanning.

constant = 143 N/m and frequency = 45 KHz). Before mounting a sample on the AFM stage, the dust or loose particles were blown off using pressurized air (purified) from the surfaces. No other sample preparation was carried out for AFM analysis.

In quantitative evaluation of surface roughness from the AFM height image, we used simple geometric parameters such as average roughness (arithmetic average of the absolute values of heights from the mean surface area), Ra. The Nanoscope III software was used for Ra calculation. Prior to analysis, height images were subjected to an “autoflatten” procedure that removes the low frequency image variations.

3.0 Results and Discussion

We have carried out a wide array of experiments to utilize AFM in the paint and coating industry. In our laboratory, we have characterized paints and coatings for various markets such as OEM (Original Equipment Manufacturer) interior automobile, OEM exterior, undercoats & topcoats of vehicle refinishing, industrial coatings, interior and exterior architectural coatings, etc. In this paper, we will present some examples where AFM has been found to be very useful in (I) fine tuning the

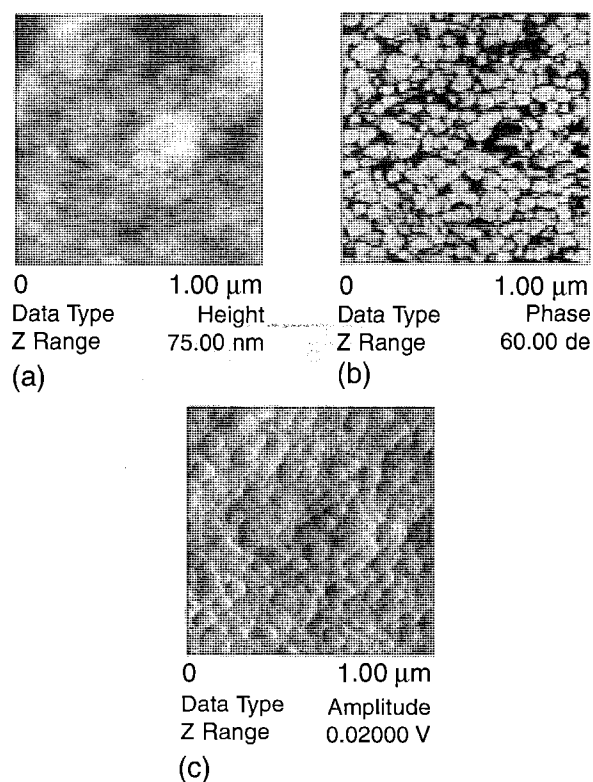


Fig. 3: AFM images of waterborne polyurethane coating for the automotive interiors: (a) height, (b) phase, and (c) amplitude film baked at 130°F. The contrast covers height corrugations in the range of 0 –75 nm, phase changes in the 0-60 degree range, and amplitude changes in the range of 0-0.02 V. Scan 1.00 micron.

paint application parameters, (II) understanding the coatings, and (III) development of high quality coatings.

3.1 Waterborne Acrylic Polyurethane Coatings for Automobile Interiors

Very low gloss and high performance coatings are designed for some interior parts (such as dashboard, steering wheel etc.) of the automobile. These coatings were sprayed on the plastic substrates. The surface morphology of these pigmented coatings, baked at different temperatures, was examined by AFM. Using tapping mode, we collected images in height, phase and amplitude modes. The height, phase, and amplitude images of the coating baked at 130° F show distinctly the particles of the polymer in a one-micron scan (Figure 3). The sectional analysis of the topography image shows spherical particles of about 75 to 100 nm in diameter (Figure 4). This coating when baked at 130°F shows a poor resistance to sun tan lotion and bug spray. To optimize application parameters, we also baked the same

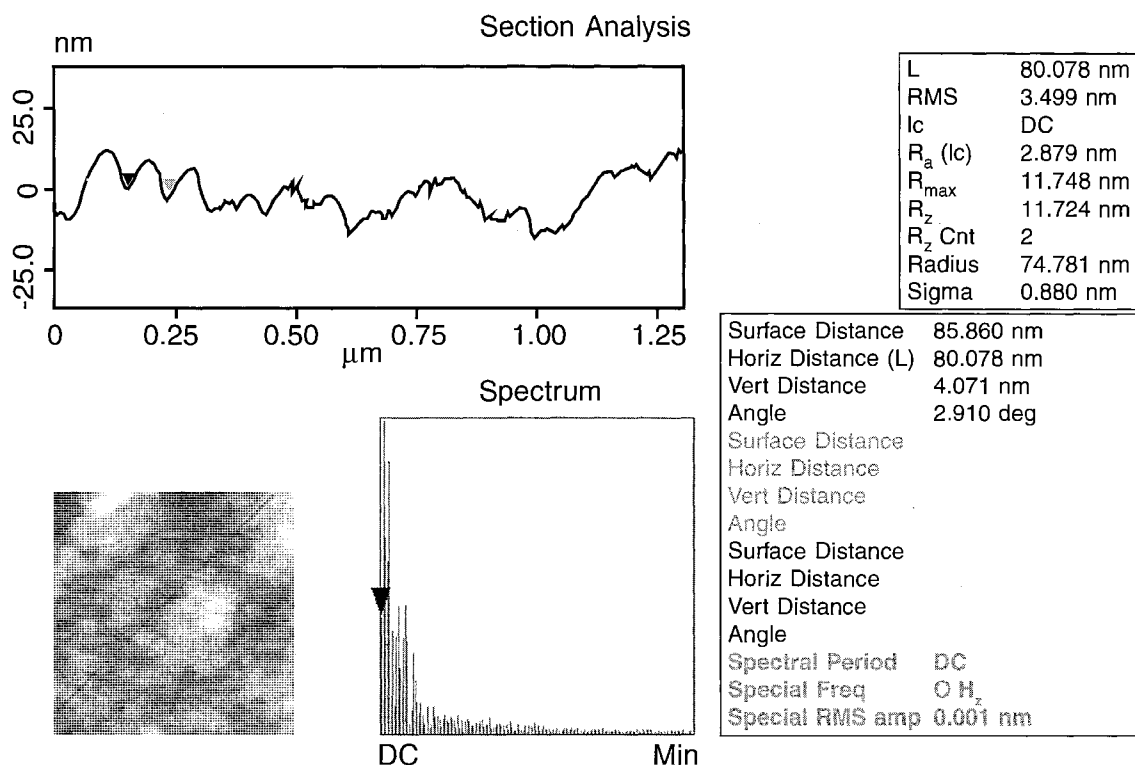


Fig. 4: Sectional analysis of height image of waterborne polyurethane coating as shown in Figure 3.

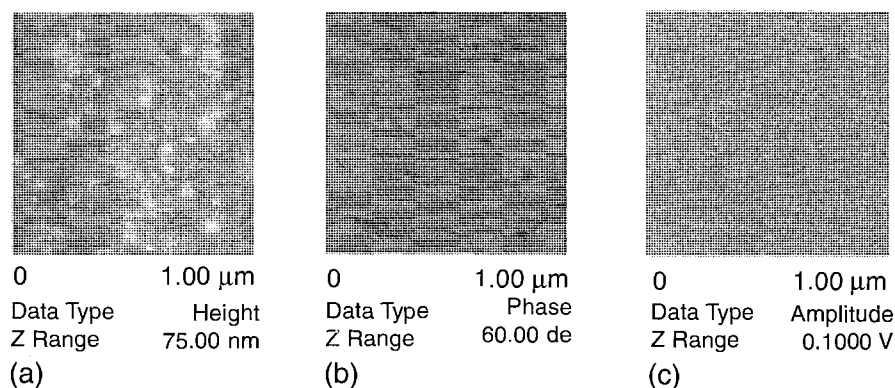


Fig. 5: AFM images of waterborne polyurethane coating for automotive interiors: height (a), phase (b) amplitude, and (c) coating baked at 180°F. The contrast covers height corrugations in the range of 0-75 nm, phase changes in the 0-60° range, and amplitude changes in the range of 0-0.02 V. Scan 1.00 micron.

coating at 180°F and then examined by AFM. Figure 5 shows that the acrylic polyurethane particles are being coalesced to a larger degree. However, one can still see that the isotropic film has not formed. However, this baked coating at 180°F provided good resistance to sun tan lotion and bug spray. The phase images of the coating baked at 180°F are distinctly different from the film

baked at 130°F. The sectional analysis of Figures 3 and 5 indicates that the interparticle distance remains the same in coatings baked at 130 and 180°F, whereas the peak to valley value is lower for the coating baked at 180°F than the coating baked at 130°F. This is further supported by the surface roughness measurements as shown in Table 1.

Table 1. Roughness Measurements of Waterborne Polyurethane Coating at Two Temperatures

Sl. No.	Baking Temperature	Roughness, R_a (nm)
1	130°F	6.4
2	180°F	4.0

Although further investigations are needed to correlate the coating properties (such as resistance to sun tan lotion and bug spray) with R_a values, but, it appears that the interdiffusion of polymeric particles at higher temperature might be playing a key role in influencing final properties of the film.

To compare the results, we have also characterized the same polyurethane pigmented coating baked at 130°F by SEM at about 40,000 magnification using 15 kV. The SEM image was very different than the AFM image. The SEM image couldn't resolve the polymeric particles. The SEM image showed very bright (white) spherical particles. These particles are in the range of 125 nm. The x-ray analysis confirmed these particles to be TiO_2 . Together AFM and SEM complement each other and provide better knowledge of coatings.

3.2 UV Curable Coating: Customer Problem-Solving

The UV curable coatings are used for several applications in automotive, floor and other applications where very durable, scratch resistance hard coatings are desired. One of the customers of UV curable coatings was having a haze problem in the lettering area of the headlamp at the robotic paint spray booth plant. We were interested to know what the haze is and also to see if haze is present on the surface or underneath the surface. We utilized AFM to investigate the haze problem in the UV coatings. We examined the parts as received from the manufacturing plant with out any sample preparation. This is where AFM offers great advantages over other surface techniques such as SEM and TEM. First, we examined the surface, where there were no defects, by AFM. The Figure 6 shows the height and phase images of the UV coating in the 10 micron scan of a typical defect free film on polycarbonate substrate. The AFM clearly shows that the film is very smooth and homogenous. It should be noted that Figure 7 shows the AFM images of the haze area. The surface is very heterogeneous and can be described as having small pox. The size of these circular depressions varies from 100 nm

to 1.6 micron. The height image corresponds to the phase image. The phase diagram indicates that the curing is not uniform and lettering areas were not cured uniformly on the surface. Because of non-uniform curing by UV light, the coating shows spots of soft and hard film. It should be emphasized that the height variation in the defect free film is only 50 nm compared to 1000 nm in the haze film. Here we discussed only one example of a "real world" problem, but it demonstrates that the AFM can be utilized in solving problems related to surface defects on real parts with out any sample preparation.

3.3 Accelerated Weathering Studies

Automotive paints are designed to tolerate severe weather conditions for the "life time" of the coatings. Typically for the refinish market, auto paint industries perform several accelerated tests (such as QUV⁸ exposure up to 3000 hrs., Xenon exposure up to 4500 KJ/m² etc.) in addition to natural weathering in Florida, Arizona and other locations. We have been investigating the application of AFM in predicting the durability of coatings. We have been successful in seeing the topographical changes in coatings in early stages of exposures, which have not been possible by other means. In this paper we are presenting the AFM work related to accelerated QUV exposed auto paint system. The topcoat was a vehicle refinish acrylic polyurethane clearcoat system containing a UV absorber as well as hindered amine light stabilizer (HALS). The undercoat (basecoat) was an acrylic grafted alkyd system. The colorcoat is a black basecoat. Typically, the film thickness of clearcoat and basecoat was about 50 and 20 μ m respectively. The Figure 8 shows height and phase images of an unexposed urethane clearcoat system. The AFM clearly shows that the film is very smooth and homogenous. It should be noted that the z-axis is only 30 nm. The Figure 9 shows the AFM images of the same system after exposure to QUV for 3000 hrs. The AFM shows that the film has degraded very badly. Many pits are seen in the film. It should be noted that the z-axis is 300 nm. The phase image also shows that the QUV light has eaten up the upper layer of the topcoat. Figures 10 and 11 are the AFM images of a similar system except that the white basecoat was used to investigate the effect of the undercoat on the morphology of the surface after exposure. The topographic and phase images (Figure 10) show that the unexposed film is very smooth, as expected. After exposure to QUV for 3000 hrs., the film (Figure 11) shows degradation but certainly much less than the previous system with the black basecoat. To quantify these changes, we used roughness measurements. The roughness data (Table-2) were

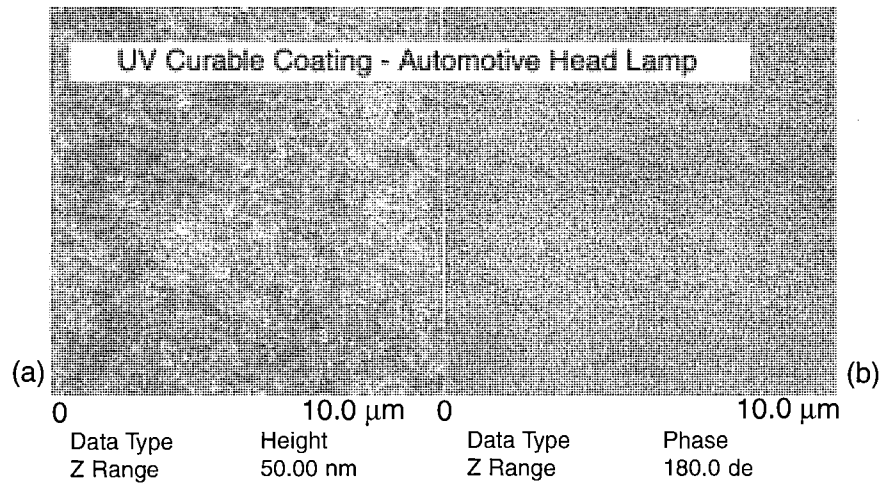


Fig. 6: (a) Height and (b) phase AFM images of UV curable coating for automotive head lamp application – defect free coating. The contrast covers height changes in the range of 0-50 nm, and phase changes in the 0-180° range. Scan 10.0 μm .

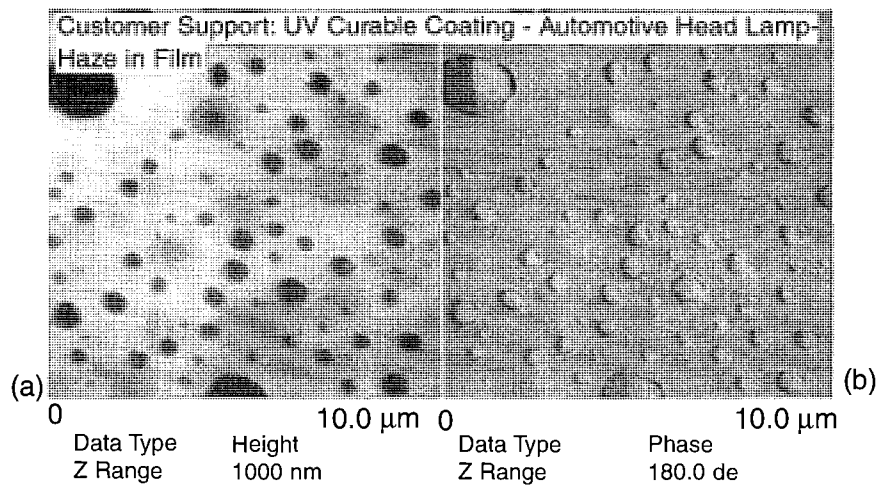


Fig. 7: (a) Height and (b) phase AFM images of UV curable coating for automotive head lamp application – haze in coating. The contrast covers height changes in the range of 0-1000 nm and phase changes in the 0-180° range. Scan 10.0 μm .

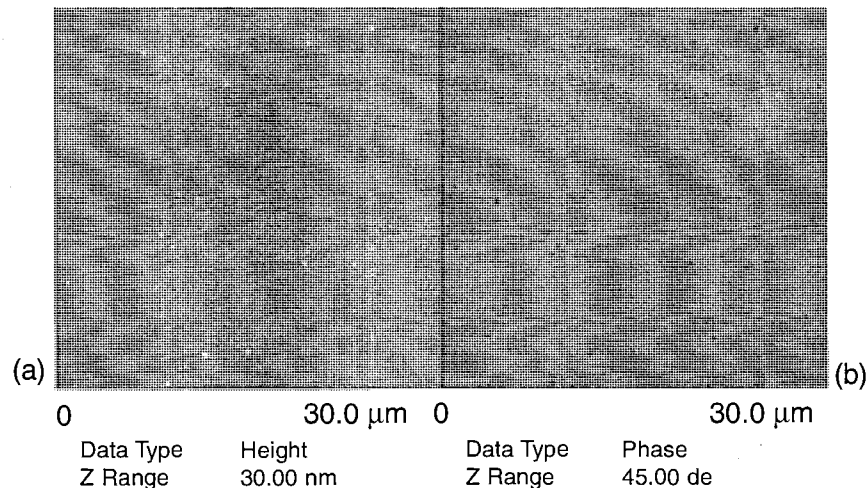


Fig. 8: (a) Height and (b) phase AFM images of automotive vehicle refinish (acrylic polyurethane clearcoat and black basecoat) – unexposed coating. The contrast covers height changes in the range of 0-30 nm and phase changes in the 0-45° range. Scan 30.0 μm .

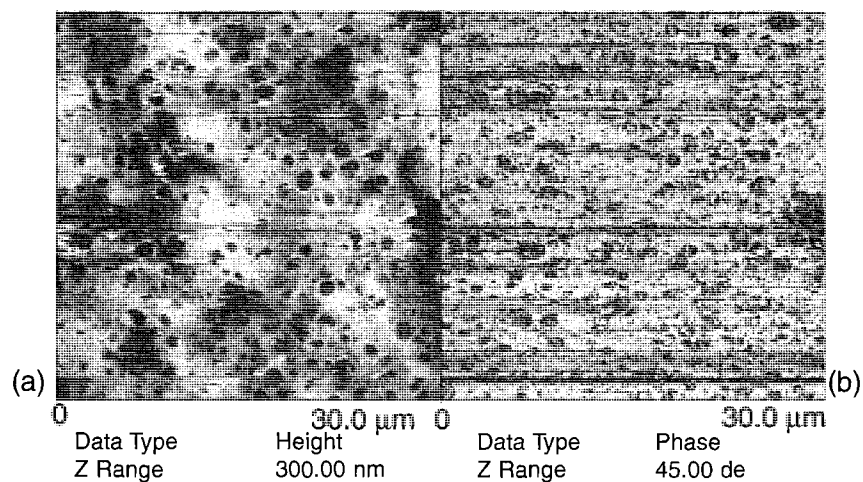


Fig. 9: (a) Height and (b) phase AFM images of automotive vehicle refinish (acrylic polyurethane clearcoat and black basecoat) – 3000 Hours QUV exposed coating. The contrast covers height changes in the range of 0-300 nm and phase changes in the 0-45° range. Scan 30.0 μm.

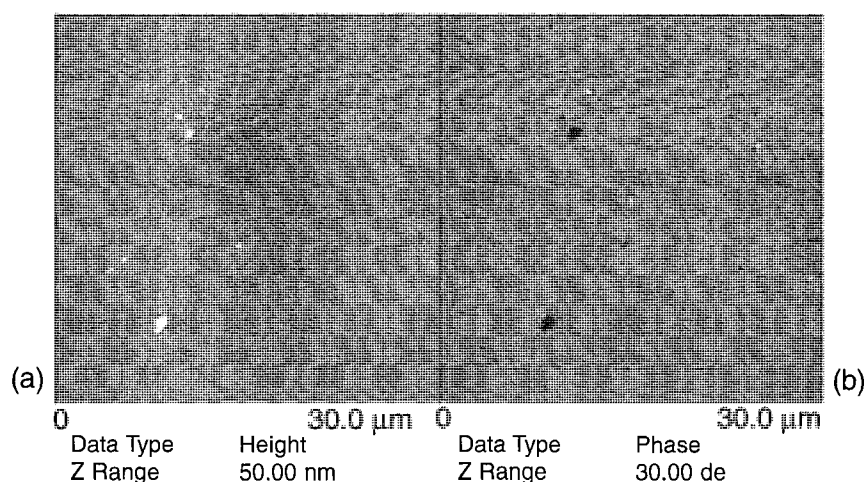


Fig. 10: (a) Height and (b) phase AFM images of automotive vehicle refinish (acrylic polyurethane clearcoat and white basecoat) – unexposed coating. The contrast covers height changes in the range of 0-50 nm and phase changes in the 0-30° range. Scan 30.0 μm.

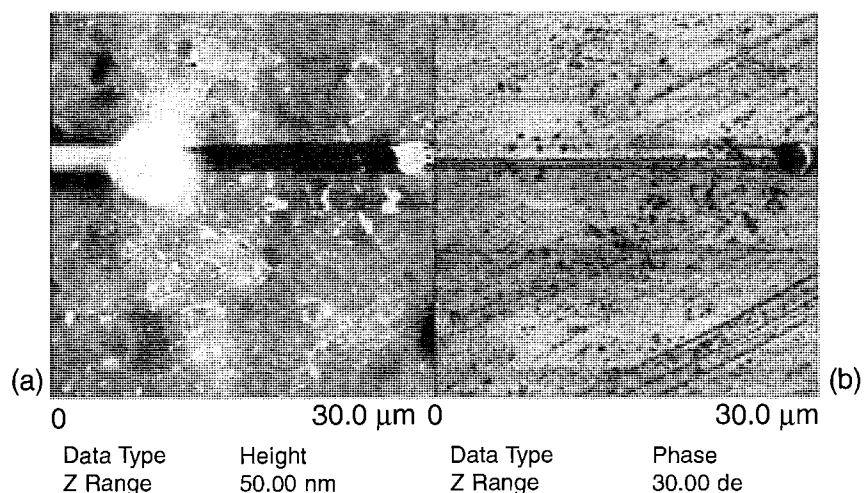


Fig. 11: (a) Height and (b) phase AFM images of automotive vehicle refinish (acrylic polyurethane clearcoat and white basecoat) – 3000 Hours QUV exposed coating. The contrast covers height changes in the range of 0-50 nm and phase changes in the 0-30° range. Scan 30.0 μm.

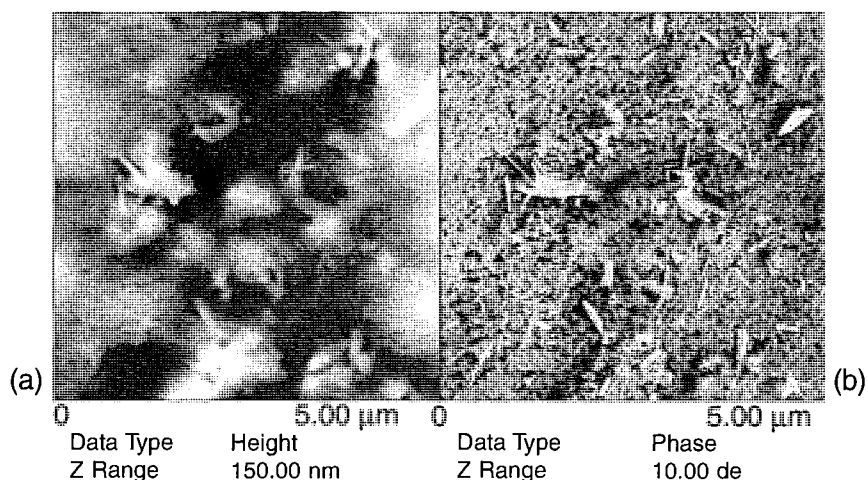


Fig. 12: (a) Height and (b) phase AFM images of industrial DTM white paint. The paint was applied and dried at 50°F/85%RH. The contrast covers height changes in the range of 0-150 nm and phase changes in the 0-10° range. Scan 5.0 μm.

Table 2. Roughness Measurements of Automotive Topcoat System for Unexposed and QUV 3000 Hrs. Exposed Panels

#	Sample	Roughness, Ra (nm)
1	Black Basecoat/Polyurethane Clearcoat (Figure 8): Unexposed	1.7
2	Black Basecoat/Polyurethane Clearcoat (Figure 9): Exposed QUV 3000 hrs	88
3	White Basecoat/Polyurethane Clearcoat (Figure 10): Unexposed	1.4
4	White Basecoat/Polyurethane Clearcoat (Figure 11): Exposed QUV 3000 hrs.	13

calculated from the height images of AFM for Figures 8-11.

Analysis of roughness data clearly indicates that unexposed acrylic polyurethane coatings are very smooth. The surface becomes quite rougher after exposure to QUV light for 3000 hrs. It also seems that the undercoat plays a crucial role in the degradation of the topcoat. The data in the Table 2 shows that the topcoat with the black basecoat degraded about 7-8 times more than the topcoat with the white basecoat. More research is needed in this area to study surfaces of topcoats with different pigmented basecoats and as well as primers.

3.4 Industrial Coatings: Direct to Metal (DTM) Paint

Industrial paints are designed to provide excellent coating properties (such as adhesion, humidity resistance, etc.) for industrial reactors, plants, manufacturing operations, etc. in a variety of industrial

settings. We have been interested in examining the paint system in different temperature and humidity conditions. In this applied research, we are presenting data for the DTM paint applied and/or dried at two different conditions. The AFM image (Figure 12) was acquired for a film which was applied and dried at 50°F (colder temperature), and 85% relative humidity (RH, High humidity) conditions. The height and phase images show the presence of needle like crystals on the surface. These needle shaped crystals are present throughout the film. The needles were found to be sodium sulfate (confirmed by SEM/EDX). We believe that when the coating is applied at a cooler temperature such as 50°F, sodium sulfate crystallizes from the paint formula. This film failed the adhesion test indicating there was a weak bond between the metal substrate and the paint film applied at 50°F/85% RH. The same paint applied at room temperature (72°F) and 67% RH (moderate humidity) and dried at 50°F/85% RH was examined by AFM under the same experimental conditions. The AFM image

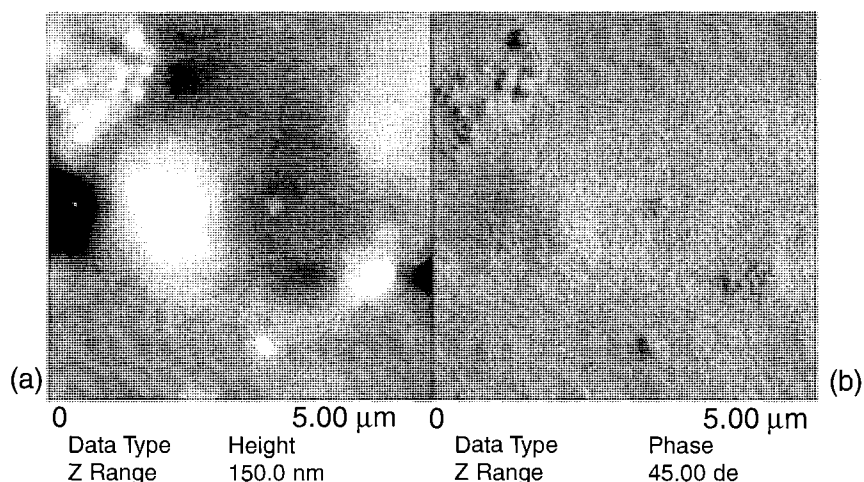


Fig. 13: (a) Height and (b) phase AFM images of industrial DTM white paint. The paint was applied at room temperature (72°F/67% RH) and dried at 50°F/85% RH. The contrast covers height changes in the range of 0-150 nm and phase changes in the 0-45° range. Scan 5.0 μm.

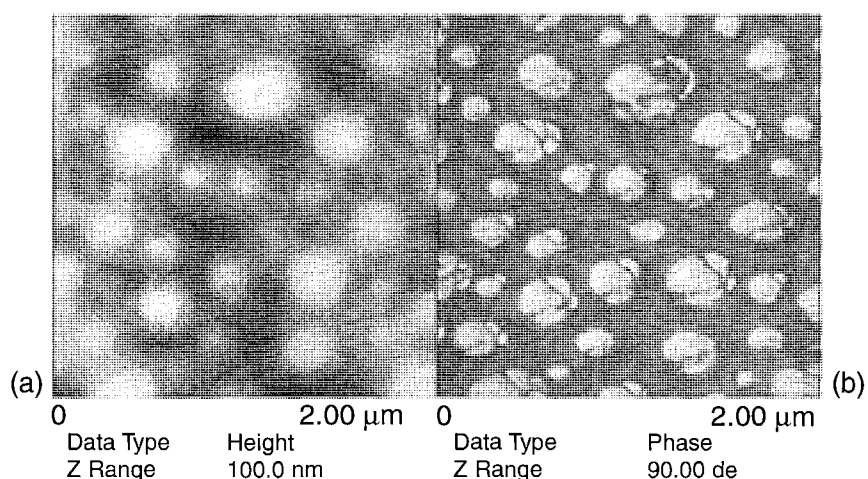


Fig. 14: (a) Height and (b) phase AFM images of acrylic non-aqueous dispersion unpigmented film. The film was dried at 24°C. The contrast covers height changes in the range of 0-100 nm and phase changes in the 0-90° range. Scan 2.0 μm.

(Figure 13) didn't show any crystal formation on the surface. The small spherical particles of approximately 80 to 90 nm in diameter are latex polymer particles. This film passed the adhesion test. This example shows that the AFM can be easily applied to solve application problems of paints and coatings.

3.5 Acrylic Non-Aqueous Dispersion (NAD) Film Formation

Coating industries in the various market sectors are very interested to evaluate surface morphological changes such as film baked (annealed) at various temperatures. To provide optimum temperature

recommendations to auto paint plants and other paint utilizing facilities in various parts of the world, we have been investigating film formation of solventborne and waterborne coatings with different types of polymer systems. In this paper, we would like to present the investigations related to unpigmented acrylic non-aqueous dispersions. The T_g (glass temperature) of the NAD polymer used was found to be 75°C by DSC. The height and phase images (Figure 14) of NAD film dried at room temperature (24°C), give a crystal clear image of the film. Figure 15 shows four AFM images of NAD films at various temperatures viz., 24, 50, 90, and 120°C. In a two micron scan, NAD particles are seen very clearly in the films dried at 24°C and also in the film baked at

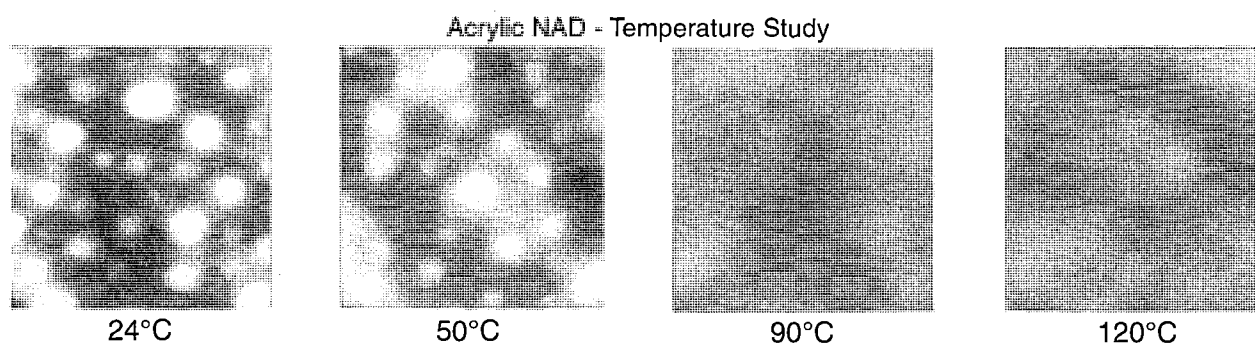


Fig. 15: Height AFM images of acrylic non-aqueous dispersion unpigmented films. The films were dried at 24, 50, 90, and 120°C. The contrast covers height changes in the range of 0-100 nm for films dried at 24 and 50°C and 0-25 nm for films dried at 90 and 120°C. Scan 2.0 μ m.

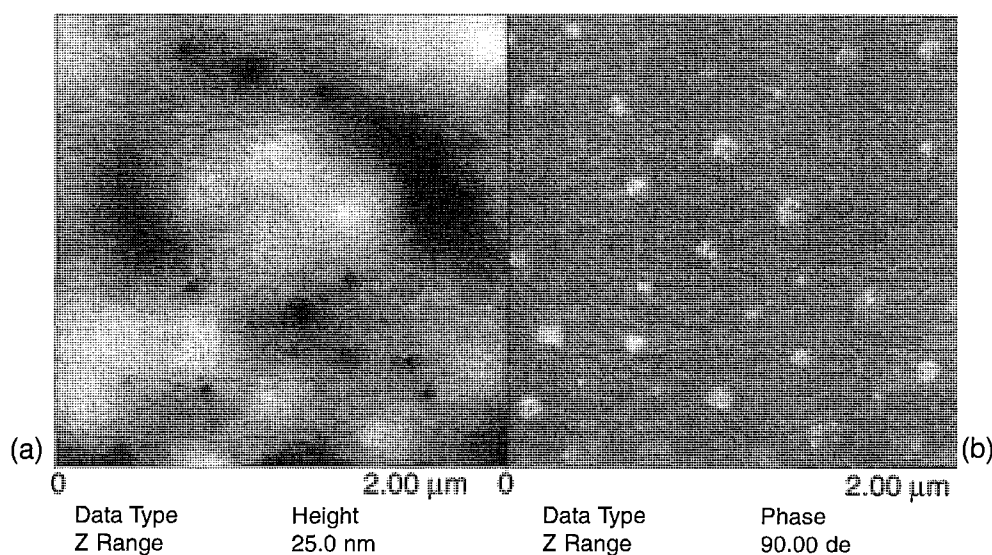


Fig. 16: (a) Height and (b) phase AFM images of acrylic non-aqueous dispersion unpigmented film using light tapping. The film was dried at 120°C. The contrast covers height changes in the range of 0-25 nm and phase changes in the 0-90° range. Scan 2.0 μ m.

50°C. As the film is annealed above the room temperature, the film gets smoother. To quantify the coalescence of the NAD particles, we used the roughness measurements from the AFM image. The Figure 18 shows a plot of roughness (R_a in nm) vs baking temperature of the film. It clearly shows that at 90°C and above, the film gets smoother. The smooth film (baked at 120°C) is still not isotropic (Figure 16). It should be noted that the height variation in Figure 16 is only 25 nm rather than 100 nm as shown in Figure 14.

We have also investigated the effect of the AFM tip force on the phase imaging for the NAD film. For this experiment, we selected the smooth NAD film

(baked at 120°C). Figure 16 shows the AFM images with the normal force (light tapping, where $A_{sp} = 0.8 A_o$, where A_o = Initial Amplitude and A_{sp} = Set Point Amplitude) while Figure 17 shows the images with the higher force (hard tapping, where, $A_{sp} = 0.4 A_o$). It is interesting to see that hard tapping provides more detailed morphological features that are not seen by the light tapping especially in the phase image.

3.6 Nanoindentation Studies

As discussed before, we are very interested to evaluate the durability of coatings in early stages of

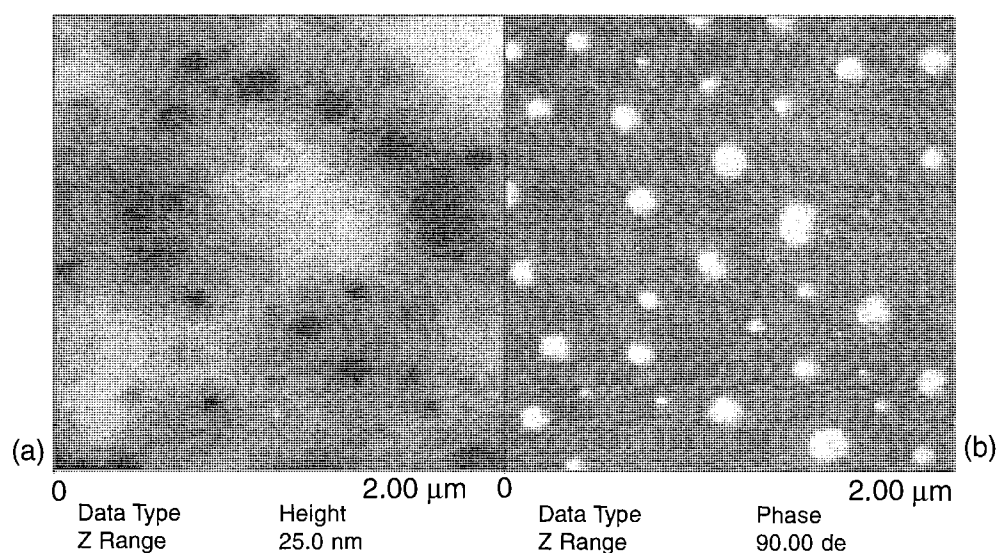


Fig. 17: (a) Height and (b) phase AFM images of acrylic non-aqueous dispersion unpigmented film using hard tapping. The film was dried at 120°C. The contrast covers height changes in the range of 0-25 nm and phase changes in the 0-90° range. Scan 2.0 μm.

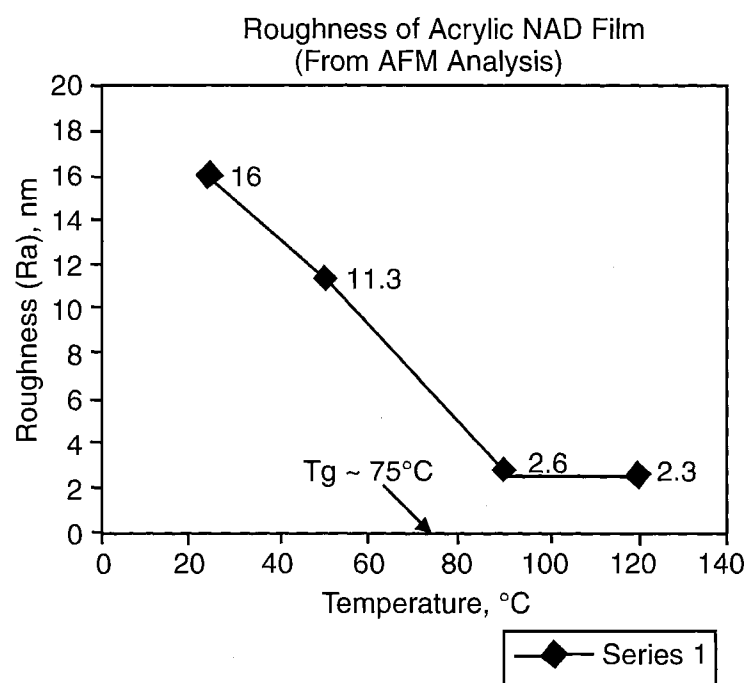


Fig. 18: Roughness (R_a) of acrylic NAD film vs. temperature of the film dried. Roughness was measured from height images.

natural and accelerated exposures. In this research, we are exploiting AFM for nanoindentation and nanoscratching studies. Here, we discuss one example of nanoindentation which was performed on unexposed and 3000 hrs QUV exposed acrylic urethane coatings.

The nanoindentation was performed (Figures 19 and 20) using a diamond tip mounted on AFM and after indentation, the surface was scanned using the same tip. The depth of indentation was measured from the sectional analysis of the AFM image. The Figure 21

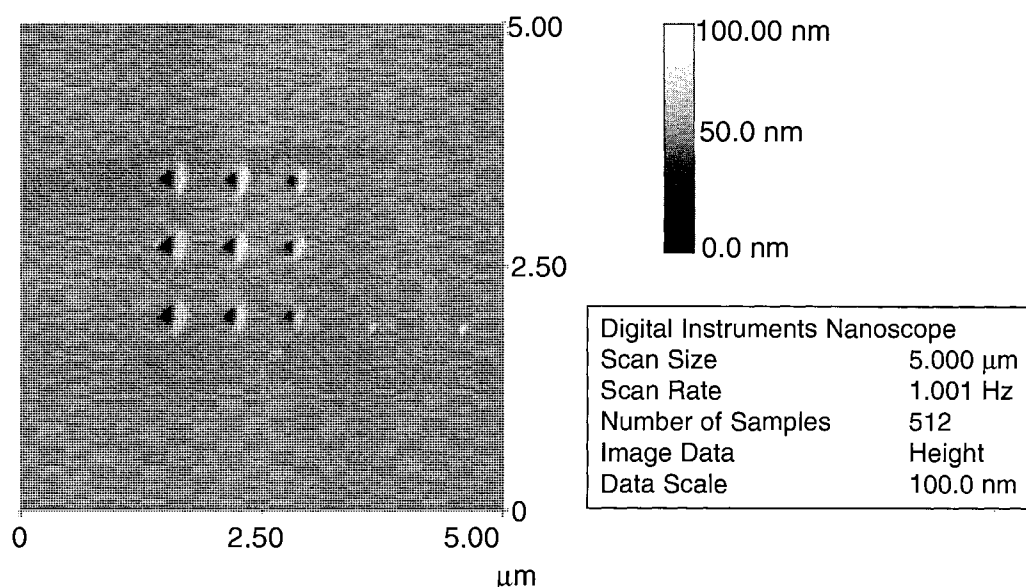


Fig. 19: Nanoindentation performed on an automotive polyurethane coating (unexposed) using three different microforces in triplicate. The contrast covers height changes in the range of 0 –100 nm. Scan 5.0 μm .

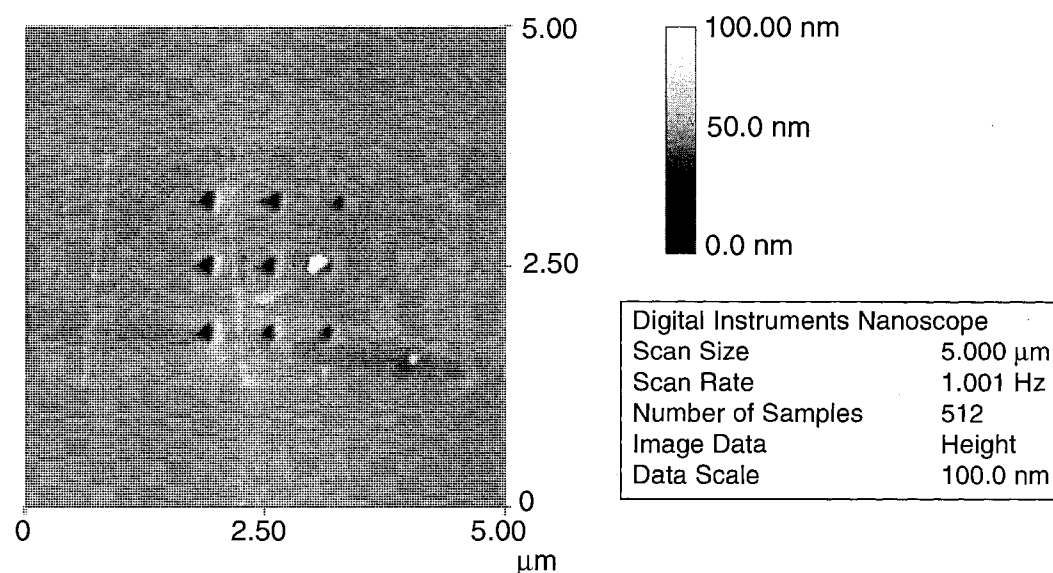


Fig. 20: Nanoindentation performed on an automotive polyurethane coating (3000 hours exposed to QUV) using three different microforces in triplicate. The contrast covers height changes in the range of 0 –100 nm. Scan 5.0 μm .

shows the depth of indentation vs. force. As expected, higher force gives a deeper indent. Also the plot shows that the exposed film is harder to indent than the unexposed film. The AFM image after the indentation allows us to see micro cracking, surface fatigue, elastic recovery, plastic deformation, etc. The nanoscratching studies have been performed similarly.

4.0 Conclusion

The AFM has been found to be a very valuable microscopic tool for paint and coating investigations. We have utilized AFM in tapping mode, phase imaging, nanoindentation and nanoscratching modes. The AFM provided high-resolution images of polymers, paints and

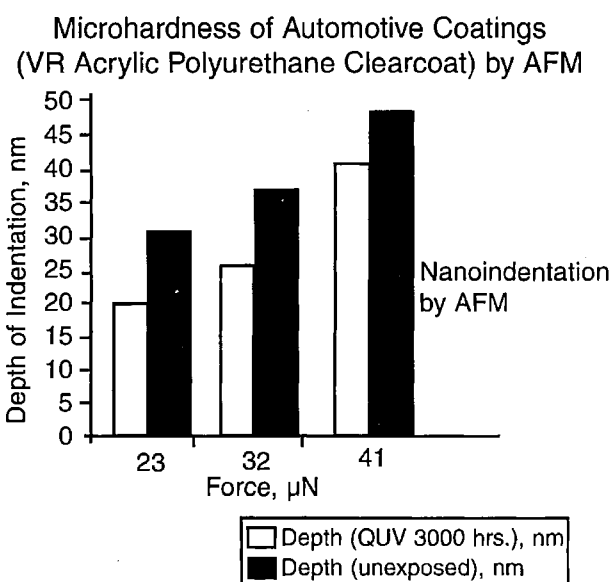


Fig. 21: Depth of indentation vs. force for an automotive topcoat (unexposed and exposed to 3000 hours QUV).

coatings without the need for sample preparation (coating and staining) in nanometer to submicron scale. Overall, AFM brings new possibilities to the paint and coating industry and allows us to see features of coatings that were not accessible before.

5.0 Acknowledgment

The author would like to thank Dr. Bob Coombes for encouragement. Management support from Sherwin-Williams Co. is highly appreciated. The author wishes to give special thanks to Dave Klimovich of Breen Technology Center for providing some of the samples for AFM studies.

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Study by Atomic Force Microscopy: Effect of the Doping Anion on the Surface Morphology of Polypyrrole Films

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Abstract

The effect of both the doping anions (perchlorate and tetrafluoroborate) and the potential limits on the surface morphology of ppy films imaged by AFM are reported using a non-aqueous solvent. Results indicated that by using a cathodic potential limit (-1.0 V) for the ppy films formation, a porous polymer structure is obtained, which occupies a higher

volume than a film electrosynthesized at -0.1 V. Formed nodules are of greater radius and shorter for the former potential limit and taller and thinner for the latter. In addition, ppy films prepared in presence of perchlorate anions presented an intermediary shape between the two above nodules. Presence of "grooves" at the ppy films surfaces electrosynthesized reaching the anodic potential of 1.8 V was observed, but the films prepared reaching 1.0 V grow without formation of grooves.

1.0 Introduction

Conductive polymeric films of polypyrrole (ppy) have been studied for their possible applications in electronics, batteries, electrochromic devices, selective membranes, sensors, and capacitors among others.¹⁻⁵ These applications depend on the ppy properties such as surface morphology and conductivity. It is known that the surface morphology and other properties of the ppy films have an important dependence on the electrosynthesis method and the doping anion.⁶⁻⁷ In previous studies, Naoi *et al.*⁸ reported the effect of different doping anions on the morphology of ppy films studied by Atomic Force Microscopy (AFM) and Scanning Electronic Microscopy (SEM), finding columnar structures in the polymer. Silk *et al.*⁹ indicated that in the ppy films with thickness below 1 μm any effect of four doping anions on the surface morphology were observed; however, for thicker films some differences on the width, height and shape of the globular features on surfaces were found. Above studies were mainly focussed on the formation and analysis of thick ppy films. Recently, Hernández-Pérez *et al.*¹⁰ studied the surface morphology of ppy films at the early stages of growth. In that work, tetrafluoroborate and *p*-toluensulfonate doping anions were used in an AFM study. In this manuscript, we describe the effect of other anions (perchlorate and tetraethylammonium) and the potential limits on the surface morphology of ppy films prepared from acetonitrile. These films were imaged by AFM.

2.0 Experimental

2.1 Ppy Film Preparation

The ppy films were prepared by the electropolymerization of pyrrole (Py) monomers from an acetonitrile solution containing 0.1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4) or 0.1 M lithium perchlorate (LiClO_4). All films were prepared by cyclic voltammetry (voltammetric method) using two pyrrole monomer concentrations of 1.85×10^{-3} M and 3.7×10^{-3} M. In all electrochemical experiments a three-electrode electrochemical cell was used with a Pt film supported on a glass electrode (area *ca* 0.25 cm^2) as working electrode, a Pt gauze (area *ca*. 4 cm^2) as counter electrode and a Ag/0.1 M AgBF_4 electrode as reference. All potentials are refereed to the Ag/0.1 M AgBF_4 electrode. The experiments were performed in inert atmosphere, after de-oxygenation of the electrochemical cell with super-pure N_2 (15 min.). The voltammetric ppy

film deposition was carried out by means of a PARC 173 potentiostat-galvanostat (EG & G) coupled both to a PARC 175 Universal programmer (EG & G) and to a Hewlett Packard 7004B x-y recorder.

2.2 AFM Imaging

The surface morphology of the ppy film on the Pt substrate was observed using an by AFM, Nanoscope III, from Digital Instruments, (DI). Imaging was performed utilizing *ex situ* approach, under laboratory atmosphere, at the room temperature. The freshly prepared ppy films were checked at the oxidative stage breaking the imposed potential at the positive limit. AFM imaging was performed in the “contact mode”, using standard geometry silicon nitride probes from DI. Images were collected in slow scan rate of 1 Hz; to avoid possible undesired interactions between the AFM tip and the polymer sample. The imaging samples were rinsed by water, acetonitrile and acetone solvents, to remove eventual surface impurities and dried in a stream of clean air. As expected, despite using the contact mode AFM imaging, no damage of the polymer surface was observed during the imaging process. Usually on each sample imaging was performed at four different locations. All images are presented in the “height” mode, with the higher part of the imaged surface colored brighter in the image. 3D image presentations were intentionally used to emphasize differences among the polymer film surface morphologies. The quantitative evaluation of the polymer film surface morphology was based on utilization of a software package for image analysis which came with the Nanoscope III software set.

2.3 Chemicals and Solutions

The pyrrole (Py) monomer (Aldrich) was purified by distillation in vacuum before each experiment. Acetonitrile solvent (HPLC grade, Prolabo), AgBF_4 (Aldrich) and LiClO_4 (Sigma) were used as received. Et_4NBF_4 (Aldrich) was recrystallized and dried in vacuum before using. In order to prepare the Py solution, the electrolyte was dissolved in acetonitrile and deoxygenated with superpure nitrogen. The Py monomer was then added. Between experiments, within the same day, Py solutions were maintained in an inert atmosphere.

3.0 Results and Discussion

The ppy films were performed using a voltammetric program beginning at the zero-current potential ($E_{t=0}$) following the forward potential until the anodic limit (E_+) and switching into the cathodic potential (E_-). The

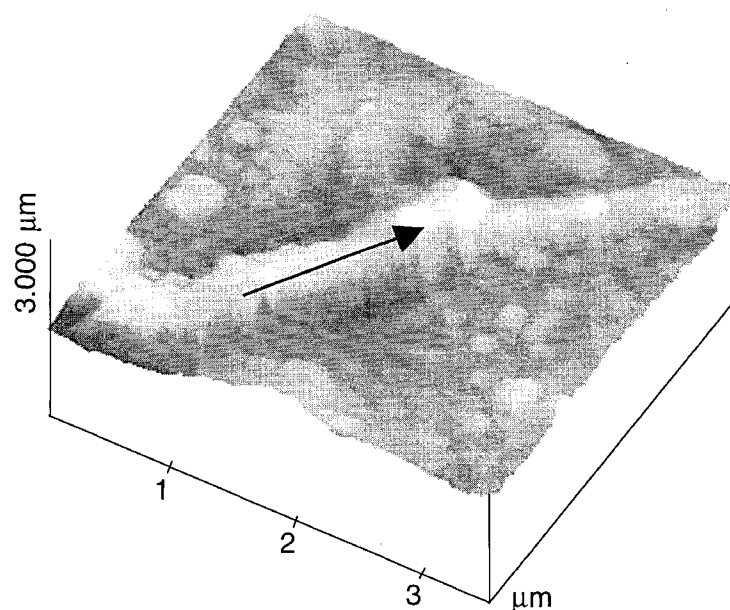


Fig. 1: AFM image of a ppy film formed in presence of 0.1 M Et_4NBF_4 using $E_- = -0.1$ V and $v = 0.1$ V/s. Arrow indicates a groove.

limits between E_+ and E_- will be considered as the potential window in which ppy films will be formed. The cyclic voltammogram of ppy film formation using the program with $E_{1=0} = -0.1$ V, $E_+ = 1.8$ V and $E_- = -0.1$ V shows the irreversible peak that was previously observed.¹⁰ The ppy films were formed in an acetonitrile solution containing 0.1 M of Et_4NBF_4 and 3.7×10^{-3} M of Py using a scan rate (v) of 0.1 V/s and five potential scan cycles (PSC). It is worthy to mention that in the above experiments¹⁰ only one PSC was used for the ppy film formation. In this article the effect of the PSC number will also be explored. In order to maintain the ppy film in its oxidized stage the potential was stopped at 1.8 V in the film formation process.

Other ppy films were prepared using the voltammetric method changing the cathodic limit at $E_- = -1.0$ V, yielding similar voltammograms to those previously reported.¹⁰ Figures 1 and 2 display the AFM images of the ppy films formed in the two cases using $E_- = -0.1$ V and $E_- = -1.0$ V respectively.

It was observed that in the two images, the films display nodules and “grooves” distributed in a random way, and they seem to be equal. However, a quantitative analysis of those images showed different characteristics which are displayed in Table 1.

The studied surfaces have a mean roughness (RMS) higher than bare platinum¹⁰ (RMS = 4.7), which indicates the formation of a thick ppy film on the Pt electrodes, because of a thin film does not change the RMS of the bare Pt electrode very much.¹⁰

Analyzing the characteristics of Table 1, it can be observed that the thickness of the ppy film increases changing the cathodic potential (E_-) from -0.1 V (Figure 1) to -1.0 V (Figure 2). This phenomenon can be explained as the conformational surface relaxation proposed by Otero *et al.*¹¹ If we apply very negative potential values E_- (-1.0 V) to the film, they will induce a free interchange of anions between the polymer and those in solution. This interchange permits a relaxation over the volume of the electrodeposited ppy, and formation of a porous ppy. Therefore, this structure might have a higher volume than those where any relaxation was promoted.

Now, in the ppy film formed using $E_- = -0.1$ V, the anions interchanged at the polymer/solution interface are not favored (or it is a slow reaction), which restrains the surface relaxation. Therefore, a ppy film with less volume and thickness will be produced; in other words, a compact film of ppy will be formed.

If we consider width, height and shape of nodules and grooves formed in different conditions, a representative shape of each nodule will be as shown in Figure 3.

The nodules formed using $E_- = -0.1$ V are sharper, (thin and tall), making to be pile up themself, building a closed surface, which is less porous than those formed using $E_- = -1.0$ V. The nodules are short and extend over a large area (wide).

As expected, the roughness changes from 10.7 (Figure 1) to 7.92 nm (Figure 2), because of the nodules are thin and tall in Figure 1 and short and wide in Figure 2.

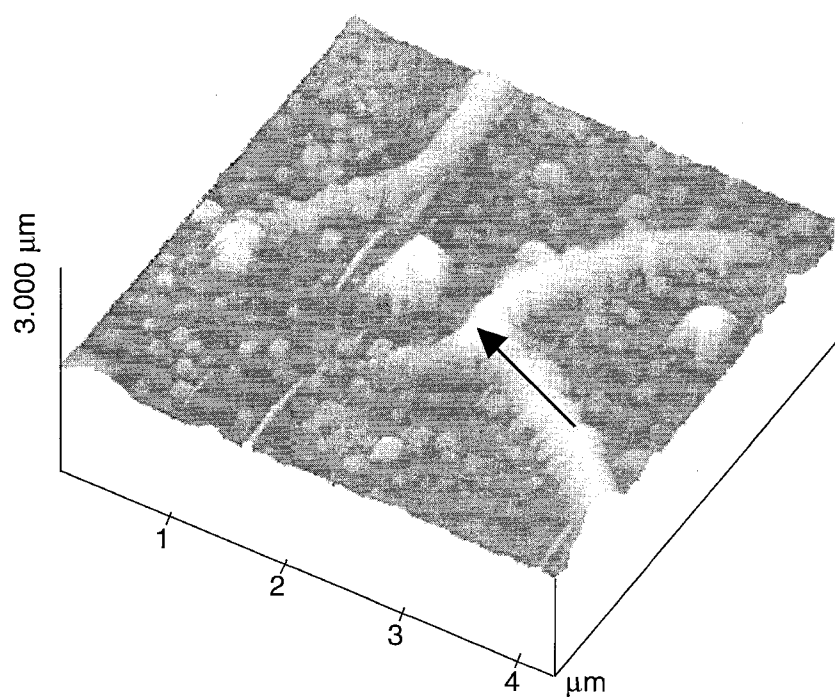


Fig. 2: AFM image of a ppy film formed in presence of 0.1 M Et_4NBF_4 using $E_{\text{f}} = -1.0$ V and $v = 0.1$ V/s. Arrow indicates a groove.

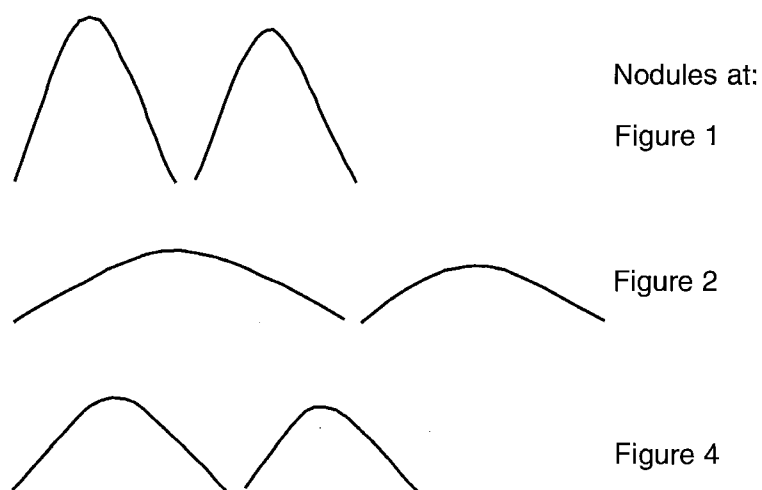


Fig. 3: Representation of the nodule shapes of each indicated figure.

Table 1. Characteristics of the Observed Surfaces in Figures 1, 2, and 4

Figure	Nodules/Grooves	Nodules/Grooves		
	Radius/(nm)	Height/(nm)	RMS/(nm)	Thickness/(nm)
1	53/447	25-34/291	10.7	33
2	93/339	18/205	7.92	118
4	64/516	26/322	10.7	54

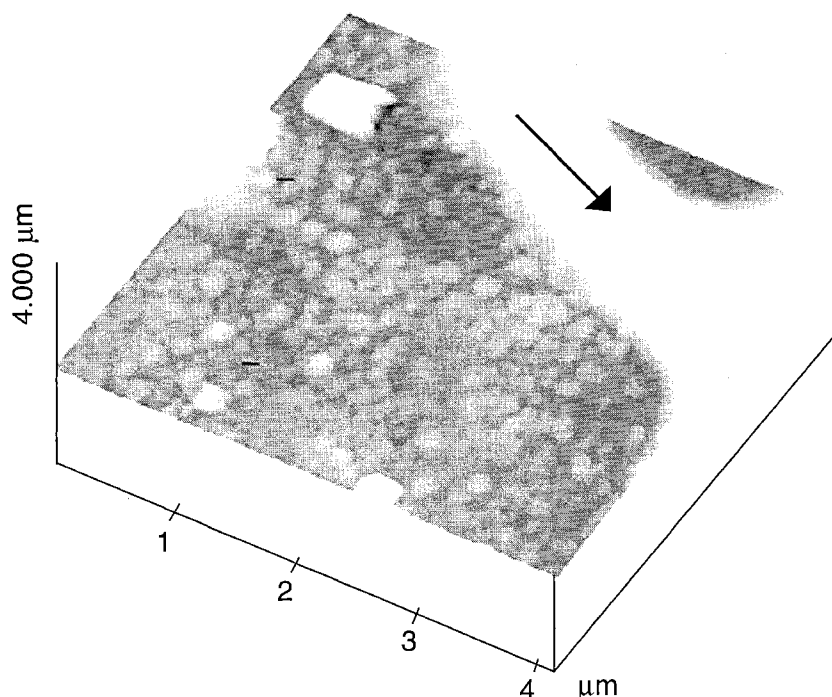


Fig. 4: AFM image of a ppy film formed in presence of 0.1 M LiClO_4 using $E_- = -1.0$ V and $v = 0.1$ V/s. Arrow indicates a groove.

3.1 Effect of the Doping Anion

The following ppy films were electrosynthesized similarly to these above, using the perchlorate as doping anion. Figure 4 shows the AFM image of a ppy film formed at $E_- = -1.0$ V with a py concentration of 1.85×10^{-3} M and 0.1 M of LiClO_4 . The main characteristics of nodules and grooves are displayed in Table 1, and the nodules shapes are represented in Figure 3. It is evident that there are important differences between the surface morphology shown in Figures 1, 2, and 4, mainly when the electrolyte changes from tetrafluoroborate to perchlorate. When the tetrafluoroborate is the counter anion the nodules are wide and short, whereas with the perchlorate as counter anion the grooves are always of higher size.

From these results, we can infer that nodules formed in the presence of the perchlorate ion look like those observed in Figure 1. In other words, the displayed nodules in Figure 4 have an intermediate shape between that observed in Figures 1 and 2.

3.2 Effect of the Anodic Limit (E_+)

To study this effect two ppy films were electrosynthesized on Pt using the same electrolyte

(LiClO_4) and the electrochemical conditions described in the experiment section (using five potential scan cycles), changing exclusively the E_+ .

Figures 5 and 6 show AFM images of the observed surfaces of the ppy films using $E_+ = 1.8$ and $E_+ = 1.0$ V respectively. Figure 5 clearly shows some grooves, however in Figure 6 these features disappear completely, when less anodic E_+ was used yielding a very homogeneous ppy film surface with a lower value of roughness (3.7 nm). The nodules have 17.1 nm height and 183.1 nm width.

Another effect that affects the ppy surface morphology is the potential scan cycle number, because of with each sweeping cycle is electrodeposited more ppy forming films with higher thickness and increment of roughness. Figure 7 shows the AFM image of a ppy film using the same conditions as Figure 6 applying 30 PSC and using Et_4NBF_4 as the doping anion. It can be observed that the RMS roughness increment goes to 712.73 nm.

4.0 Conclusions

A very cathodic potential (-1.0 V) of electrosynthesis produced porous ppy films with higher volume than were electrosynthesized using $E_- = -0.1$ V. The surface morphology has wide and short nodules

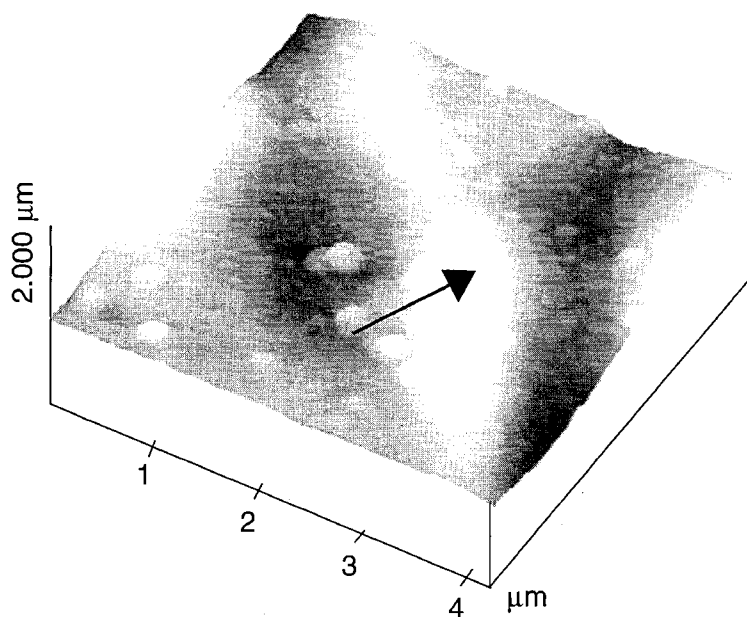


Fig. 5: AFM image of a ppy film formed in presence of 0.1 M Et_4NBF_4 using $E_+ = 1.8$ and $E_- = -0.1$ V and $v = 0.1$ V/s. Arrow indicates a groove.

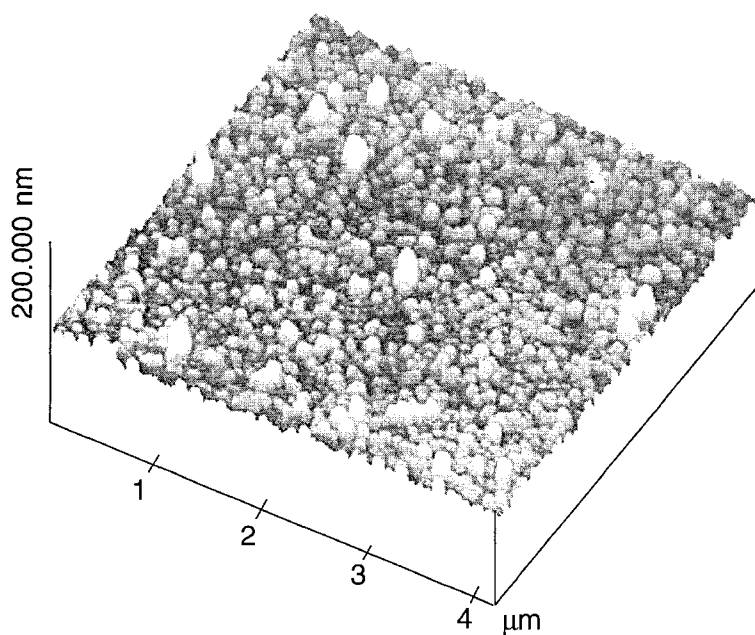


Fig. 6: AFM image of a ppy film formed in presence of 0.1 M LiClO_4 using $E_+ = 1.0$ V, $E_- = -0.1$ V and $v = 0.1$ V/s.

when $E_- = -1.0$ V; whereas for E_- near or equal to $E_{I=0}$, the shape is tall, thin and sharp.

There are important differences between the formed nodules and grooves observed on the ppy surfaces using either tetrafluoroborate or perchlorate as doping anions.

It was found that using an anodic limit of +1.0 V, the ppy film surface is free of grooves showing only the nodules homogeneously distributed.

It was established that diverse experimental conditions afforded different surface morphologies of

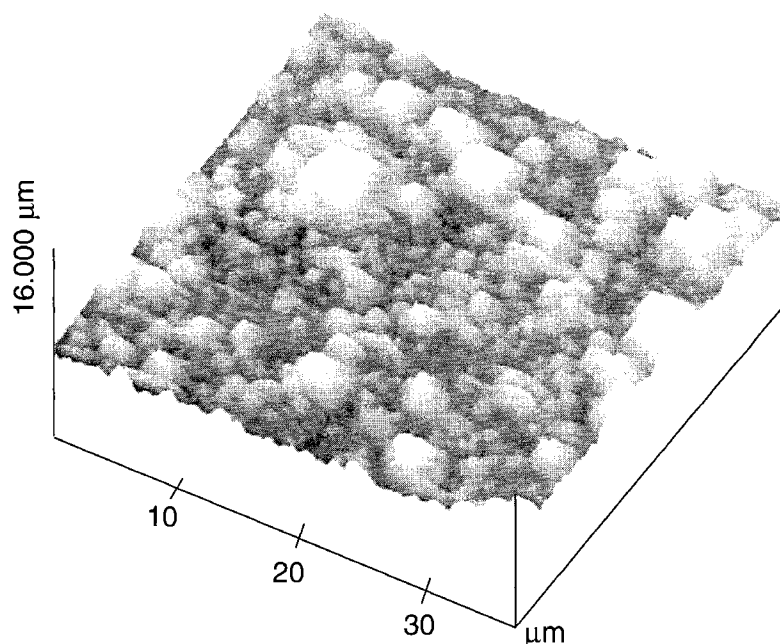


Fig. 7: AFM image of a ppy film formed in presence of 0.1 M Et_4NBF_4 using $E_+ = 1.0$ V, $E_- = -0.1$ V and $v = 0.1$ V/s. 30 potential scan cycles.

the obtained ppy films. This is very important in the surface engineering of the ppy films as it is applied in an industrial process, such as in the electronics, batteries, and electrochromic devices engineering. In example, whether we select an specific experimental condition (here studied), an unique ppy surface morphology will be obtained. This will present nodules and grooves of specific size and shape which will used in a determined applications.

5.0 Acknowledgments

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Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM): Complementary Techniques for High Resolution Surface Investigations

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Abstract

There are many analytical techniques which may be used for materials characterization depending on the type of information needed. For high resolution surface investigations, two commonly used techniques are Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Each of these techniques resolves surface structure down to the nanometer scale. However, the image formation mechanisms

are quite different, resulting in different types of information about the surface structure. The occurrence of the SEM and AFM side-by-side is becoming more common in today's analytical laboratories. A comparison of these techniques has been conducted with respect to the surface structure and composition of the specimen, as well as the operating environment, which demonstrates how these analytical techniques provide information which is complementary in nature.

1.0 Introduction

1.1 History

The first SEM was constructed in 1938 by rastering the electron beam of a Transmission Electron Microscope (TEM) to essentially form a Scanning Transmission Electron Microscope (STEM).¹ In 1942, the first SEM for bulk samples was developed which contains many of the basic principles of today's SEMs. The development of the AFM was preceded by the development of the Scanning Tunneling Microscope (STM) in 1981.² Although STM provides the ability to view the atomic lattice of a sample surface, it is limited to conductive and semiconductive samples. To image insulators as well as conductors, the Atomic Force Microscope (AFM) was developed in 1986 and has since become the most popular form of the Scanning Probe Microscopy (SPM) techniques.³

2.0 Methods

2.1 Scanning Electron Microscopy

The operation of the SEM consists of applying a voltage between a conductive sample and filament, resulting in electron emission from the filament to the sample. This occurs in a vacuum environment ranging from 10^{-4} to 10^{-10} Torr. The electrons are guided to the sample by a series of electromagnetic lenses in the electron column. A schematic of a typical SEM is shown in Figure 1. The resolution and depth of field of the image are determined by the beam current and the final spot size, which are adjusted with one or more condenser lenses and the final, probe forming objective lenses. The lenses are also used to shape the beam to minimize the effects of spherical aberration, chromatic aberration, diffraction, and astigmatism.

The electrons interact with the sample within a few nanometers to several microns below the surface, depending on beam parameters and sample type. Electrons are emitted from the sample primarily as either backscattered electrons or secondary electrons. Secondary electrons are the most common signal used for investigations of surface morphology. They are produced as a result of interactions between the beam electrons and weakly bound electrons in the conduction band of the sample. Some energy from the beam electrons is transferred to the conduction band electrons in the sample, providing enough energy for their escape from the sample surface as secondary electrons. Secondary electrons are low energy electrons ($<50\text{eV}$), so only those formed within the first few nanometers of

the sample surface have enough energy to escape and be detected. High energy beam electrons which are scattered back out of the sample (backscattered electrons) can also form secondary electrons when they leave the surface. Since these electrons travel farther into the sample than the secondary electrons, they can emerge from the sample at a much larger distance away from the impact location of the incident beam which makes their spatial distribution larger. Once these electrons escape from the sample surface, they are typically detected by an Everhart-Thornley scintillator-photomultiplier detector. The SEM image formed is the result of the intensity of the secondary electron emission from the sample at each x, y data point during the rastering of the electron beam across the surface.

2.2 Atomic Force Microscopy

AFM consists of scanning a sharp tip on the end of a flexible cantilever across a sample surface while maintaining a small, constant force. The tips typically have an end radius of 5 to 20 nm, although this may vary depending on tip type. The scanning motion is conducted by a piezoelectric tube scanner which scans the tip in a raster pattern with respect to the sample (or scans the sample with respect to the tip). The tip-sample interaction is monitored by reflecting a laser off the back of the cantilever into a split photodiode detector. By detecting the difference in the photodetector output voltages, changes in the cantilever deflection or oscillation amplitude are determined. A schematic of this can be seen in Figure 2.

The two most commonly used modes of operation are contact mode AFM and tapping mode AFM, which are conducted in air or liquid environments. Contact mode AFM consists of scanning the probe across a sample surface while monitoring the change in cantilever deflection with the split photodiode detector. A feedback loop maintains a constant cantilever deflection by vertically moving the scanner to maintain a constant photodetector difference signal. The distance the scanner moves vertically at each x, y data point is stored by the computer to form the topographic image of the sample surface. This feedback loop maintains a constant force during imaging, which typically ranges between 0.1 to 100 nN.

Tapping mode AFM consists of oscillating the cantilever at its resonance frequency (typically $\sim 300\text{ kHz}$) and lightly "tapping" on the surface during scanning. The laser deflection method is used to maintain a constant root-mean-square (RMS) amplitude voltage on the photodiode detector, which in turn maintains a constant applied force during imaging. A feedback loop

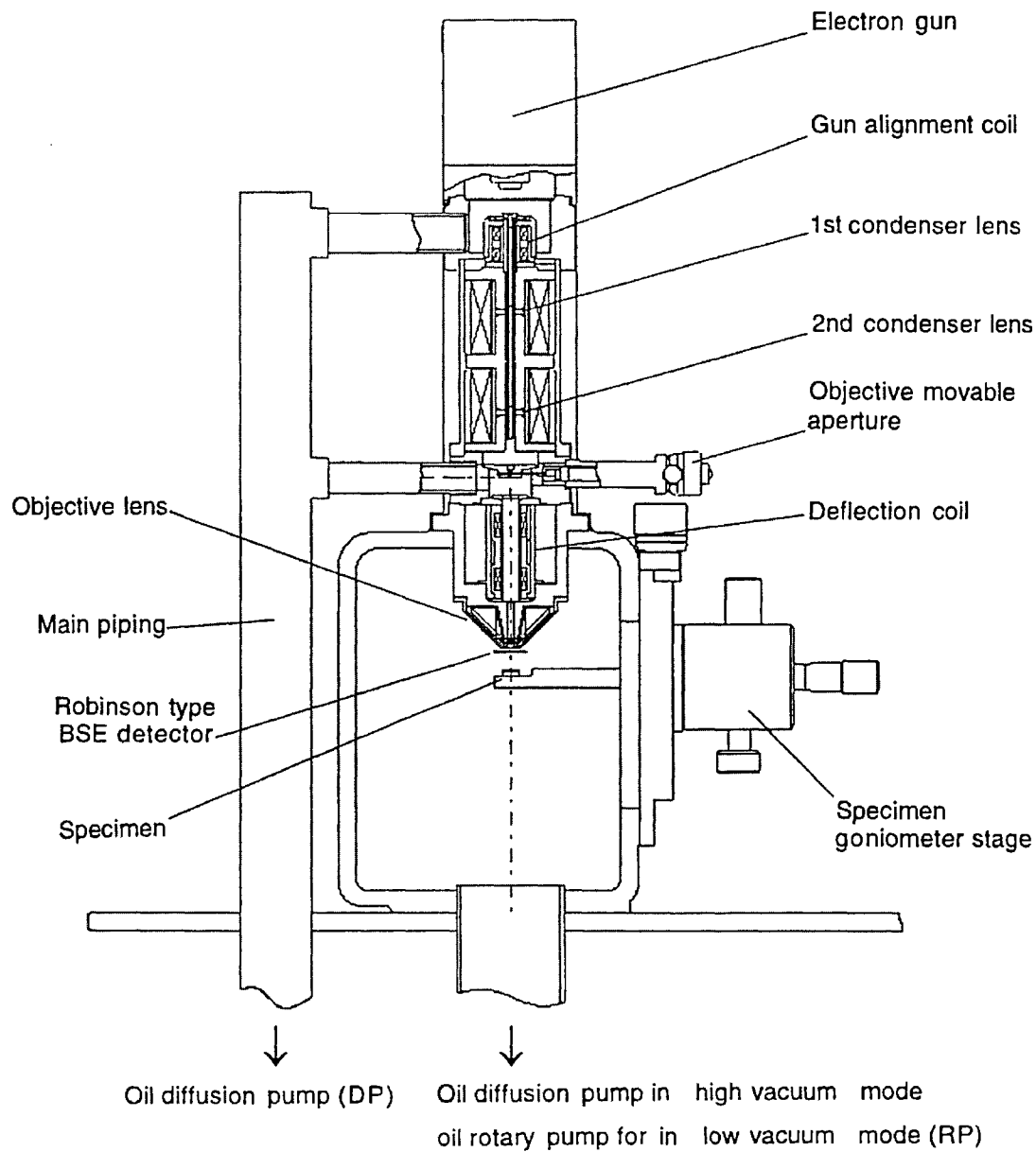


Fig. 1: Schematic of the primary components of a typical SEM.

maintains a constant oscillation amplitude by moving the scanner vertically at every x, y data point to form the topographical image. The advantage of tapping mode with respect to contact mode is that it operates with a lower normal force applied to the sample surface, and it eliminates the lateral, shear forces present in contact mode. Both of these factors make it possible for tapping mode to image soft, fragile, and adhesive surfaces without damaging them, which can be a drawback to contact mode AFM.

3.0 Results

There are a number of different ways to compare and contrast SEM and AFM. Although investigations

that use SEM and AFM to characterize a material are common, there are just a few studies that directly discuss the complementary nature of the techniques.⁴⁻⁹ A comparison of these techniques will be conducted with respect to 3 factors:

1. Surface Structure,
2. Composition. and
3. Environment.

3.1 Surface Structure

Although both SEM and AFM are similar in lateral resolution, there are situations in which one technique can provide a more complete representation of the sample surface, depending on the information desired.

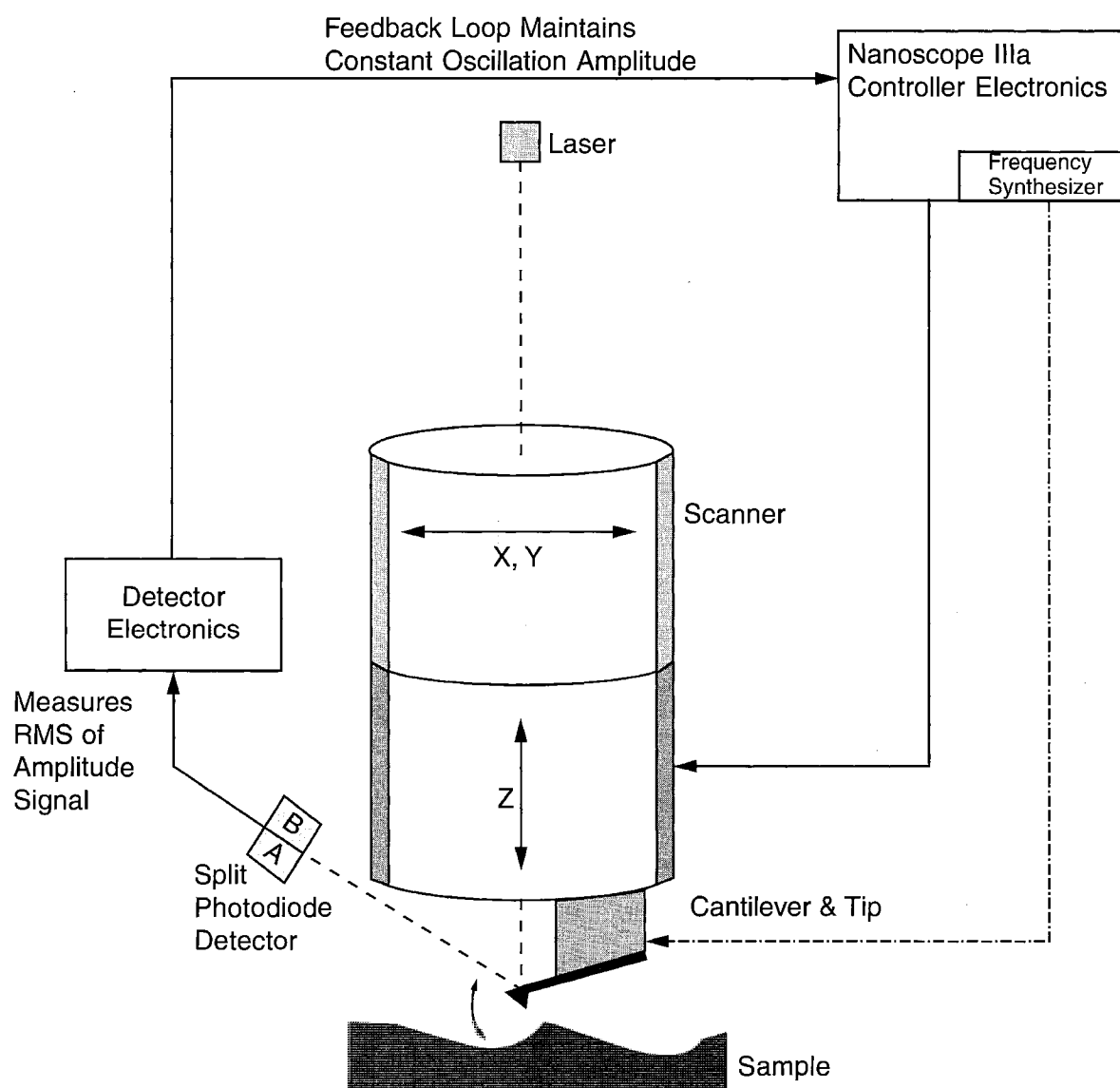


Fig. 2: Schematic of the major components of an AFM showing the feedback loop for tapping mode operation.

One principal difference is in how the two techniques process vertical changes in topography. Below we will discuss measurements of different vertical scales of topography, beginning with smooth surfaces and working up to rough surfaces to determine how the surface topography affects the ability of each technique to perform the measurement.

3.1.1 Atomically Smooth Surfaces

Atomically smooth surfaces can occur naturally, such as on mineral surfaces, or by processing, such as polishing and epitaxial growth on semiconductor, data storage, and optical surfaces. A tapping mode AFM image of an epitaxial silicon surface is shown in Figure 3. Since the AFM has a vertical resolution of $<0.5 \text{ \AA}$, it can resolve the $1.4 \text{ \AA}$ monoatomic silicon steps on the surface as well as calculate an RMS roughness of

$0.7 \text{ \AA}$.¹⁰ On a sample this smooth, the SEM has difficulty resolving these features due to the subtle variations in height.

3.1.2 Thin Films

On most thin films, the SEM and AFM produce a similar representation of the sample surface. A common application of surface investigations of thin films consists of determining changes in morphology with variations of deposition parameters, such as temperature, pressure, time, etc. Figure 4 shows SEM and AFM images of a polysilicon thin film at approximately the same lateral magnification. The two images show similar surface structure, however, they differ in the other types of information that can be acquired on this sample. The three dimensional nature of the AFM can be used to calculate changes in roughness and surface area

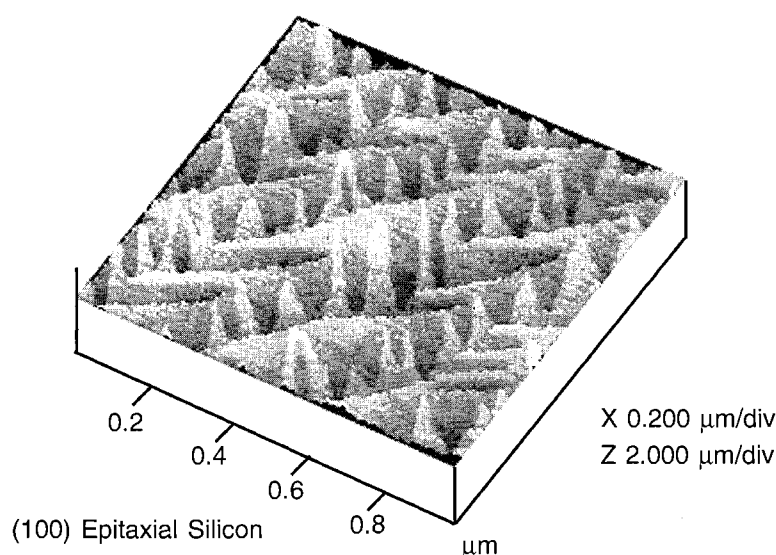


Fig. 3: Tapping mode AFM image of 1.4 Å monoatomic steps on epitaxial silicon deposited on Si (100). 1 μm scan.

variations due to differences in deposition parameters. For the SEM, a large area view of the surface structure can be acquired all at once (such as several mm's), whereas a $100 \times 100 \mu\text{m}$ area is typically the largest area viewed by an AFM. These images are an example of "rugged" polysilicon films which are used as capacitors in memory devices. By making these films rough, the surface area is increased which makes it possible to hold more charge without increasing the lateral dimensions of the capacitors on the chips. By adjusting the deposition parameters and using the AFM to analyze the surface area of the films, the deposition parameters needed to produce a film with the maximum surface area were determined.¹¹

3.1.3 High Aspect Ratio Structures

Semiconductor processing commonly requires measurements of high aspect ratio structures such as trenches and via holes. In a SEM, these structures are typically measured in cross section by cleaving the wafer and imaging the sample on end to obtain the dimensions of the structure. A common example of this is seen in Figure 5a. In contrast, the AFM image of a trench or via is made by scanning over the sample surface. The ability of the AFM to measure these structures nondestructively makes it possible for the wafer to be returned to the production line after the measurement is acquired. An AFM image of vias in photoresist is shown in Figure 5b. To image some higher aspect ratio structures, the proper tip shape may be needed for the AFM to scan narrow openings and steep sidewalls. Although the SEM measurement is destructive to the sample, its ability to

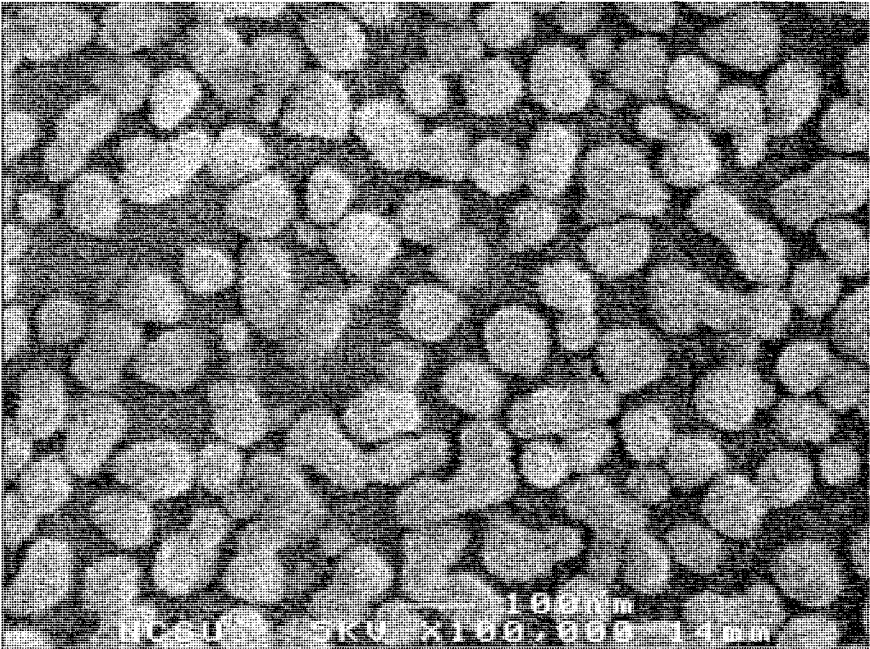
image the undercuts of these lines (Figure 5a) is a useful application that AFMs are not typically designed to perform.

3.1.4 Rough Surfaces

One of the key advantages of the SEM with respect to other types of microscopy is its large depth of field. This ability makes it possible to image a very rough surface with mm's of vertical information within a single image. A SEM image of non-woven polyethylene oxide fibers can be seen in Figure 6. The depth of field and small beam size makes it possible to image the fibers far below the top layer. This ability also makes it possible to measure very rough surfaces over larger lateral areas as well. Although the AFM can measure vertical surface variations below 0.5 Å, its ability to measure a tall structure comes from how far the scanner can move vertically. Standard scanners typically have 5 to 6 μm of vertical range, however, in some configurations the vertical range approaches 10 μm. For scanning areas that have heights of greater than 5 to 10 μm's of variation, the SEM would be better suited for the analysis.

3.2 Composition

Both SEM and AFM provide compositional information through a variety of techniques. SEM is the only one of the two techniques which provides elemental analysis, however, both SEM and AFM are associated with techniques which can provide compositional information through analyzing materials and physical properties of the sample.



(a)

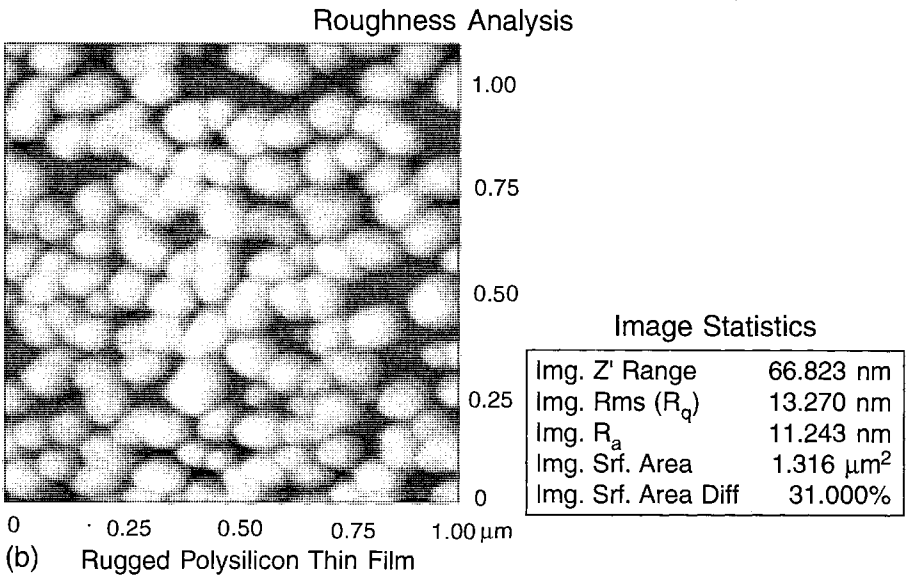


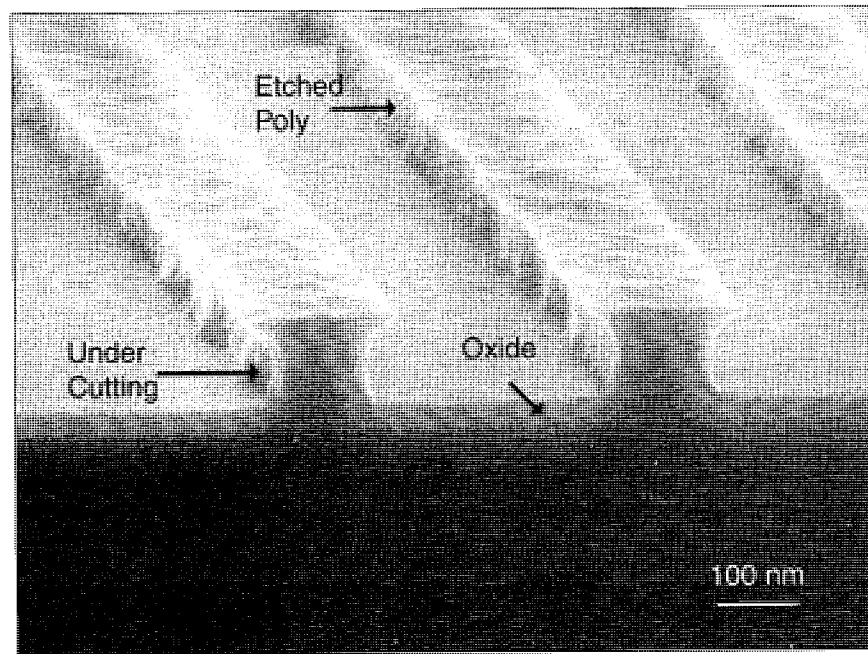
Fig. 4: (a) SEM and (b) tapping mode AFM images of the same rugged polysilicon thin film. The roughness measurement of the AFM data is shown in 5(b). (a) 100,000X, Bar = 0.1 μm , and (b) 1 μm scan.

3.2.1 SEM

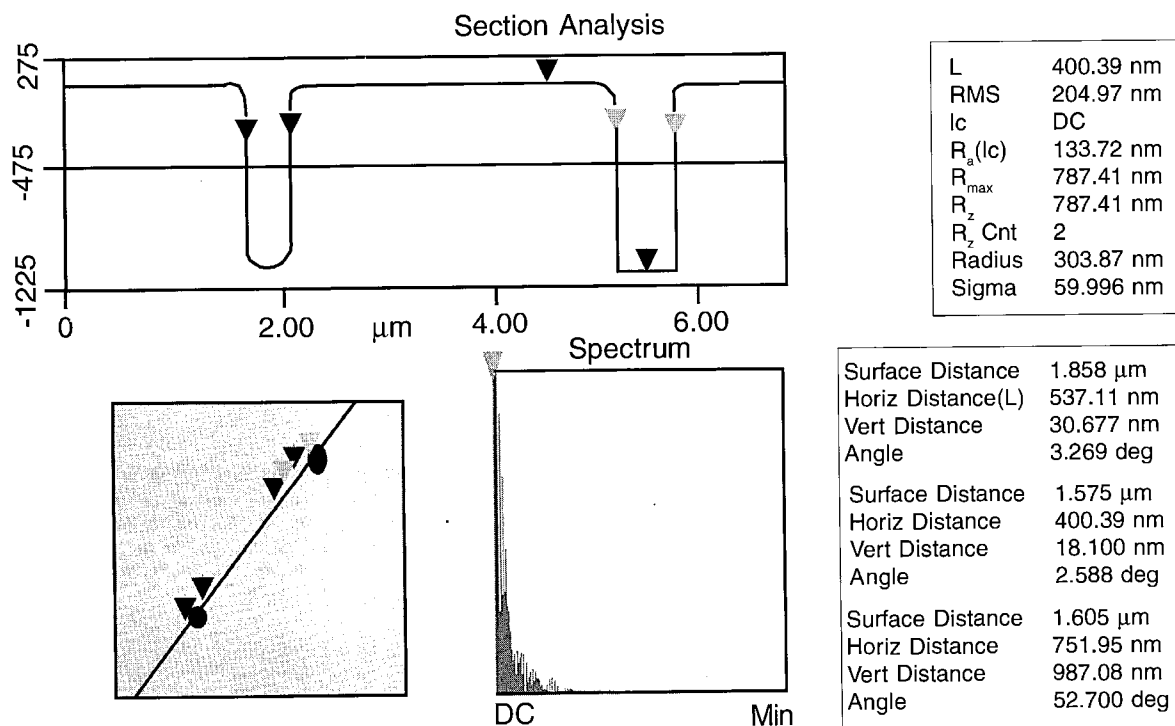
Along with the secondary electron emission which is used to form a morphological image of the surface in the SEM, a number of other signals are emitted as a result of the electron beam impinging on the surface. Each of these signals carries information about the sample which provides clues to its composition.

Two of the most commonly used signals for investigating composition are x-rays and backscattered

electrons. X-ray signals are commonly detected to provide elemental analysis by the attachment of an Energy-Dispersive Spectrometer (EDS) or Wavelength-Dispersive Spectrometer (WDS) to the SEM system. X-ray emission results from inelastic scattering between the beam electrons and the electrons of the sample atoms. This interaction results in the ejection of an inner shell electron from the atom, creating a vacancy that is filled by an outer shell electron. This jump from an outer to



(a)



(b)

Fig. 5: (a) Cross-sectional SEM image of polysilicon lines which shows undercutting due to reactive ion etching. Scale bar = 100 nm and (b) Cross-sectional measurement of developed and incompletely developed vias in photoresist acquired by tapping mode AFM. In order to image the high aspect ratio structures on the sample, a silicon tip machined with a focus ion beam was used to scan the vias. 6.2 μ m scan.

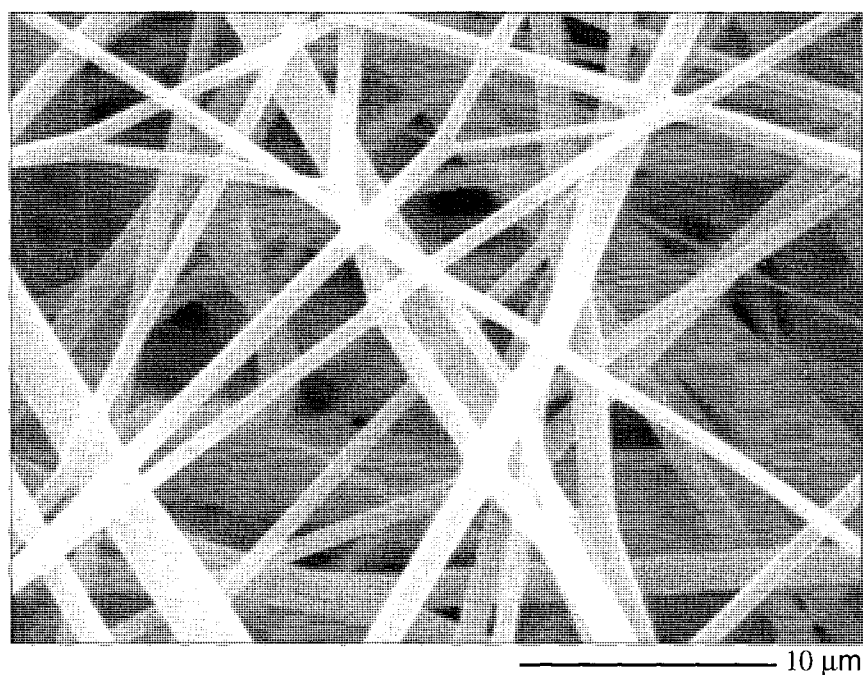


Fig. 6: SEM image of a non-woven textile sample of polyethylene oxide fibers. The large depth of field of the SEM makes it possible to image fibers which are 10's of μm 's below the upper layer of fibers. Bar = 10 μm .

inner shell results in a change in energy that produces either an x-ray or Auger electron. The emitted x-ray has energy equal to this change. A typical x-ray spectrum collected with an EDS system is shown in Figure 7.

Backscattered electrons are the result of beam electrons being scattered back out of the sample. In this case, the incident beam electrons undergo a number of scattering events within the specimen in which very little energy is lost, allowing these electrons to go much deeper into the sample than secondary electrons and still emerge from the sample surface to be detected. The percentage of beam electrons that become backscattered electrons has been found to be dependent on the atomic number of the material, which makes it a useful signal for analyzing the material composition.

3.2.2 AFM

Although an AFM does not provide elemental analysis, it can supply compositional information by differentiating materials based on physical properties, such as stiffness, elasticity, compliance, friction, adhesion, magnetic and electrostatic fields, carrier concentration, temperature distribution, spreading resistance, and conductivity. Many of these techniques consist of looking at another signal while performing standard AFM imaging, or performing slight variations on the standard imaging methods. One of the most common techniques for mapping differences in materials

properties is Phase Imaging. Phase Imaging is conducted during tapping mode AFM operation by monitoring the phase lag between the oscillating drive signal used to resonate the cantilever and the detection signal from the photodiode detector. Phase Imaging can indicate differences in viscoelasticity and adhesion across the imaged area. This technique is commonly applied to mapping the distribution of polymers in a multi-polymer system, or mapping filler distribution, such as silica or carbon black, in a polymer matrix, and to map heterogeneity on other composite materials. An example of phase imaging on a polyethylene film is shown in Figure 8.

Although the AFM is applied so that it is nondestructive to the sample surface, it can be used to study differences in mechanical properties by performing nanoindentation to investigate hardness differences between materials. This technique uses a diamond tip mounted on a stiff, stainless steel cantilever. A tapping mode AFM image is collected with the probe to determine the area of interest for indentation, the nanoindentation is then made at a specified force, and an image is then collected of the indented area.

3.3 Environment

One of the primary differences between SEM and AFM is the environment in which they are performed,

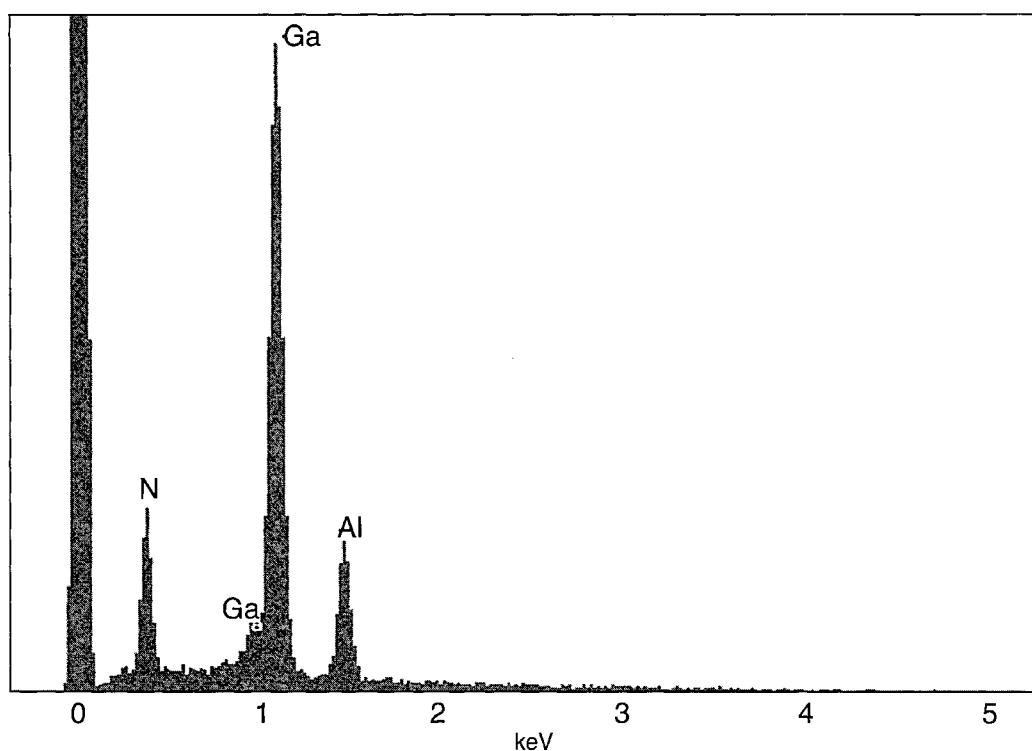


Fig. 7: EDS X-ray spectrum of an AlGaIn thin film on SiC substrate showing the presence of N, Ga, and Al.

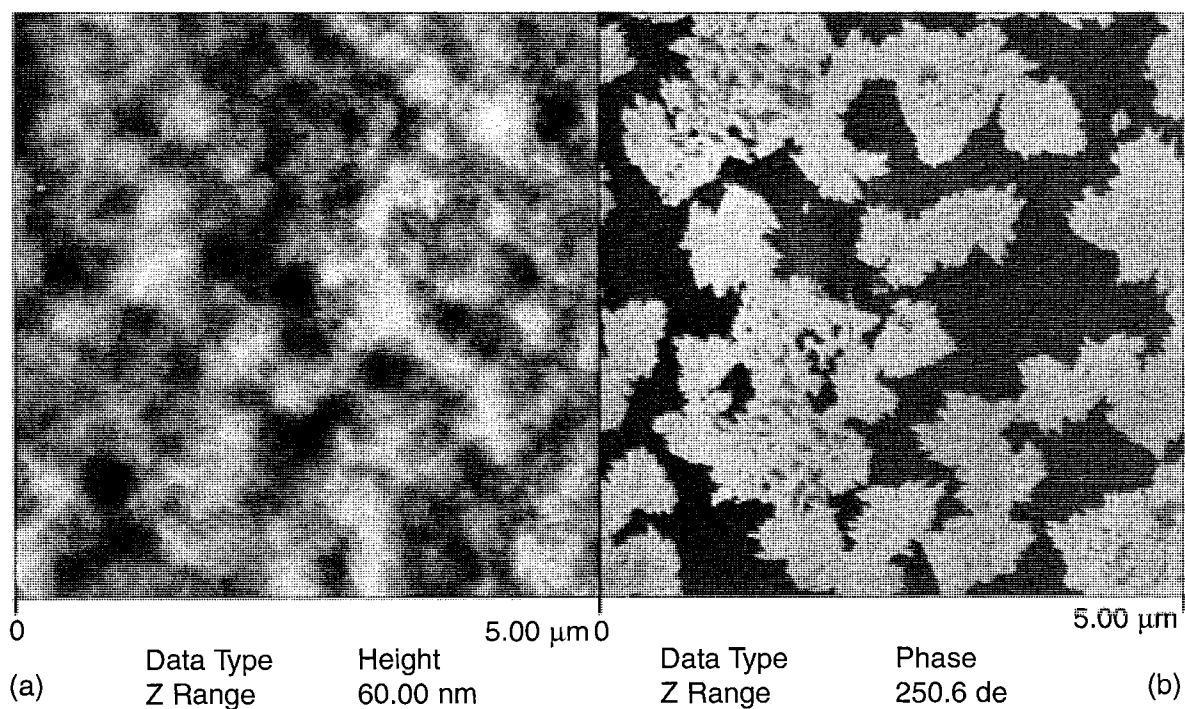


Fig. 8: AFM images of two components which are used to form a polyethylene (PE) film. The phase image (b) clearly shows the distribution of the two polymers due to differences in stiffness which is not evident from the topographic image (a). 2 μm scan.

i.e., SEM is conducted in a vacuum environment, and AFM is conducted in an ambient or in liquid environment. There are several reasons why environment is an important issue. First, there is a frequent need in fields such as biology and biomaterials to study hydrated samples. These two techniques compensate for this need by different means: an environmental chamber for a SEM, and a fluid cell for the AFM. Second, the SEM is required to work in a vacuum environment due to the nature of the technique which brings up the issues of vacuum compatibility of the sample, the conductivity of the surface, and vacuum maintenance. To image poorly conductive surfaces without sample charging may require conductive coatings or staining, which may alter or obscure the features of interest; or it may require low voltage operation, or an environmental chamber, which may sacrifice resolution.

4.0 Conclusion

SEM and AFM are complementary techniques that provide a more complete representation of a surface when used together than if each were the only technique available. These techniques overlap in their capabilities to provide nanometer scale lateral information. However, they deviate in the fact that the AFM can provide 3-dimensional images, with height information at a vertical resolution of $<0.5\text{\AA}$, whereas the SEM has the ability to image very rough samples due to its large depth of field and large lateral field of view, but only in two dimensions. The SEM can provide elemental analysis using x-ray detection, whereas the AFM can provide compositional information based on physical properties. The fact that the two techniques operate in different environments can be a strength when used together since the AFM does not encounter vacuum issues and may image samples in an enclosed liquid environment. The vacuum environment of the SEM makes it possible to conduct a number of techniques that require vacuum, such as X-ray analysis. By having both techniques side-by-side in an analytical facility, the overall scope of analytical capabilities is broadened, adding to the flexibility of the facility.

5.0 References

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Electrodeposition of Polypyrrole on Aluminum Alloy

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Abstract

Polypyrrole (PPy) is a technologically important conductive polymer. Al alloy is a metal that is very easily oxidized before and during PPy deposition, and the oxide layer makes further PPy deposition difficult. In this study, an in-situ AFM technique was used to examine the influence of surface preparation on the PPy deposition process. PPy deposition was carried out on Al alloys after various pretreatments and at various constant current densities. It was found that PPy deposition on the aluminum alloy was

facilitated by hexane pretreatment. It is suggested that hexane cleaning controls the formation of an oxide layer before deposition.

1.0 Introduction

The study of polypyrrole (PPy) and other conductive polymers has become an important topic in recent years because conductive polymers are promising materials which can be used in corrosion protection

coatings, batteries, sensors, and various biological applications.¹⁻⁵

Conductive polymer coatings such as PPy are being examined in our laboratory as possible replacements for the traditional chromate-containing primer coatings currently used in the aircraft coating industry. The chromate-containing coatings offer excellent corrosion protection of aluminum alloys. However, chromium (VI) is a highly toxic compound that is harmful to human health, and there is increasing interest in eliminating or greatly reducing its use in aircraft coatings.

One of the goals of our research is the development of methods for making high quality PPy coatings on aircraft aluminum alloy such as Al 2024-T3. The direct electrodeposition of PPy onto the alloy is an attractive approach. However, an oxide layer is easily formed on the Al alloy prior to and during PPy electrodeposition. This oxide layer is an insulation layer that seriously affects the quality of the PPy film by blocking electron transfer between the aluminum substrate and the growing polymer.⁶ Experience has shown that hexane pretreatment can improve the quality of the films. In a traditional 3-electrode cell, a good PPy film can form on a hexane-cleaned surface, but cannot form on a water-cleaned surface. In this study, we concentrated on the deposition process that occurred on Al alloy surfaces after different surface pretreatments.

It has been found that conductive polymer electropolymerization is a nucleation and growth process,⁷⁻¹⁰ and in many cases polypyrrole films possess a cauliflower appearance.¹¹⁻¹³ However, studying conductive polymer deposition with in-situ atomic force microscopy (AFM) technique is difficult, so most investigators use ex-situ AFM rather than in-situ AFM to examine the PPy films.¹⁴⁻¹⁸ In this study, we used in-situ AFM to study PPy deposition carried out on an Al alloy surface after different pretreatments and under different current densities.

2.0 Experimental

2.1 Electrodeposition

Pyrrole purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, U.S.A.) was distilled under reduced pressure. Sodium p-toluenesulfonate, pTS, from Aldrich Chemical Company was used as the electrolyte and dopant and Milli-Q water was used as solvent. The substrate was an aluminum alloy, Al 2024-T3, purchased from Q-Panel Co. Two groups of samples were prepared. One group of samples were wet polished to 1 μm , finishing with aluminum oxide powder, then ultrasonically cleaned in hexane for 3 minutes and

followed by 30 minutes immersion in hexane. The other group of samples were polished as above and then ultrasonically cleaned in water for 3 minutes. The electrodeposition solution concentration was 0.1 M pyrrole and 0.1 M pTS solution.

2.2 Atomic Force Microscopy (AFM) Studies

The AFM used in this work was a Nanoscope IIIa, MultiMode AFM (Digital Instruments, Santa Barbara, California) with a J scanner (125 μm scan region). In-situ deposition was carried out in a Digital Instruments electrochemical cell supplied with the microscope. Because of the electrode geometry of that cell, a maximum current density of 0.5 mA/cm^2 was used for in-situ deposition. During the PPy deposition process, the potentiostat was switched off at different time intervals to collect AFM images. For each time interval, 50 and 10 μm AFM images were collected, although all are not shown here. Optical micrographs were captured from the video microscope on the AFM.

3.0 Results and Discussions

Figure 1 is a group of 50 μm in-situ AFM time series images showing PPy deposition on a water pretreated Al alloy surface. After 30 seconds, there was no PPy deposit (Figure 1b). Instead, a large crater formed. The very first AFM scan after 30 seconds deposition indicated there was a PPy deposit growing in the crater, but it was wiped away due to contact by the AFM tip in subsequent scans. Al 2024-T3 is an alloy that contains Cu, Mg, Si and other elements. These elements form different phases. The crater shown in Figure 1 would be an easily dissolved phase under this condition. Figure 1c shows that after 30 minutes of deposition, a deposit filled the crater. It should be noted that although deposits grew in the crater, no deposit formed on other areas of the surface in the field of view. Evidently, some characteristic of the surface prohibited PPy deposition. The most obvious hypothesis is that an oxide layer formed during the surface pretreatment with water. An oxide layer would be an insulating barrier, breaking the conductive link of the PPy with the substrate and stopping PPy electrodeposition. However, when the anodic area was dissolved, fresh metal was exposed and PPy easily deposited on it. As a result, PPy deposits were observed in the crater. The corresponding 10 μm AFM images in Figure 2 verify that no significant PPy deposition occurred after 10-minutes of electrolysis.

Optical images in Figure 3 show the region around the tip area in a lower resolution. The horizontal size of all optical images is 400 μm . Figure 3 shows that except

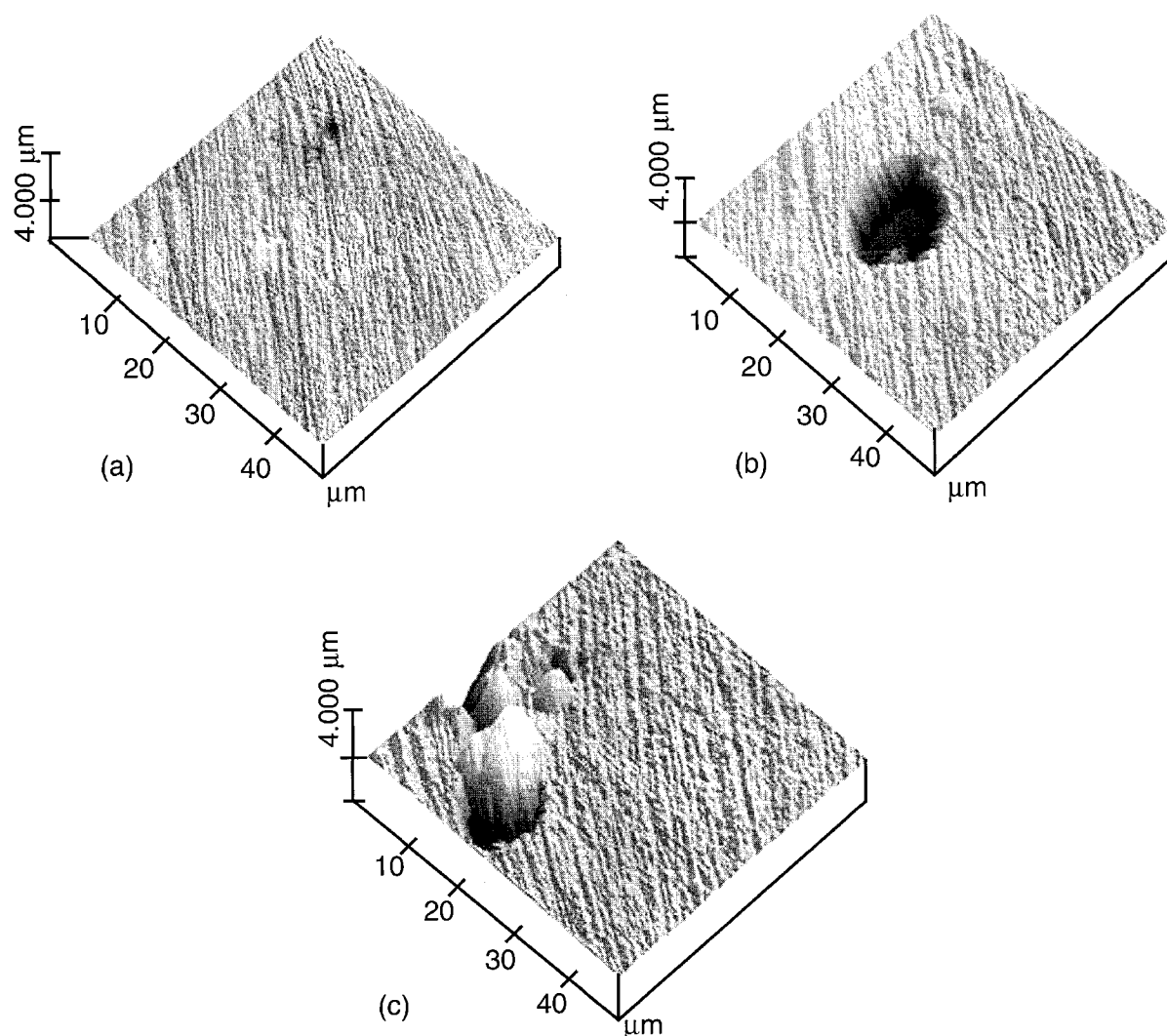


Fig. 1: 50 μm in-situ AFM images showing PPy deposition with 0.5 mA/cm^2 on a water pretreated Al alloy surface. (a) before deposition, (b) 30 seconds deposition, and (c) 30 minutes deposition. The deposition occurred preferentially on the fresh surface in the crater.

for one black spot of deposit that appeared on the surface after 5 minutes deposition, the surface had no change after 30 minutes. Obviously, it is difficult to deposit PPy on a water-cleaned surface. It is possible that water pretreatment promoted the formation of an oxide layer on the surface prior to deposition. During the above experiment, we observed with the optical microscope during initial stages of electrolysis that a few dark colored thread like products floated above the substrate. They may have been polypyrrole polymer suspended in the solution. Although we could not record this phenomenon with the optical microscope, the observation indicated that PPy was difficult to deposit on the substrate with an oxide layer, even though PPy apparently polymerized on microscopic areas of the electrode. According to Naoi and coworkers,⁶ a conductive polymer on an oxide layer may have an electronic link with the metal through

defects and cracks in the oxide layer. Thus, it was possible that the black spot of deposit observed in Figure 3 formed on an oxide film defect region.

Three 10 μm AFM height images in Figure 4 show PPy deposition on a hexane-pretreated surface. In contrast to the water-pretreated surface, PPy nucleation occurred after 30 seconds. In Figure 4b, the substrate surface was covered with numerous small deposit particles. With prolonged deposition time, these nuclei increased in size significantly. After 90 seconds, the small polymer particles developed to be large spherical deposits (Figure 4c). PPy polymer with this appearance has been previously reported.¹⁶ Film growth occurred by the growth and coalescence of these deposited particles.

The corresponding optical images in Figure 5 also show that after 30 seconds, the area surrounding the tip was covered with polymer deposits (Figure 5b), though

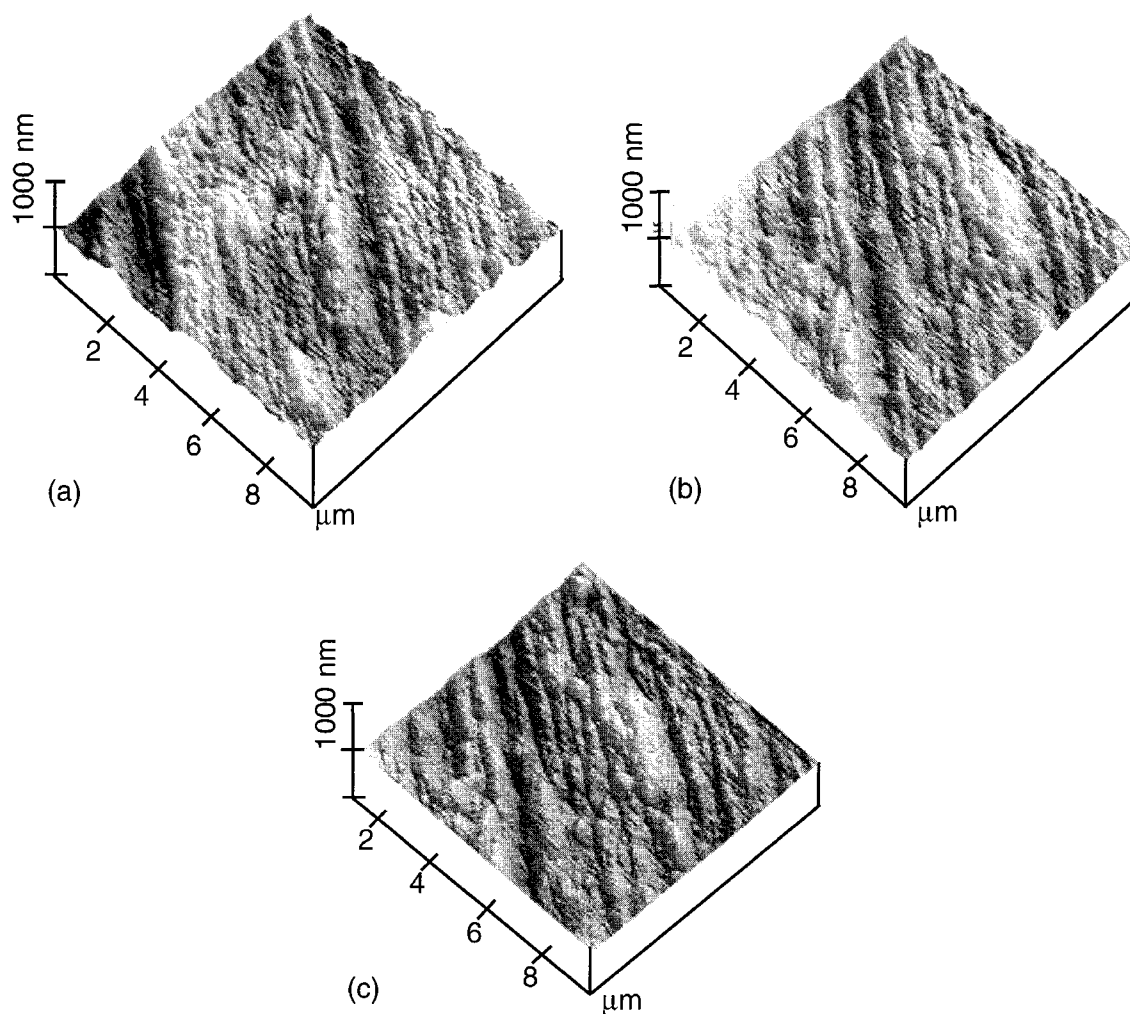


Fig. 2: 10 μm in-situ AFM images showing the Al alloy surface under 0.5 mA/cm^2 current density on a water pretreated Al alloy surface. (a) before the current applied, (b) 30 seconds after the current was applied, and (c) 10 minutes after the current was applied. No obvious surface change during 30 minutes deposition.

this layer was not uniform at that time. The lighter region was a thin deposit while the black region was a thick deposit, indicating that the PPy film developed three dimensionally. After 90 seconds, the imaged area was fully covered with a thick deposit layer (Figure 5c).

By comparing PPy deposition carried out on a water-pretreated surface with that on a hexane-pretreated surface, we found that PPy nucleation (and subsequent growth) on the water-pretreated surface was much more difficult. We conjecture that PPy nucleation on the water-pretreated surface was inhibited because a thicker oxide layer formed prior to polymer deposition. This oxide layer blocked active sites for electron transfer between the Al substrate and the pyrrole in solution. In contrast, this oxide formation was limited by hexane pretreatment, so initial PPy nucleation was more facile on the hexane-pretreated Al surface.

Figure 6 shows another group of optical images that were collected from another in-situ PPy deposition

experiment under the same conditions on a hexane-pretreated surface. Similarly, the first deposits were found after 20 seconds electrolysis, and they developed in size and concentration in the initial deposition period (Figures 6a and b). The difference was that the initial nucleation rate in this experiment was lower than on the surface shown in Figure 5. The possibility for this difference may be the non-uniform microstructure of the Al alloy surface.

It is also observed in Figure 6 that after 1.5 minutes, most deposited polymer remained constant in size and shape throughout the remainder of the experiment (Figures 6b and c). With repeated experiments under the same conditions, initial nucleation time varied between 1.5 and 5 minutes, but PPy nucleation always occurred in the early stages of these experiments. Since oxidation of the alloy surface inevitably occurs concurrently with PPy deposition, the increasing oxide layer apparently prevents PPy deposition at later stages in the deposition period.

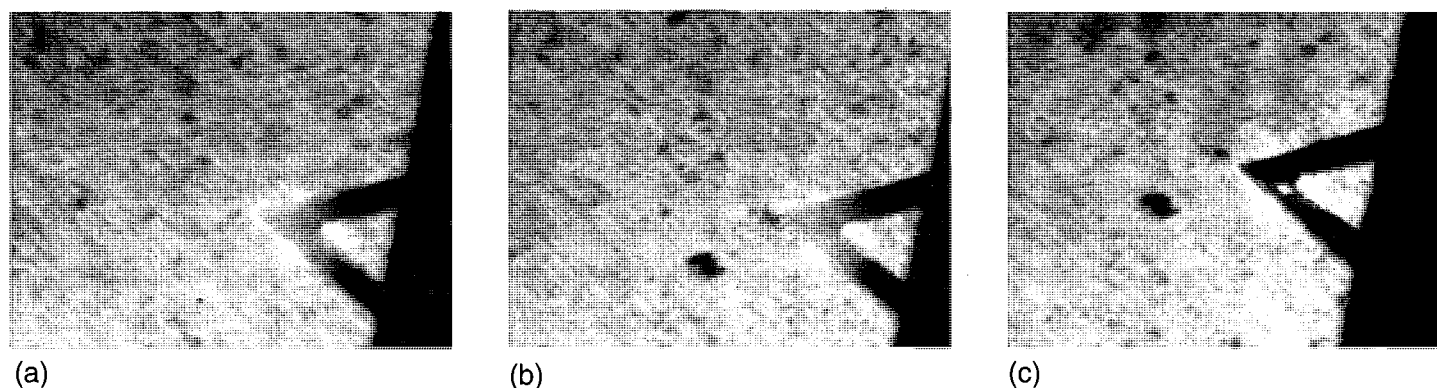


Fig. 3: Optical images, only one small deposit island was observed during 30 minutes deposition. The deposition was not successful elsewhere on the surface. (a) before deposition, (b) 5 minutes deposition, and (c) 30 minutes deposition.

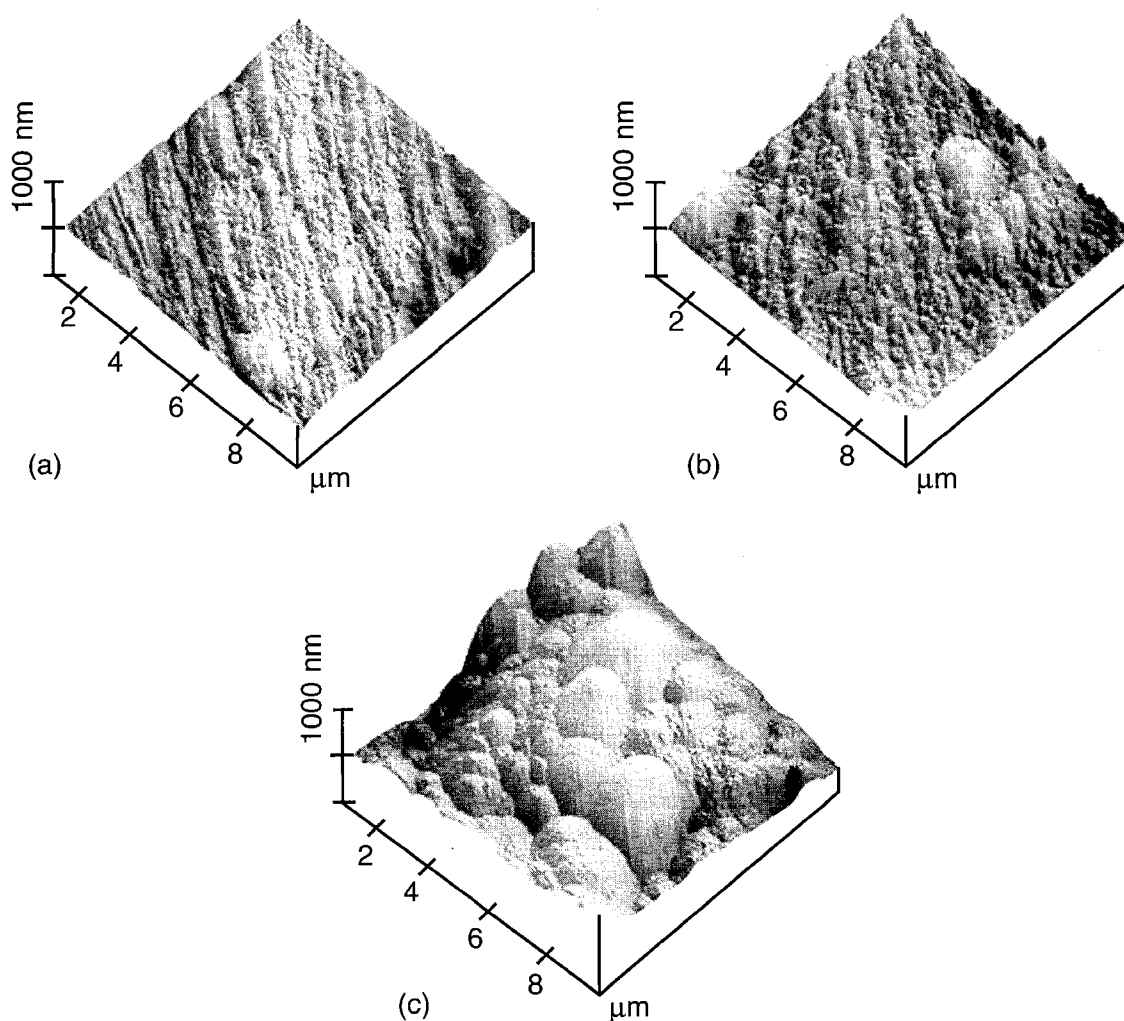


Fig. 4: 10 μm in-situ AFM images showing PPy deposition with 0.5 mA/cm^2 on a hexane pretreated Al alloy surface. (a) before deposition, (b) 30 seconds deposition, and (c) 90 seconds deposition.

Additional experiments were performed using a lower current density for PPy deposition, in order to further reduce Al oxidation during polymer deposition. Figure 7 shows the surface topography change during

electrodeposition at 0.2 mA/cm^2 and Figure 8 shows the corresponding optical images. Before deposition, the hexane-pretreated surface was free of oxide particles (Figure 7a). During the first 5 minutes of electrolysis,

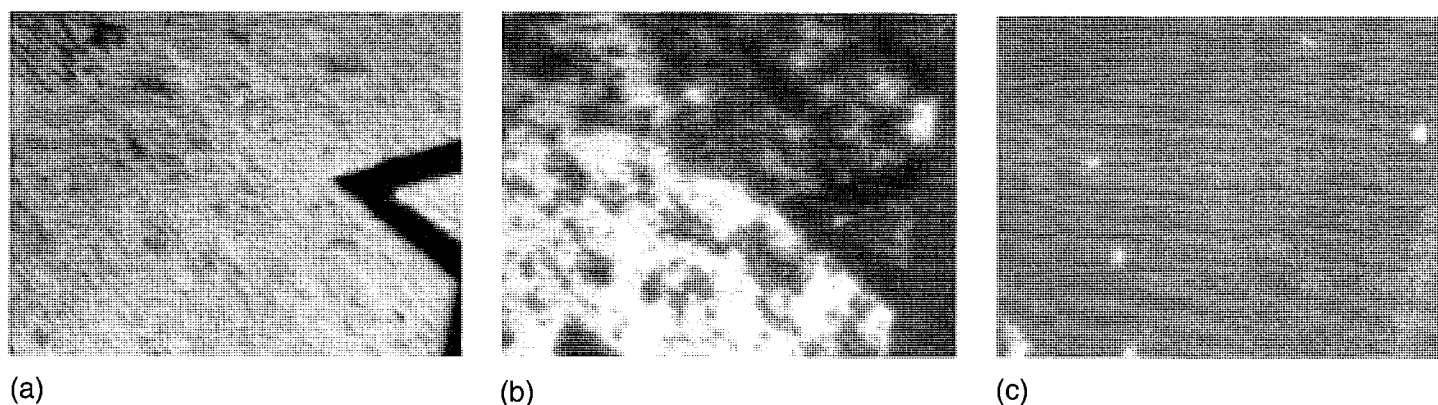


Fig. 5: Corresponding optical images showing PPy deposits fully covering the substrate surface in the field of view in 90 seconds. (a) before deposition, (b) 30 seconds deposition, and (c) 90 seconds deposition.

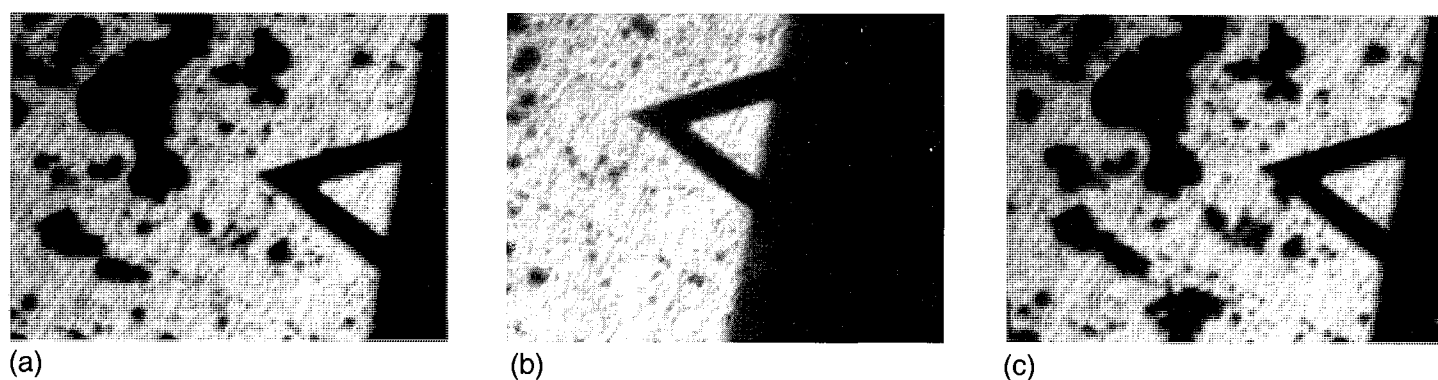


Fig. 6: Optical images obtained from the other in-situ study under the same condition showing that PPy deposits mainly occurred in the initial deposition period. (a) 20 seconds deposition, (b) 90 seconds deposition, and (c) 10 minutes deposition.

small particles developed on the surface (Figure 7b). These particles may be oxide particles rather than polymer particles because little or no polymer deposition was observed in the tip area in the optical images at that time (Figure 8b) (an air bubble distorted the tip shape in Figures 8a and b).

In contrast to PPy electrodeposition at $0.5\text{mA}/\text{cm}^2$, the deposition at $0.2\text{mA}/\text{cm}^2$ did not show observable deposition in the initial electrolysis period (Figure 8b). Instead, PPy deposits developed on the surface later in the electrolysis period (Figure 8c), with some deposited islands developing rapidly between 5 and 10 minutes electrolysis. Unfortunately, the tip was damaged under the bubble force after 12 minutes deposition, so this experiment was terminated at that time. In a second in-situ experiment under the same conditions, the continuous deposition of polypyrrole was observed to 30 minutes.

It was anticipated that use of a lower current density would promote polymer nucleation and growth with reduced metal oxidation and resultant oxide growth. However, the use of a lower current density did not appear to improve the nucleation and growth process under these conditions.

Above results show that since a thick oxide layer formed on water pretreated surfaces, PPy deposition on a water pretreated surface is more difficult than on a hexane pretreated surface. As a result, a fast deposition at the initial deposition stage was observed on the hexane pretreated surface but not on the water pretreated surface. Oxidation occurred during PPy deposition causes the continued deposition difficult, so the expanding of the deposition areas in the late deposition period was not found on both surfaces. Reducing deposition current density reduces the oxidation rate during deposition, so

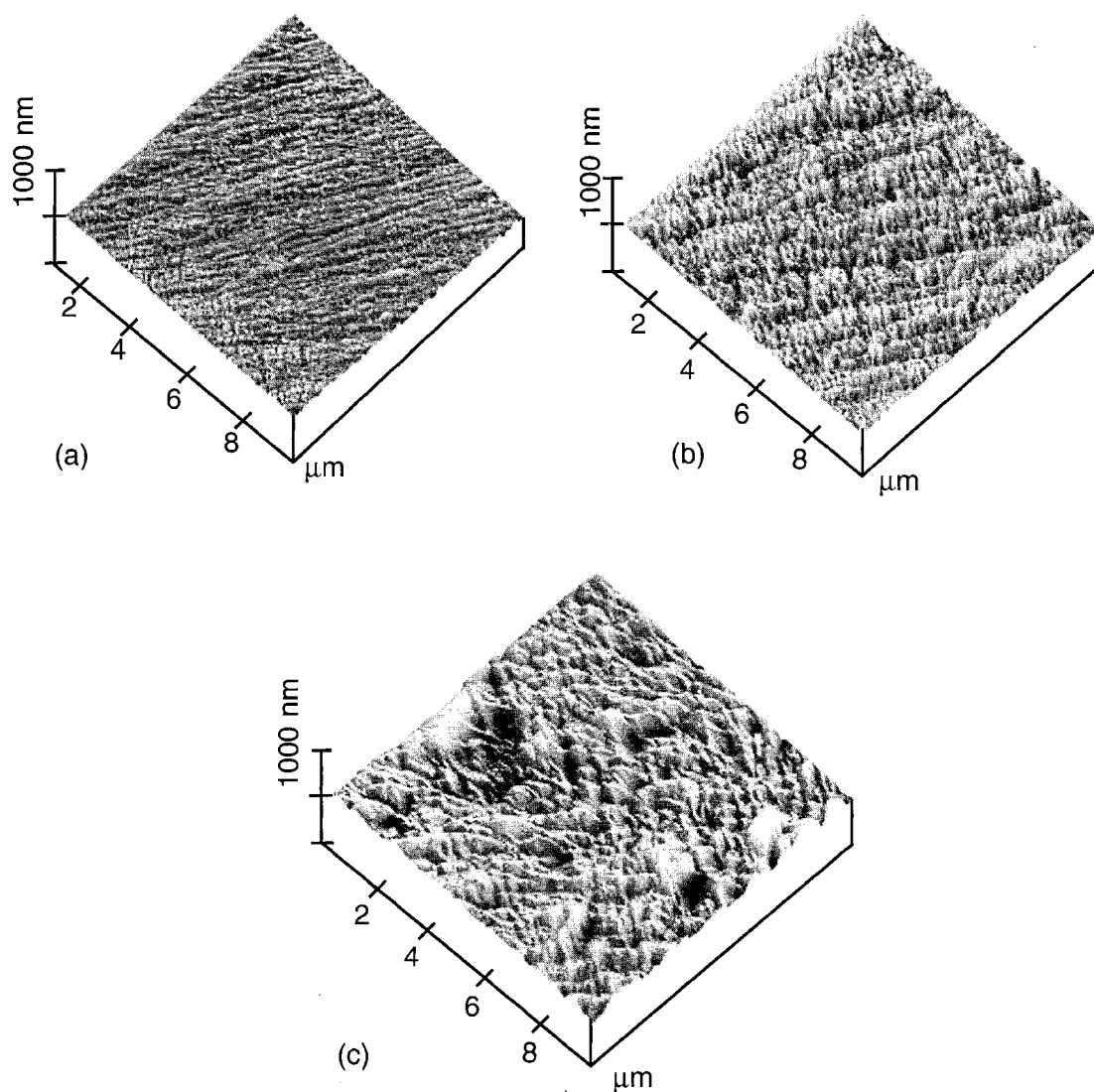


Fig. 7: 10 μm in-situ AFM images showing a no polymer deposit area under 0.2 mA/cm^2 on a hexane pretreated Al alloy surface. (a) before the current was applied, (b) 5 minutes after the current was applied, and (c) 10 minutes after the current was applied.

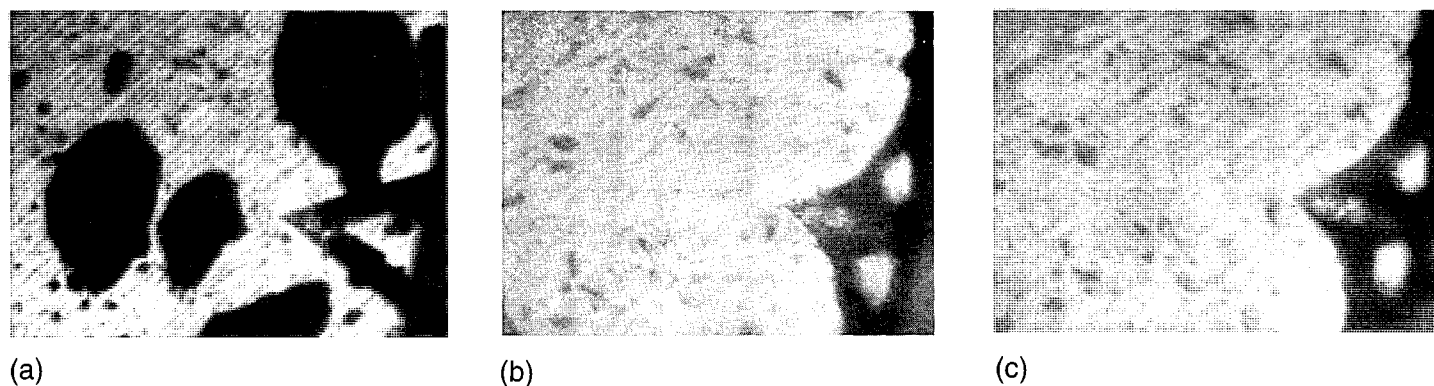


Fig. 8: Optical images show that PPy deposition took a longer time to occur under 0.2 mA/cm^2 current density and the deposition continued to 10 minutes when the experiment terminated. (a) 30 seconds deposition, (b) 5 minutes deposition, and (c) 10 minutes deposition.

continued deposition at the late deposition period was observed when a low deposition current was used.

4.0 Conclusions

Hexane pretreatment improved the PPy deposition, apparently by minimizing the formation of an oxide layer on the Al 2024-T3 surface and promoting nucleation sites for polymer formation. By contrast, surface preparation in water leads to a sufficiently thick oxide layer that nucleation of polymer deposition is hindered. Simply reducing the current density does not appear to alleviate this problem. This study provides the background for understanding polymer deposition on active metals using electron transfer mediation, work that is in progress and will be reported in due course.

5.0 Acknowledgment

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New Technology in Atomic Force Microscopy (AFM) for Faster Scanning Speeds and Shorter Time-to-Result

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Abstract

Atomic force microscopy (AFM) has been usually slow in scanning speed when compared to scanning electron microscopy (SEM). Also, the typical density of data points stored in a scan line, as well as the number of scan lines per image, have been limited such that upon zooming into an AFM image to “see” detail on a smaller length scale, one often loses some information. (This is commonly referred to as image pixelization). A new generation of AFM controllers (and associated software and file-handling capability), together with a new type of AFM probe, is now able to address these

bottlenecks in such a way that the overall time-to-result is reduced. This new technology 1. enables faster scanning speeds to reduce image capture time and, 2. obviates the need for multiple scans on different length scales to see detail. The fast-scanning technology relies on a new kind of AFM probe, and new electronics for moving that probe up and down the features of the sample surface.¹ The new image formats enable data densities much higher than previously attained, and allow flexibility in distributing this increased data density in X and Y unevenly, so that more detail can be captured in one of the two planar dimensions at the expense of the other. The technology is described and examples are discussed.

1.0 Introduction

Tapping mode AFM is the most commonly used method of AFM imaging.² Typical scanning speeds for capturing AFM images in tapping mode in air are under 3 Hz per scan line, more often 1 or 2 Hz, depending on the roughness and the material of the sample surface.² Scan speeds in contact mode, which is not as widely used as tapping mode, are usually higher, but typically no faster than 5 Hz per scan line. Typically, an AFM image (tapping mode or contact mode) consists of 256 or 512 lines, each consisting of 512 data points a 256×512 or a 512×512 image. A typical 512 line tapping mode AFM image taken at 1 Hz scan rate (1 scan line per second) takes about 8.5 minutes to capture. Image capture times are not affected by the number of data points in a given scan line only by the number of scan lines per image. The exact reasons why contact mode AFM is usually faster than tapping mode AFM—on the same sample, with the same scan size—are beyond the scope of this paper; indeed, they are not all clear, and they are the subject of ongoing research. However, there are some features of the AFM that are well understood to limit the scanning speed in both contact mode and tapping mode. One reason for the slow scan speeds in AFM is that the speed of the feedback loop response in adjusting the relative out-of-plane (vertical) position of the AFM tip relative to the sample is limited by the speed of the Z-actuator. The Z-actuator is typically a piezoelectric tube or stack that is on the order of centimeters in size, and relatively heavy. This combination makes the Z-actuator a speed bottleneck. A more agile Z-actuation scheme can improve the speed of scanning.

It is sometimes desirable to zoom into a captured AFM image and be able to see more features and measure detail real features, and measurement of real events, rather than what the computer fills in the gaps by extrapolating between the actual data points that exist in the original image. This requires that there be more pixels in the captured image than are initially visible on the computer screen that is, prior to the zoom. Another way to say this is that there be a higher density of data points per unit length in a given direction (or per unit area) in the captured image.

In this paper, new technology for scanning and capture of AFM images is discussed which show both a more agile Z-actuation scheme and the capability to capture images with higher density, symmetrically (same density in both in-plane dimensions) or asymmetrically.

The combination of these two improvements, enables faster time-to-result AFM imaging and analysis

by reducing the time required to capture a single image, and also by reducing the need for multiple scans of an area on progressively smaller regions within that area in order to record the detail.

2.0 Dual Z-Actuation

The scheme that is used to improve the agility of the Z-actuation in AFM imaging uses two actuators and a nested feedback loop, which consists of a faster feedback loop nested inside a slower feedback loop. The output of the faster loop drives the faster of the two actuators. The output of the slower loop drives the slower of the two actuators. The two actuators are shown schematically in Figure 1. The traditional tube scanner portion of the actuator, commonly referred to as the Z-tube is assisted by the new, much smaller, more agile actuator that is integrated into the AFM cantilever. Scanning electron microscope (SEM) micrographs of a micro-actuated (active) probe are shown in Figure 2.

The electronics that control the motion of the Z-tube and the micro-actuated probe include an architecture known as the nested feedback loop. At any given time, two signals are sent from the AFM controller to the two actuators; these are the outputs of the nested feedback loop. The error signal for the small (fast) actuator, also called the primary error signal, comes from comparing the output of the detector that monitors the up-down (vertical) motion of the AFM cantilever, with the controller's setpoint. The error signal for the larger (slower) Z-tube actuator comes from the signal the controller sends to the micro-actuator. The bulk of the fast adjustments to the vertical (Z) position of the tip are affected by the micro-actuator integrated into the AFM cantilever, the fast actuator. This lifts much of the burden off the bulky and slow Z-tube, leaving the Z-tube to carry on the slower actuation of the tip.

The small, fast actuator has a small range, only a few hundred nanometers. The Z-tube carries the large adjustments in height as it has a much larger range typically several micrometers, but less than 10 μm .

Images in Figure 3 were captured on a sample of aluminum with an AFM operating the same probe with and without the use of the micro-actuator integrated into the AFM lever. The scan rates are 1 and 5 Hz for the slow scan and the fast scan. The slow scan was done the "old-fashioned way," i.e., with the Z-tube in charge of all the vertical adjustments of the AFM tip. The fast scan was done with both actuators, the Z-tube and the micro-actuator involved in the vertical adjustments. In the absence of the micro-actuated probe and nested feedback, the 5 Hz scan lost much of the fidelity and the features were distorted and immeasurable (not shown).

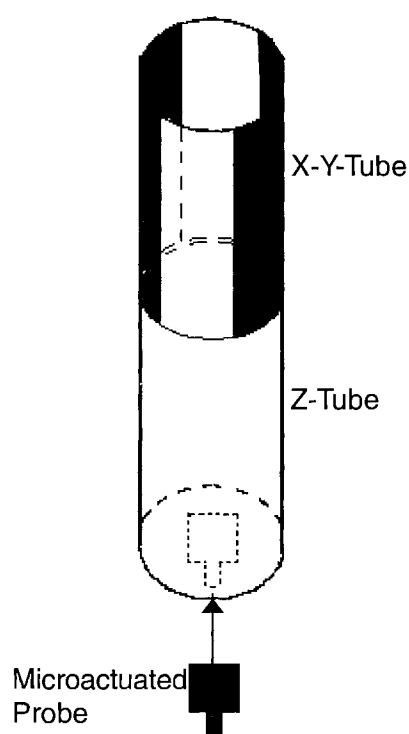


Fig. 1: Dual Z-actuation. A Z-tube, together with a much smaller micro-actuated (active) probe, adjusts the position of the AFM tip in the Z-direction. A micro-actuated AFM probe has a piezoelectric micro-actuator element integrated into it. This actuated probe is much smaller than the Z-tube, and more agile.

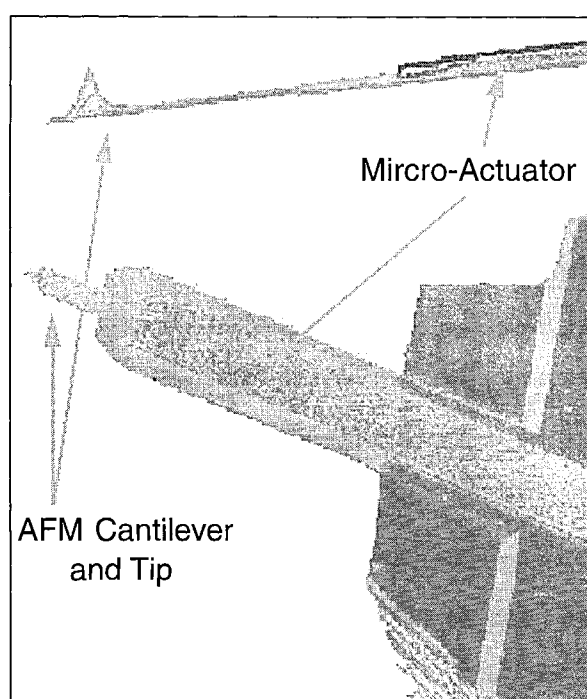


Fig. 2: Two SEM micrographs of a micro-actuated probe (Nano Devices, Inc., Santa Barbara, CA, U.S.A). The cantilever part (small extension at the end) is about 100 μm long.

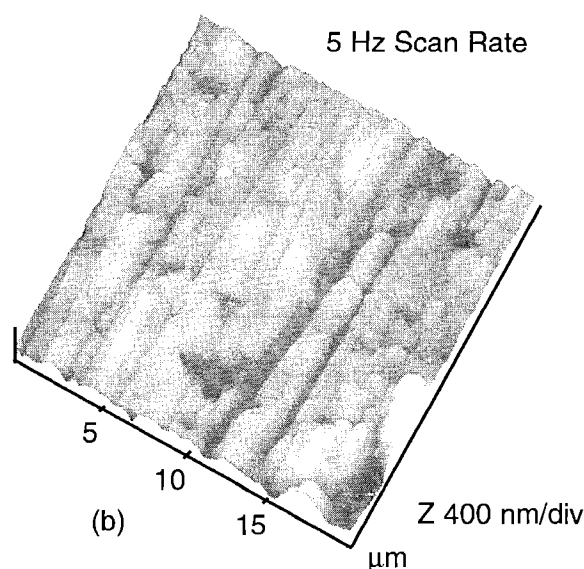
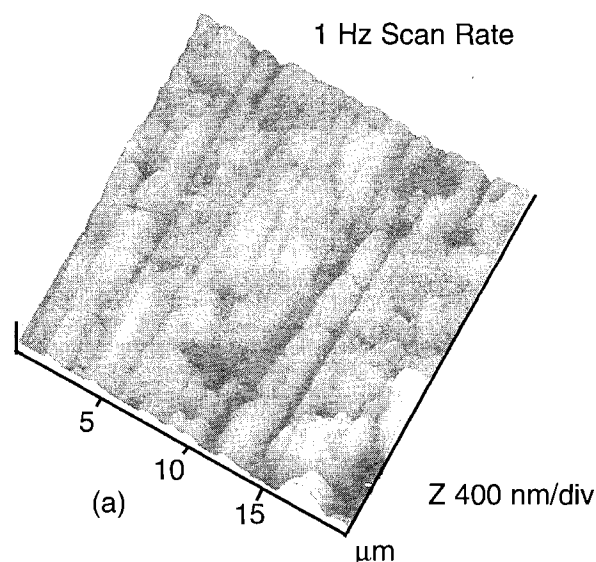


Fig. 3: (a) Slow and (b) fast-scanning images of an area on a sample of aluminum. The same probe was used to capture both images, but a single actuator (the Z-tube) was used to complete the slow scan, and a dual-actuator and nested feedback loop were used to enable the fast-scan image.

The improvement in the scan speed that comes with the nested feedback-loop-enabled dual Z-actuation varies from sample to sample. We have been able to demonstrate scan speed improvements better than an order of magnitude on some samples, while on others, no more than 3 or 4 times improvement has been possible so far.

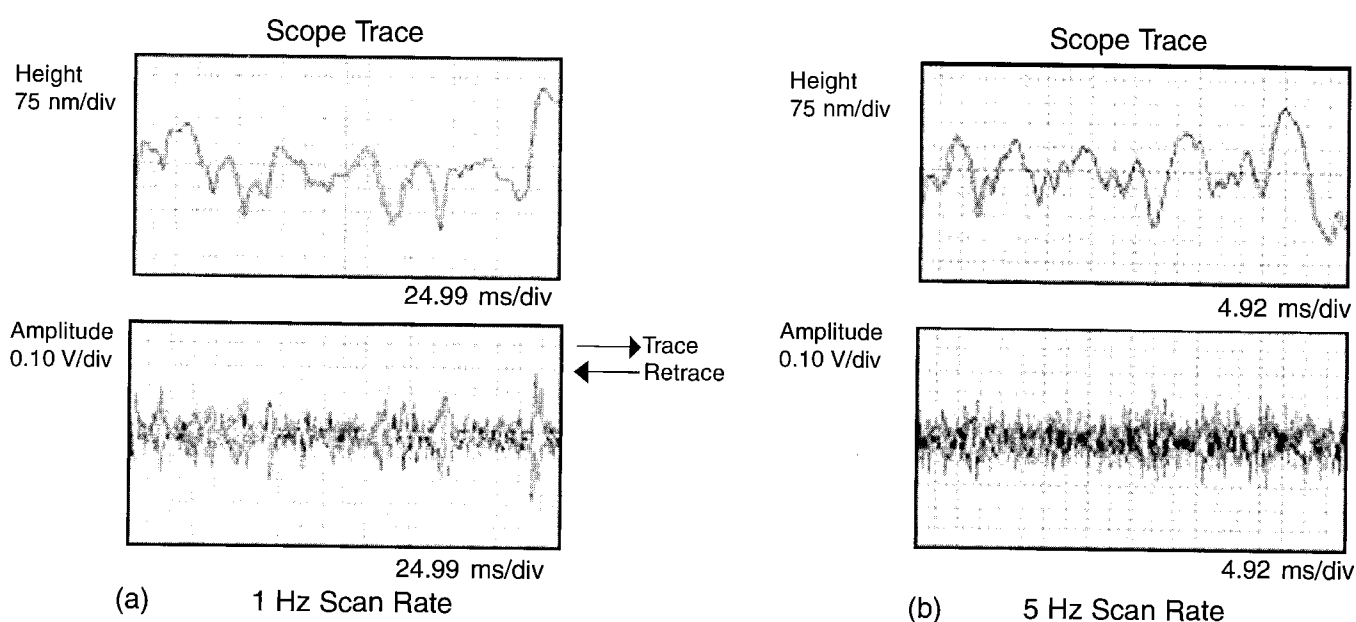


Fig. 4: Error signal for the Z-tube-only (a) scanning of the same height variation is larger than the error signal for the dual-actuation/nested-feedback-loop and (b) scanning at 5 times faster scan speed.

Another benefit of the nested-feedback-loop-enabled dual-Z actuation is that at a given scan speed, the AFM tip follows the sample surface more accurately, resulting in higher-fidelity images. This is deduced from observing the primary error signal of the feedback loop. This error signal, as mentioned earlier, comes from comparing the up-down movement of the AFM cantilever (tip) with the feedback loop's setpoint. The larger this error signal, the less accurately the tip follows the sample surface. In Figure 4, we show two sets of single-scan-line data, Scope-Trace data. The top curves show the topography the same height variation is present in both sets; approximately 450 nm peak-to-valley. The error signal for each case is shown below the topography curve. The highest peaks in the error signal of the slow-scan (1 Hz), done with the Z-tube only, are higher than any peaks in the error signal for the fast-scan (5 Hz), done with dual actuation/nested feedback loop. This shows that the Z-tube alone (operating at one-fifth the scan rate) is unable to adjust the AFM tip's vertical position in accordance with the surface height variation as well as the dual-Z/nested-feedback-loop can do.

3.0 Increased Data Point Density

The improvement in the data point density allows one to zoom into a captured AFM image, and learn more about the surface qualitatively and quantitatively. The enabling technology is hardware and software that allows

recording, storing, visualizing, and analyzing larger amounts of information (more pixels) in a given image file. (OneScan™, from Digital Instruments, Veeco Metrology, Santa Barbara, CA, U.S.A.).

Here, we show an example. In Figure 5, the rectangular image is from an area $10 \times 1.25 \mu\text{m}$ on a polymer that shows both long-range and short-range morphology. What makes this image different than a typical AFM image is that in each scan line (left-right) there are 4096 data points present. Also, there are 512 lines of data, which results in the same density of data points per unit length in both in-plane directions X and Y. A zoom into the center region of this image is shown in the square image. In the absence of this level of data density, the detail visible in the square image would only be possible with an additional scan that covers the square image. That is, the AFM operator must scan and capture another image.

The one tradeoff in this technology has to do with averaging. At a given scan speed, say 1 Hz, a number of sampling-data-points are averaged to make up a given AFM image data point. The number of the sampling-data-points that are averaged is smaller if the number of AFM image data points per scan line is increased. In cases where the signal (e.g., topography of the sample) is near the noise floor of the AFM, then the benefit that comes with the averaging of sampling-data-points is reduced at higher AFM image data points. This is the subject of ongoing research and development.

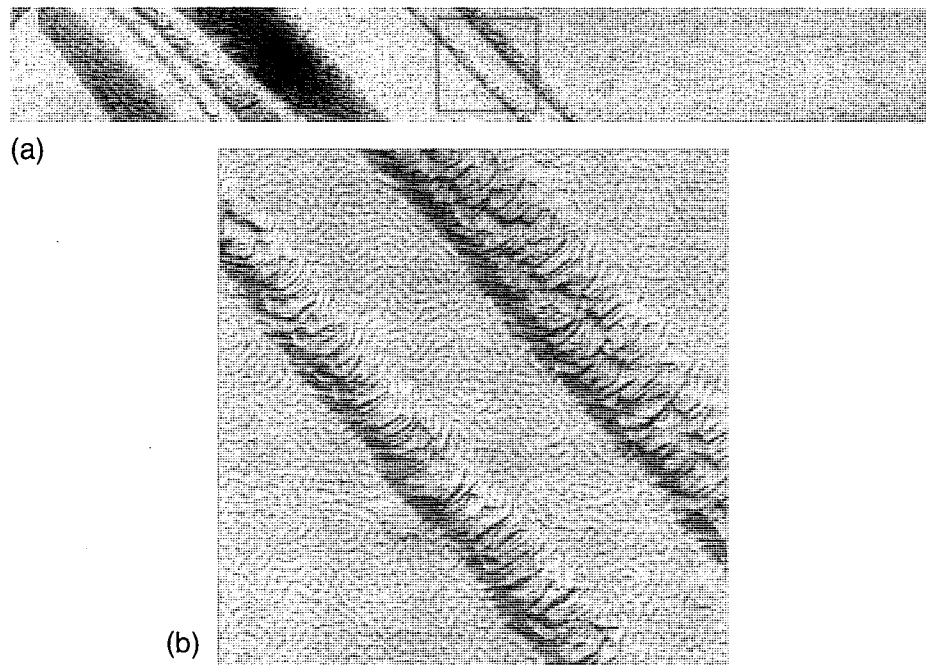


Fig. 5: (a) Long-range and (b) short-range morphology on a polymer sample captured in the same AFM image, with 4096 data points per scan line (left-right) and 512 scan lines (top-bottom.)

4.0 Summary

This paper discussed two new technological advances in AFM that enable faster time-to-result. One technology makes use of a new actuation scheme for adjusting the out-of-plane (Z) position of the AFM tip with two rather than a single actuator, the small actuator is responsible for fast adjustments, and the traditional Z-tube, which has long been present in the AFM scanners, but which is slow in response, is thus assisted in the task of following the AFM tip to the sample surface. The second technological improvement is software and hardware that allows AFM images with much higher density of data points be captured and handled, so that without the need for repeated scans at

progressively smaller areas, one can see and measure details within one and the same image.

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Surface Treatments for Corrosion and Joining

Formation of Bilayer Polypyrrole-Polyaniline Composite Coating for Corrosion Protection of Steel

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Abstract

Bilayer polypyrrole-polyaniline coatings were coated on low carbon steel by electrochemical polymerization technique. In this study, a two-step deposition process was applied in order to improve corrosion resistance of low carbon steel. Initially, a primer coating composed of polyaniline-polypyrrole composite coating was deposited. Subsequently, polypyrrole topcoat was deposited onto composite coating to form

(Pani/PPy)-PPy bilayer coating. The formation of polypyrrole top layer was monitored by Infrared Spectroscopy and Scanning Electron Microscopy. DC polarization test was used to determine the corrosion performance bilayer coatings. It was shown that the corrosion performance of the bilayer coating is significantly higher than that for the single layered polyaniline-polypyrrole composite coatings. Thus, significant improvement of corrosion performance of the polyaniline-polypyrrole composite coating is achieved by introducing polypyrrole bilayer.

1.0 Introduction

Intrinsically conducting polymers (ICP) such as polypyrrole and polyaniline have become very attractive in the scientific community because of their chemical stability, environmental viability and very good corrosion resistance. Polyaniline, polypyrrole and their composites have been investigated for corrosion protection of reactive metals such as aluminum, steel.¹⁻¹⁰ The mechanism of corrosion protection of conducting polymeric coatings is also being investigated. It is proposed that an electric field generated by conducting polymeric coating could restrict the flow of electrons from the metal to an oxidizing species, thereby preventing the oxidation of metals.¹¹ These ICP coatings can also form a dense, low-porosity film, which act as a physical barrier for against the oxidizing species.¹² It was also proposed that conducting polymeric coatings catalyze the formation of protective layers of metal oxides on the metal surface, thereby preventing corrosion of metal.¹³

It was observed that, corrosion performance of these conducting polymeric coatings is strongly dependent on the synthesis conditions such as electrolyte type, electrolyte concentrations, pH, applied potential, reaction time and concentration of the monomers.⁸ Previous reports have shown that oxalic acid is one of the electrolytes that to form adherent conducting polymeric coatings on low carbon steel for the corrosion protection.¹⁴⁻¹⁷ Beside this, it has been reported that anti-corrosion coating of polypyrrole and composites of polypyrrole was formed by using LiClO_4 as the electrolyte.¹⁰

In this study, to improve the corrosion resistance of polyaniline/polypyrrole coatings, a two-step electrochemical deposition process was used to apply corrosion protective coating on low carbon steel. Polyaniline-polypyrrole composite coating was initially applied as the primer layer. Followed by the application of the topcoat of polypyrrole by electrochemical deposition technique. We report the formation of polypyrrole top layer and its effect on corrosion performance of low carbon steel.

2.0 Experimental

2.1 Materials

Low carbon steel was purchased from Q-Panel and was used as a working electrode where the polymeric coatings were deposited on. Aniline (99.5% pure) and pyrrole (98% pure) were purchased from Aldrich Chem. Co. and were used as received without any further

purification. Oxalic acid (98% pure, Aldrich) was used in the electropolymerization of the monomers as the supporting electrolyte.

2.2 Electropolymerization

Aqueous electropolymerization was performed using a single compartment polypropylene electrochemical cell. A 0.5 mm thick QD low carbon steel panel was used as the working electrode (25.8 cm^2) and two stainless steel plates were used as the counter electrodes. A saturated calomel electrode (SCE) was used as the reference electrode. An EG & G Princeton Applied Research, Model 273A Potentiostat/Galvanostat was used as the source of power supply for the electropolymerization. Controlled potential coulometry was used to form coatings on steel substrate.

2.3 Sample Preparation

2.3.1 Polyaniline-Polypyrrole Composites Coating (First Layer (Primer))

An applied potential of 0.80 V vs. SCE was used. The feed ratio of aniline to pyrrole in the electropolymerization cell was kept 3:7 respectively, where the total co-monomer initial concentration was 0.125 M. The concentration of oxalic acid was kept constant at 0.2 M. The substrates coated with polyaniline-polypyrrole composites were taken out of the electrochemical cell at predetermined reaction times. The coated samples were rinsed thoroughly with methanol in order to eliminate any loosely contacted species and then prepared for electrochemical deposition of polypyrrole as a second layer. The detailed experimental procedure and characterization of polyaniline-polypyrrole composite coating was reported in our previous study.¹⁸

2.3.2 Polypyrrole Bilayer (Top) Coating

The steel panel, which was previously coated with polyaniline-polypyrrole composite, was coated with polypyrrole in order to prepare a bilayer (top) coating. The experimental conditions were kept same as the first layer. The applied potential was 0.8V vs. SCE and the concentration of oxalic acid was kept 0.2 M. The reaction time was set to 300 seconds where the best corrosion performance was achieved.

2.4 Characterization

The chemical structure and the composition of the coatings were investigated using Bio-Rad FTS-40 FTIR spectrometer (Bio-Rad, Richmond, CA). Reflection-

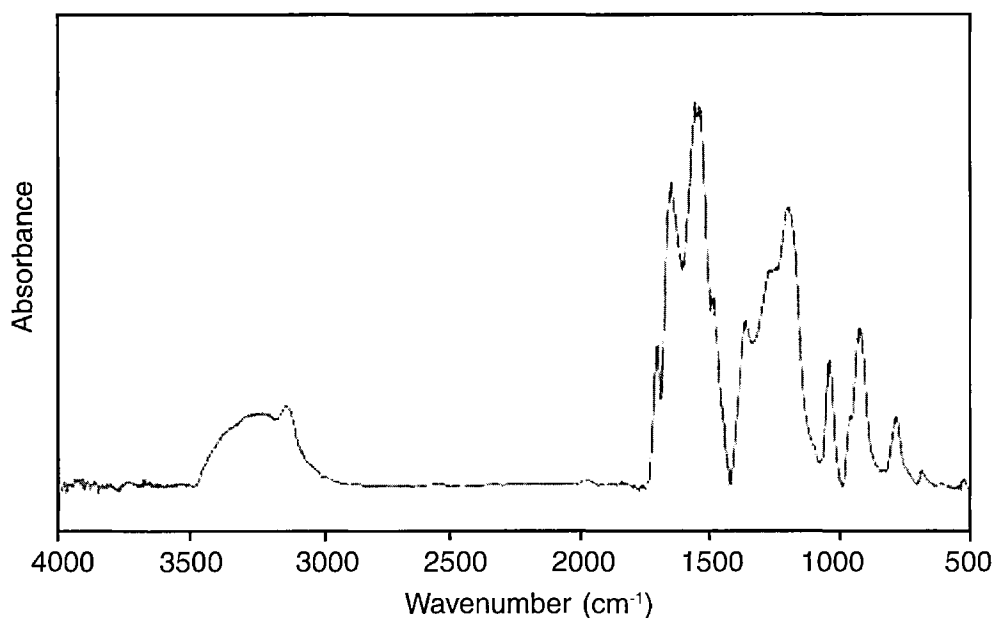


Fig. 1: Infrared spectra of polyaniline-polypyrrole composite coating (30% aniline - 70% pyrrole as a feed monomer ratio) formed on low carbon steel at an applied potential of 0.8 V vs SCE using oxalic acid as electrolyte.

absorption infrared spectra (RAIR) of the coatings were obtained from 4000 to 400 cm^{-1} using a resolution of 4 cm^{-1} and averaged over 256 scans. The morphology of the coatings was examined by scanning electron microscopy (SEM). All the micrographs were taken at an accelerating voltage of 15 kV and at a working distance of 25 mm from the detector.

2.5 DC Polarization Tests

Corrosion performance of the coatings was studied by DC Polarization tests. The DC Polarization tests were performed by using 3.5 wt.% NaCl solution at neutral pH medium. The corrosion rate of the samples was calculated by using PAR Model 352 corrosion software and EG & G PAR model 273A potentiostat/galvanostat. Four different points were tested on each sample and the average results were reported.

3.0 Results and Discussion

3.1 Formation of Polypyrrole Bilayer (Top) Coating

In our previous investigation, we have studied the electrochemical deposition of polyaniline-polypyrrole composite coatings on low carbon steel.¹⁸ Figure 1 shows the infrared spectra of polyaniline-polypyrrole composite coating formed by using a molar feed ratio of 30% aniline

- 70% pyrrole. IR peaks shown at 1704 cm^{-1} and 1650 cm^{-1} are due to absorption of C=O group present in the oxalic acid. The broad peak observed at around 3250-3100 cm^{-1} is due to presence of secondary amine and may also be due to the absorption of O-H group of oxalic acid. The peaks at 1600 cm^{-1} and 1500 cm^{-1} are due to the absorption of quinoid deformation and benzenoid deformation of aniline group respectively. This indicates that the polyaniline present in the composite has emeraldine structure (partially oxidized form). IR absorption peaks at 1050, 980, and 950 cm^{-1} are due to ring deformation of pyrrole ring, which confirm the presence of polypyrrole in the composite. The intense absorption peaks at 1590-1540 cm^{-1} come from the C=C stretch of pyrrole ring. The peak at around 1400 cm^{-1} is due N-H deformation of pyrrole unit.

In this study, we coated polypyrrole as a second layer onto polyaniline-polypyrrole composite by electropolymerization technique. Figure 2 shows the infrared spectra of the bilayer coating as a function of reaction time. The formation of polypyrrole starts at very short reaction times. In our previous studies we have shown the dissolution of steel and formation of iron (II) oxalate passive layer on the electrode in the presence of oxalic acid.¹⁹ The absence of IR peaks at 1360 and 1315 cm^{-1} due to the C-O group from in iron (II) oxalate reveals that there is no dissolution of electrode (low carbon steel) during the formation of second layer onto composite coating. The intensity of secondary amine

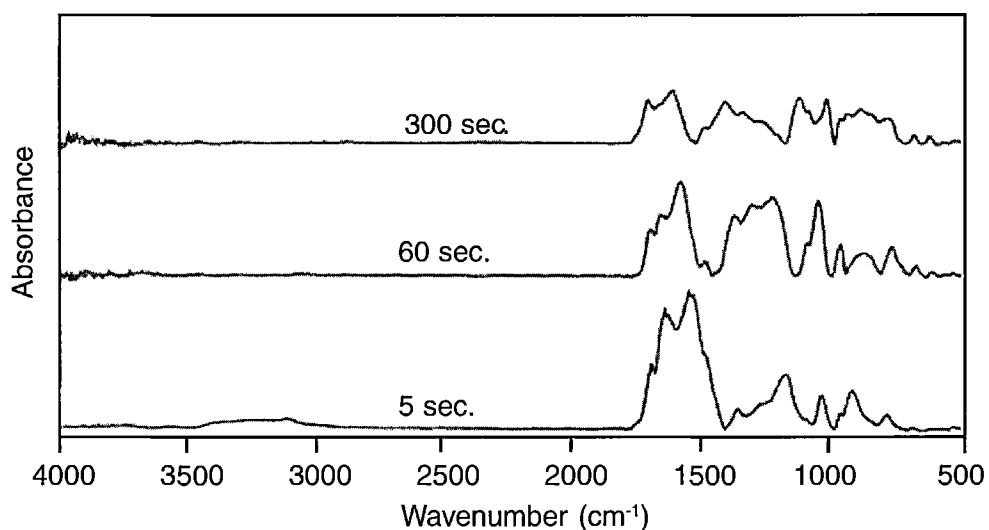


Fig. 2: Infrared spectra of the polypyrrole bilayer coating as a function of reaction time formed at an applied potential of 0.8 V vs SCE using oxalic acid as electrolyte.

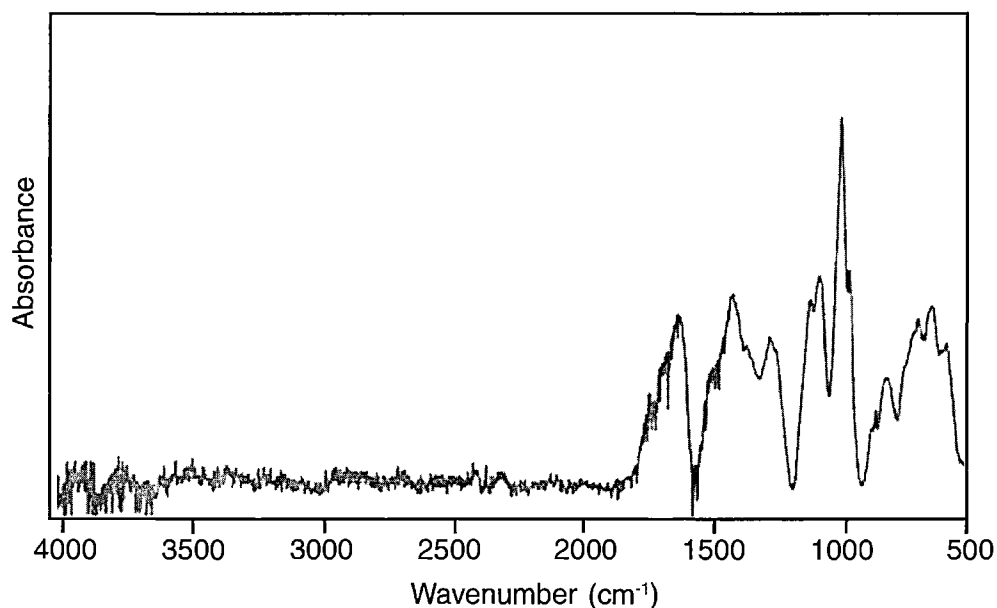


Fig. 3: Infrared spectra of polypyrrole coating formed on low carbon steel at an applied potential of 0.8 V vs SCE using oxalic acid as electrolyte.

peak at 3250 cm^{-1} is decreased and disappeared at longer reaction times. Beside this, polypyrrole peaks at 1050, 980, and 950 cm^{-1} have become strong in the IR spectra. The C=N stretch at 1600 cm^{-1} , C–N stretch at 1500 cm^{-1} and N–H deformation of pyrrole ring at 1400 cm^{-1} absorption peaks are also more pronounced. The infrared spectrum of polypyrrole, synthesized under the same condition is also shown for comparison in Figure 3. It is

clear that the formation of polypyrrole as a second layer onto polyaniline-polypyrrole coating was achieved. SEM micrographs discussed in the next section also confirm the formation of polypyrrole successfully. However, the infrared spectra of pure polypyrrole and bi-layered polypyrrole are not identical. There are some shifts in the absorption bands of polypyrrole peaks. This may be due to possible interactions between the first layer

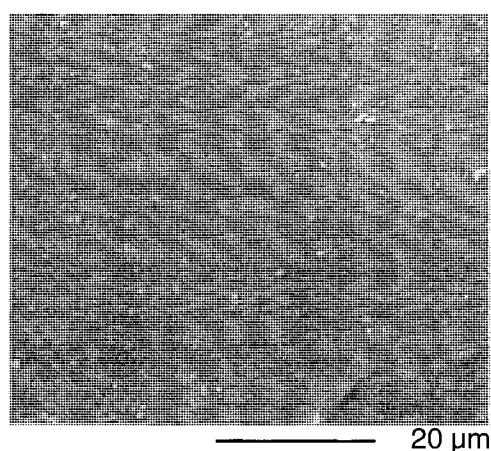


Fig. 4: SEM micrograph of polyaniline-polypyrrole composite coating (feed monomer ratio, aniline 30% - pyrrole 70%) formed on low carbon steel at 0.8 V vs SCE.

(polyaniline-polypyrrole composite) and the second layer (polypyrrole). The possible interaction between two layers is still under investigation.

Figure 4 shows the SEM micrographs of polyaniline-polypyrrole composite coating (monomer feed ratio; aniline 30% - pyrrole 70%) formed on low carbon steel. The granular morphology of the polyaniline along with globules of polypyrrole coexists together. The changes in morphology of coating as the polypyrrole top layer was deposited are investigated. Figure 5 shows the formation of polypyrrole as a function of reaction time. As the reaction proceeds, the size of globules increases and porous morphology was obtained which is identical to the morphology of pure polypyrrole shown in Figure 6. This result confirms the formation of polypyrrole onto polyaniline-polypyrrole composite coating, in agreement with IR results. It is shown that the morphology of polypyrrole was not change much irrespective of the substrate (whether it is coated on steel surface or on polyaniline-polypyrrole composite coating). The dissolution steel and formation of iron (II) oxalate on the steel surface at the beginning of reaction, which occurred in the electrochemical deposition of polyaniline-polypyrrole composite coating, was not observed during the formation of second layer.¹⁸ In the SEM micrographs iron (II) oxalate crystals were not observed. This finding is in agreement with infrared results in which iron (II) oxalate peaks at 1360 cm^{-1} and 1315 cm^{-1} due to C–O group were not recorded in any of the spectra of bi-layer system. This result reveals that, the presence of first layer (polyaniline-polypyrrole composite) protects against the dissolution of steel during

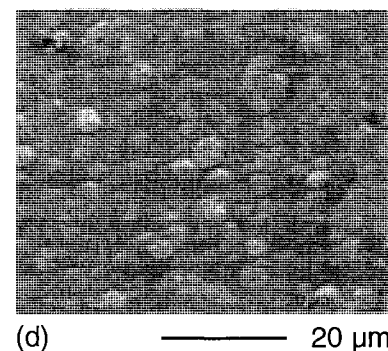
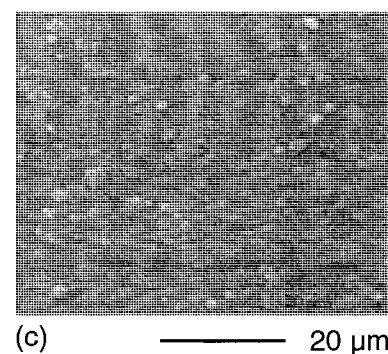
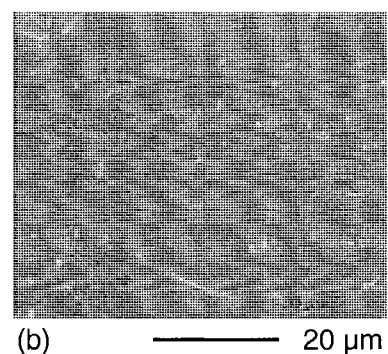
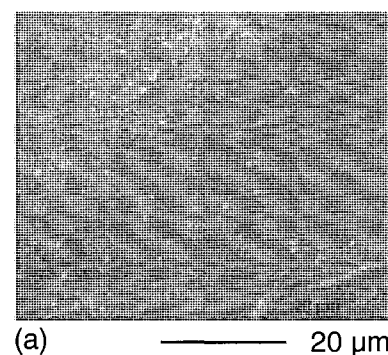


Fig. 5: SEM micrograph of polypyrrole bilayer formed onto polyaniline-polypyrrole composite coating as a function of reaction time (a) time = 0, (b) time = 5 sec., (c) time = 60 sec., and (d) time = 300 sec.

the formation of second layer. Thus, we can conclude that iron (II) oxalate does not form in the interface of polyaniline-polypyrrole composite coating and polypyrrole coating.

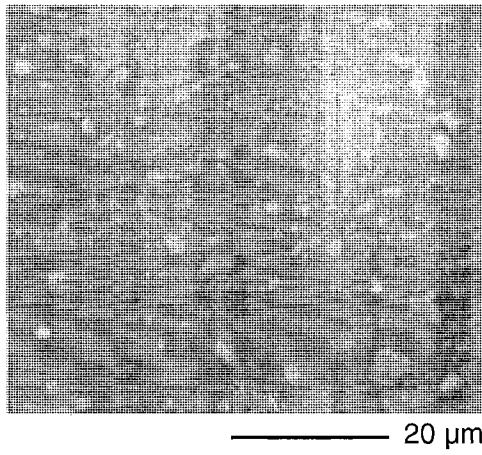


Fig. 6: SEM micrograph of polypyrrole coating formed on low carbon steel at 0.8 V vs SCE.

3.2 Corrosion Performance of the Coating

The behavior of the DC polarization curve gives information about the nature of the corrosion protection of the coatings. The DC polarization curve will show whether the coatings show an anodic protection or cathodic protection. When a protective coating is formed on the steel surface, the coating could provide protection against corrosion by either decreasing the rate of anodic reaction (cathodic protection) or cathodic reduction (anodic protection). This could be easily predicted from the behavior of the Tafel curves. If there is cathodic protection, E_{corr} shifts negatively to E resulting in a negative potential shift called cathodic overpotential. On the other hand, if there is anodic protection, the potential change positive with respect to E_{corr} .

Moreover, Tafel plots can also be used to calculate the corrosion rate of the metals from the following equation:²⁰

$$I_{corr} = [1/(2.303 R_p)] [(\beta_a \beta_c) / (\beta_a + \beta_c)]$$

where; I_{corr} is the corrosion current density (in A/cm²), R_p is the corrosion resistance (in Ω .cm²), β_a is the anodic Tafel slope (in V/decade) and β_c is the cathodic Tafel slope (in V/decade). From this equation corrosion current can be converted into corrosion rate (in mm per year) using the following equation:

$$\text{Corrosion Rate (mmpy)} = (32.721 I_{corr} (EW) / Ad)$$

where; EW is the equivalent weight of the oxidized elements (in grams/equivalent), A is the surface area of the specimen (in cm²), d is the density of the specimen (in g/cm³).

Figure 7 shows the Tafel curves of the bare steel, polyaniline-polypyrrole composite coating and bilayer system. It is clearly shown that E_{corr} values for the coated samples are shifted to more positive values when compared to bare steel sample. The E_{corr} value of about -572.6 mV for bare steel is shifted to -344.8 mV for polyaniline-polypyrrole composite coating and becomes more positive for the bilayer system ($+307.9$ mV). This suggests that the bilayer system gives corrosion protection by preventing cathodic reduction. In addition to this, Figure 7 shows how much better the corrosion performance of the bilayer coating is, compared to polyaniline-polypyrrole composite coating and bare steel. The I_{corr} value is reduced by two orders of magnitude when steel is coated with bilayer system. This means that the corrosion rate of steel was significantly reduced as a result of the low corrosion current density. Table 1 summarizes the tafel results of the coatings. These results indicate that bilayer system has better corrosion performance over polyaniline-polypyrrole composite coating. In our previous study we reported the improvement of corrosion protection of steel by polyaniline-polypyrrole composite coatings.²¹ By applying top coating we have achieved additional improvement of corrosion performance of polyaniline-polypyrrole composite coating. It can be concluded that polypyrrole coating could act as an additional protection layer, which improves the overall corrosion performance of the coating. Additionally, polypyrrole bilayer may also function as a physical barrier, which can reduce the diffusion of ions and water through to metal surface. Having conjugated double bond structure and presence of $-NH$ polar group may also give anodic inhibitor property to polypyrrole bilayer coating. These factors explain the anodic inhibition of the coating where E_{corr} value of -572 mV for bare steel is shifted to more positive value ($+307.9$ mV) for bilayer system.

3.2.1 Effect of Reaction Time

The corrosion performance of bilayer coating is investigated as a function of reaction time in order to optimize the process. Figure 8 shows the tafel plots of bilayer system as a function of reaction time. The tafel plots of composite coating and plain steel were also included for comparison. It is seen that as the formation of polypyrrole coating proceeds, the corrosion current decreases. The corrosion rate of the coatings as a function of reaction time is shown in Table 1. The excellent corrosion resistance of the coating was observed at about 300 seconds deposition. Table 1 also shows the increase of E_{corr} values and decrease of I_{corr} values as the reaction time increases from 5 to 300 seconds.

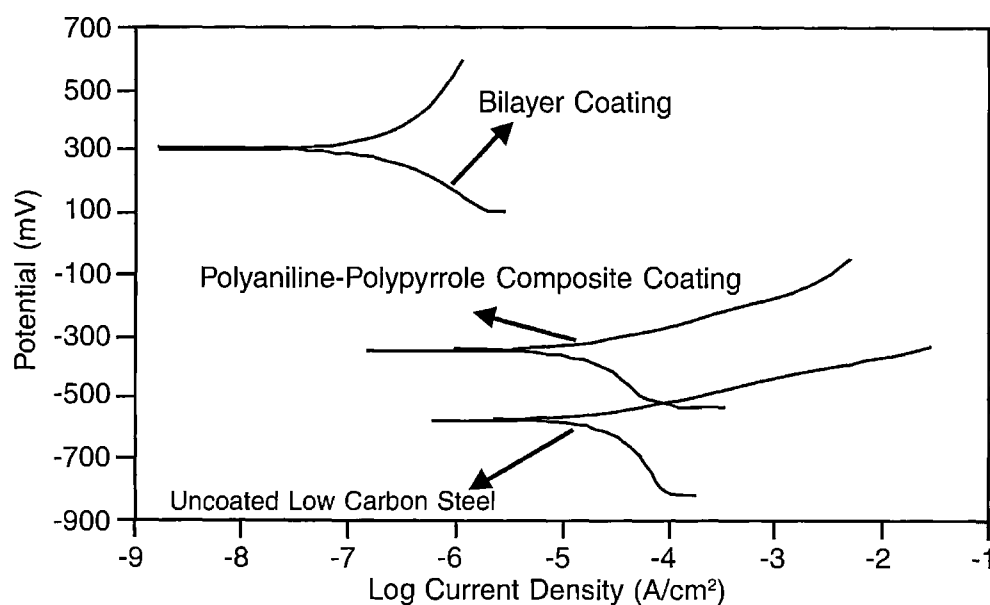


Fig. 7: Tafel plots of low carbon steel coated with polyaniline-polypyrrole composite coating and bilayer coating.

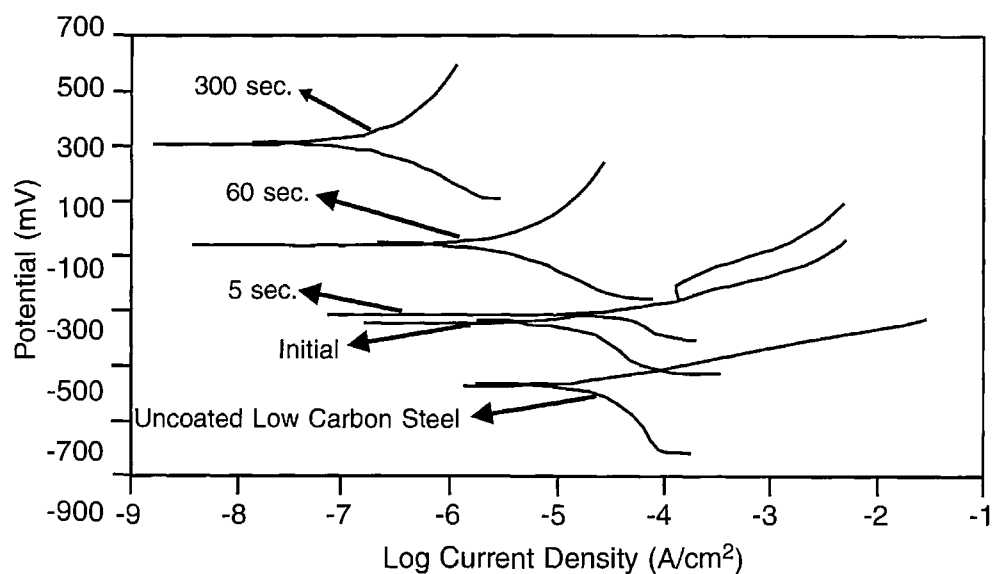


Fig. 8: Tafel plots polypyrrole bilayer coating as a function of reaction time formed at an applied potential of 0.8 V vs SCE.

Table 1. Tafel Results of the Coating

Sample	E_{corr} (mV)	I_{corr} (A/cm²)	Corrosion Rate (mmpy)
Low Carbon Steel	-572.6	9.05×10^{-5}	1.05
PANi-Ppy Composite Coating	-344.8	1.59×10^{-5}	0.238
Bilayer Coating at 5 sec.	-307.3	5.47×10^{-5}	0.816
Bilayer Coating at 60 sec.	-57.6	2.90×10^{-6}	0.0433
Bilayer Coating at 300 sec.	307.9	2.18×10^{-7}	0.00325

4.0 Conclusion

The formation of polypyrrole top coating onto polyaniline-polypyrrole composite primer coating was achieved for the corrosion protection of low carbon steel. The structure and the morphology of the bilayer coating were determined by infrared spectroscopy and scanning electron microscopy techniques. The corrosion performance of polypyrrole bilayer coating was investigated using DC polarization tests. It was found that bilayer coatings show better corrosion resistance than polyaniline-polypyrrole composite coatings. The corrosion resistance of steel is significantly improved by depositing (PANi/PPy)-PPy bi-layered coating.

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Corrosion Protection of Al 2024-T3 by Particulate Filled Conducting Polymer Coatings

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Abstract

Electrochemical synthesis of particulate-filled polyaniline (PANi) and polypyrrole (PPy) films on Al 2024-T3 was carried out under aqueous conditions. A variety of fillers including clay, carbon black (CB), short carbon fiber, YSZ, and SiO₂ were studied. Both cyclic voltammetry and constant current techniques were employed in electrochemical deposition of the filled conducting polymer composite

coatings. To further improve the corrosion resistance of the coatings, multilayers of filled conducting polymer films were formulated. The amount of charge consumed during electrodeposition was obtained from the cyclic voltammograms. DC polarization tests were performed on the coated substrates in a 3.5% NaCl solution. The results showed that the presence of fillers such as clay, short carbon fiber and YSZ improved the corrosion resistance of PPy/PANi-coated aluminum. Multilayer coatings also showed significant enhancement in the corrosion performance of the coatings.

1.0 Introduction

Polymers with conjugated π -electron double bonds in their backbones display unusual electronic properties, and belong to a class of novel materials called intrinsically conducting polymers (ICPs). These polymers become highly conductive in the doped states. Since the discovery of the conducting polymers in the 70's,¹ they have found wide application in such areas as primary and secondary batteries, sensors, light emitting diodes, electromagnetic shielding, and electrochromic systems.

Among the vast applications of electronically conductive polymers, corrosion inhibition of metals is an entirely new one and is of great industrial importance. Corrosion of metals is a serious problem encountered in industry, and it costs tens of millions of dollars annually. In the past few years, several conductive polymers such as polypyrrole, substituted polypyrrole and polyaniline have been shown to provide excellent protection for Al alloys and steel.²⁻¹¹ Despite the attractive properties of conducting polymers, there are problems limiting their wide commercial application including poor processibility, limited film thickness and the poor stability of the doped polymers. The practical application of conducting polymers cannot be fully realized if they cannot be processed from raw material to the final product. Studies have begun in this area and promising results have been achieved by formulating inorganic filler-conducting polymer nano-composites.¹² It is of interest to functionalize and stabilize these polymers by incorporating a variety of inorganic materials, such as metal oxides, clay, carbon black, and carbon fibers in order to improve their properties and impart new properties. However, there is not much study on the use of filled ICP composites for improving processibility and corrosion resistance of conducting polymers. Furthermore, there have not been many reports on electrochemical deposition of these filled composites for the purpose of corrosion protection of metals.

Our preliminary results showed that it is possible to improve corrosion resistance of conducting polymer coatings on metals through incorporation of inorganic fillers. Over the past ten years, it has been shown that incorporation of metal oxides and other inorganic particles into conducting PANi/PPy can be achieved. Yoneyama and co-workers did the pioneering work¹³⁻¹⁵ in this area. They successfully incorporated WO_3 , SiO_2 , Ta_2O_5 , and SnO_2 particles into electrochemically synthesized polypyrrole film. However, there is not much work done on the effects of these fillers on the corrosion protection of metals. This paper will explore the effect of inorganic particles on the corrosion performance of

the conducting polymer coatings based on PANi/PPy systems polymerized in aqueous solutions. The inorganic fillers included carbon black, short carbon fiber, SiO_2 , YSZ, and clay. To further improve the corrosion resistance of the coatings, multilayered coatings were formulated, and the corrosion protection mechanism is proposed.

2.0 Experimental

2.1 Materials

Aluminum 2024 panels were purchased from Q Panel Lab Product (Cleveland, OH) and were cleaned in an ultrasonic bath containing hexane and dried in air before use. Aniline, pyrrole, oxalic acid and the metal oxide powders were purchased from Aldrich Inc. (Milwaukee, WI) and were used as received. Coisite® Clay Na^+ was obtained from Southern Clay Products, Inc. (Gonzales, Texas). Short carbon fibers were purchased from Applied Science Inc. (Cedarville, Ohio) and were ground before use.

2.2 Sample Preparation

In the case of single-layered composites, aniline/pyrrole and oxalic acid were dissolved in water to make solutions of 0.1M aniline/pyrrole and 0.2-0.3 M oxalic acid, and each of the fillers was suspended in 250 ml of the aniline solution by stirring and ultrasonication. Electrochemical deposition was carried out in a one-compartment electrochemical cell with two stainless steel sheets as the counter electrodes and saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetry (CV) and constant current methods were used to form the composite films. A scan rate of 20 mV/s and a potential range of 1.0-3.0 V (vs. SCE) were used in CV. CV experiments were conducted by using a computer-controlled EG & G PAR 273A potentiostat/galvanostat equipped with Model 270 electrochemical software. Galvanostatic electro-deposition was performed by applying a current density of 2-10 mA/cm². A 363 potentiostat/galvanostat was used to provide DC current. The resulting coatings were then washed with methanol and heated in an oven at 100°C for 0.5 hr.

For multilayer composites, the first layer is PANi-Ppy composite. 10% pyrrole, 90% aniline, and 0.3M oxalic acid were mixed in the solution and a current density of 10 mA/cm² and deposition time 1.5 minutes were used. The second layer is carbon fiber-filled Polypyrrole, and the vol% of carbon fiber was varied from 0.75, 1, 1.5, and 2%. A current density of 2 mA/cm²

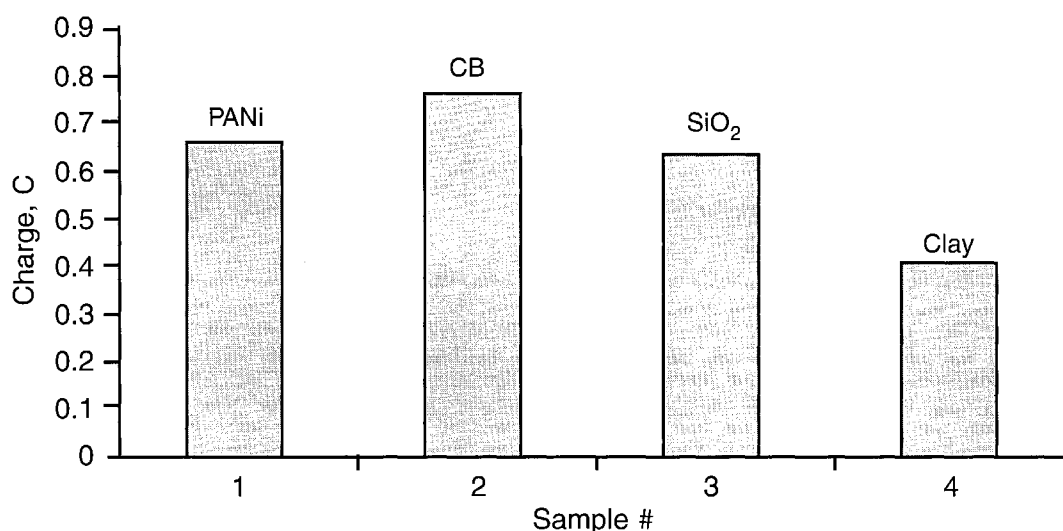


Fig. 1: Effect of fillers on the amount of charge consumed during polyaniline deposition.

five minutes were used. The other multilayer systems including first layer-polyaniline and the second layer-filled polyaniline were formulated under similar conditions by the constant current method.

2.3 Corrosion Test

A Tafel corrosion test was carried out in a flat cell containing a 3.5% NaCl solution using the PAR Model 352 corrosion software and EG & G PAR model 273 A potentiostat/galvanostat. Four different spots were tested on each sample and the average data were reported.

3.0 Results and Discussion

3.1 Effect of Fillers

For the filler incorporation to occur, the oxide surfaces have to be negatively charged, and such conditions can be achieved if the pH of the suspensions is greater than the isoelectric point of the fillers. In our study, several pH values were used for the deposition of YSZ (IEP around pH 4-5), and the pH was adjusted by using triethylamine. At pH 1.6 and 1.9, respectively, thick films were formed, while at pH of 2.5, 3.0, and 6.04, very thin films were obtained. It is known that polyaniline deposition occurs at low pH values. Therefore, for some of the systems, the pH was maintained at about 1.69.

Cyclic voltammetry and constant current methods were used in electrodeposition of the composite films.

In the former technique, PANi films formed are thick, uniform and dark green in color after drying at 100°C. Films formed by constant current were thinner and light shiny green in color, and this was the case for all filler systems. Only the constant current technique was used for PPy deposition, and the resulting films were black in color in all cases.

Cyclic voltammetry as a deposition technique not only provides the coatings, but also gives other useful information concerning PANi formation. The parameter that indicates the polyaniline polymerization rate is the charge consumed during the oxidation of aniline (area under the anodic peaks on CV curves). The charge can be calculated using the area under the anodic peak on the CV charts (equation 1).

$$\text{Area} = \int I(E) \cdot dE = Q \cdot \frac{E}{t} \quad (1)$$

where $I(E)$ is current, which is a function of E , potential, Q is the charge consumed, and E/t is scan rate (in this case, 20 mV/s). Therefore, the charge consumed during polyaniline deposition can be calculated as

$$Q = \frac{\text{Area}}{E/t} \quad (2)$$

Figure 1 shows the effect of different fillers on the charge consumed during the polymerization of aniline. It can be seen that a maximum charge is consumed when aniline is polymerized in the presence of carbon black. Therefore, one can infer that CB enhances the deposition of PANi. This observation is in agreement with literature reports.¹⁶ Polymerization of aniline in the presence of

clay involved the consumption of the least amount of charge, indicating that, to some extent, clay may inhibit PANI deposition. There was no significant charge consumption change during the polymerization of aniline in the presence of SiO₂ when compared with the control aniline system containing no fillers. However, whether the inhibition phenomenon is beneficial or adverse to the corrosion protection property of the coating needs further study.

3.2 Corrosion Test

The equilibrium open circuit potential (OCP) of a polymer-coated electrode can be considered to be the corrosion potential. OCP of a polymer film also indicates the surface characteristics of the film. The corrosion current density I_{corr} is a parameter that represents the corrosion resistant property of a polymer film, and the corrosion rate r in mmpy (millimeter per year) of material can be calculated from I_{corr} , as shown in (equation 3).¹⁷ Therefore, both parameters are indicators of surface property and corrosion resistance of films.

$$r = 3.27 \frac{ai}{nD} \text{ (in mmpy)} \quad (3)$$

where 3.27 is the proportionality constant, I_{corr} is corrosion current density in $\mu\text{A}/\text{cm}^2$, a is atomic weight in grams/mole, D is density of the specimen in g/cm^3 , n is the number of equivalents transferred.

Both I_{corr} and E_{corr} can be obtained from DC polarization curves (Tafel plots). The Tafel plots were generated by applying potential (E_{app}) from equilibrium potential (E_{eq}) towards the negative and positive potentials against a Ag/AgCl reference electrode. The potential difference between applied potential and equilibrium potential is the overpotential. The Butler-Volmer Equation¹⁸ (equation 4 and 5) shows the relation between polarization current density and overpotential.

$$i_a = i^0 \left[\exp\left(\frac{\beta nF}{RT} \cdot \eta_a\right) - \exp\left(-\frac{\alpha nF}{RT} \cdot \eta_a\right) \right] \quad (4)$$

$$i_c = i^0 \left[\exp\left(\frac{\alpha nF}{RT} \cdot \eta_c\right) - \exp\left(-\frac{\beta nF}{RT} \cdot \eta_c\right) \right] \quad (5)$$

where i_a and i_c are anodic and cathodic current density respectively; i^0 represents reaction current density in both anodic and cathodic direction at E_{eq} , and is called exchange current density. The anodic overpotential is obtained from the difference between E_{app} and E_{eq} , $\eta_a = E_{\text{app}} - E_{\text{eq}}$, and cathodic overpotential is obtained from: $\eta_c = E_{\text{eq}} - E_{\text{app}}$. α is the transference coefficient for cathodic reaction, while β is transference coefficient for

anodic reaction, and both α and β are positive and less than 1 ($\alpha + \beta = 1$); n is the number of electrons. Under the conditions of high overpotential, the relation between overpotential and the logarithm of polarization current density is a straight line, given by the Tafel Equation:

$$\eta = a + b \cdot \log I \quad (6)$$

where η is the electrochemical polarization overpotential; a is overpotential per unit polarization current density; b is the slope of Tafel polarization curve. The first term, a , is related to the intrinsic characteristics of the electrode system and reaction process while the second term, $b \cdot \log i$, is related to polarization current density. Corrosion current density I_{corr} is obtained from the extrapolation of the two Tafel straight lines (cathodic and anodic) to E_{eq} , which represents the corrosion resistant ability of the electrode. Tafel plots can only be constructed under strong polarization conditions, which means overpotential in the range of 100-250 mV.

The Tafel plot can give both the corrosion current and open circuit potential and other parameters such as R_p (polarization resistance). The Tafel slopes, β_a for anodic branch and β_c for cathodic branch, can also be obtained from Tafel plots. In this study, Tafel tests were carried out in 3.5% NaCl water solution.

3.3 Single-Layer Systems

Among all the fillers used, clay, YSZ, SiO₂, and CeO₂ showed favorable corrosion properties, while TiO₂ and WO₃ did not show any significant effect on the corrosion property of polyaniline. The polyaniline coatings formed in the presence of clay showed the best corrosion resistant property. In our former report, it has been found for the first time, that incorporation of Na⁺ Cloisite® clay into PANi films by electrodeposition provided higher corrosion resistance for Al 2024 than pure PANi.^{19, 20} As shown in Figure 2, Tafel plots of the nano-composite film shifted to the left, which indicates lower corrosion current and lower corrosion rate than the pure PANi. It can be seen that films formed in the presence of clay showed nearly an order of magnitude lower corrosion current than the PANI film. Therefore, the presence of clay improved the corrosion resistance of polyaniline coatings.

Another interesting conducting polymer, filled PPy system was also studied. Shown in Figure 3 are the Tafel plots for different filler systems including a pure PPy coating. The corresponding I_{corr} and E_{corr} of the systems were plotted in Figure 4. As shown in these two figures, there was a significant decrease in the corrosion current from 17 to 10 μA for PPy-clay and PPy-YSZ systems. However, there was no significant change in the corrosion

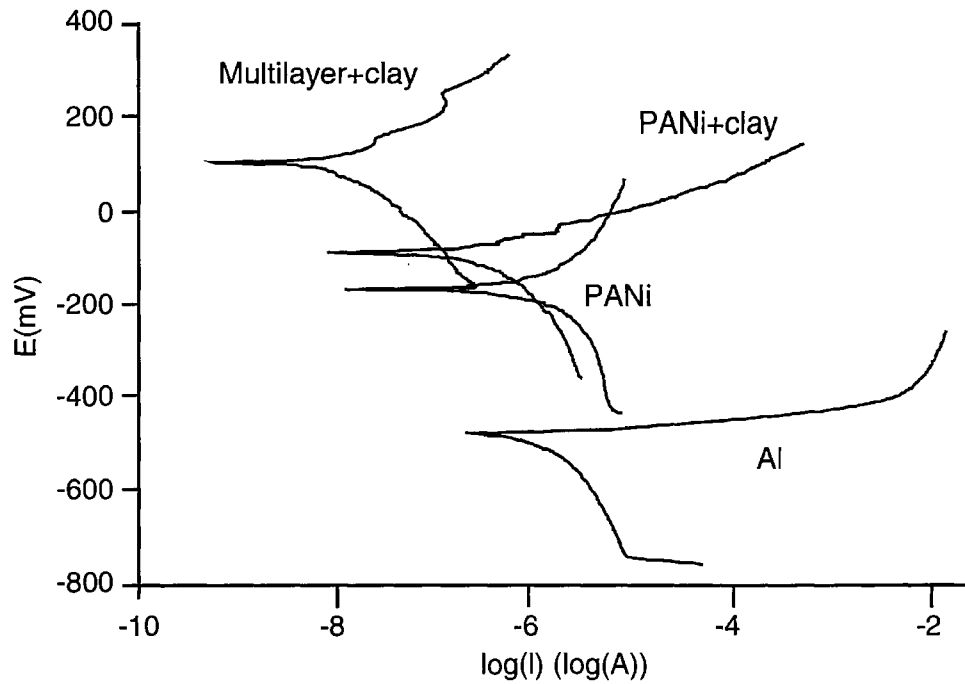


Fig. 2: Tafel plots of clay filled composite coatings on Al 2024.

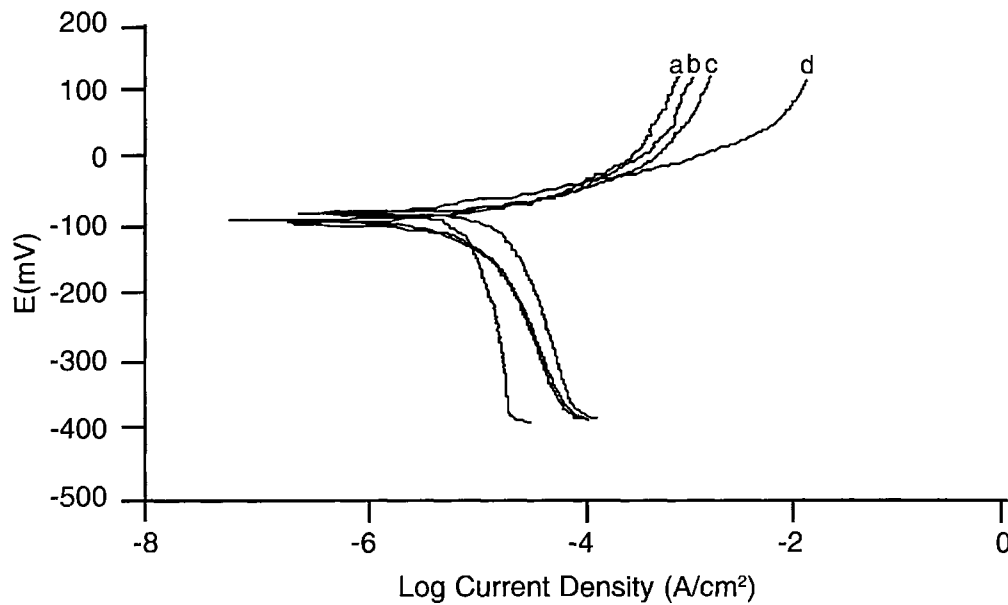


Fig. 3: Tafel plots of particulate-filled pyrrole coatings on Al 2024-T3: (a) PPy + SiO₂, (b) PPy + clay, (c) PPy, and (d) PPy + YSZ.

potential. This indicates that incorporation of the fillers enhances the corrosion resistance of the coatings.

4.0 Multilayer Systems

By formulating graded coatings containing nano-sized inorganic fillers, further improvement in the corrosion performance of the PPy and PANi coatings

has been achieved. As shown in Figure 2, the clay-filled multilayered system provides more than a two order of magnitude decrease in corrosion current. The corrosion (open circuit) potential (OCP) also showed a dramatic increase. In fact, the multi-layered system containing clay particles showed a noble behavior with OCP as high as 100 mV(vs. SCE) (300 mV higher than that for PANi coating). Both the decrease in corrosion current

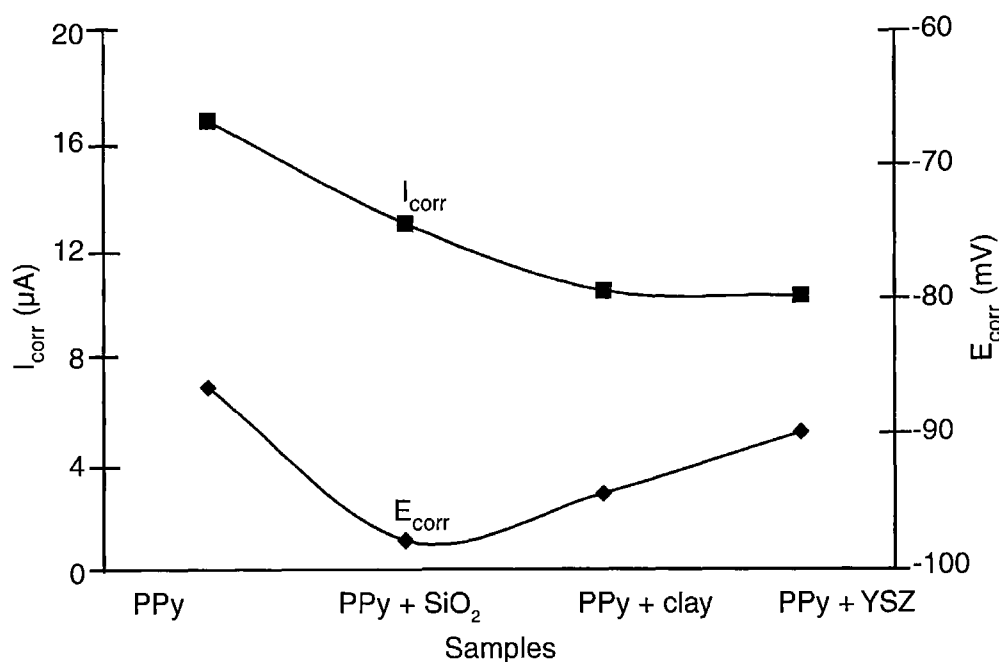


Fig. 4: I_{corr} and E_{corr} for particulate-filled polypyrrole coatings.

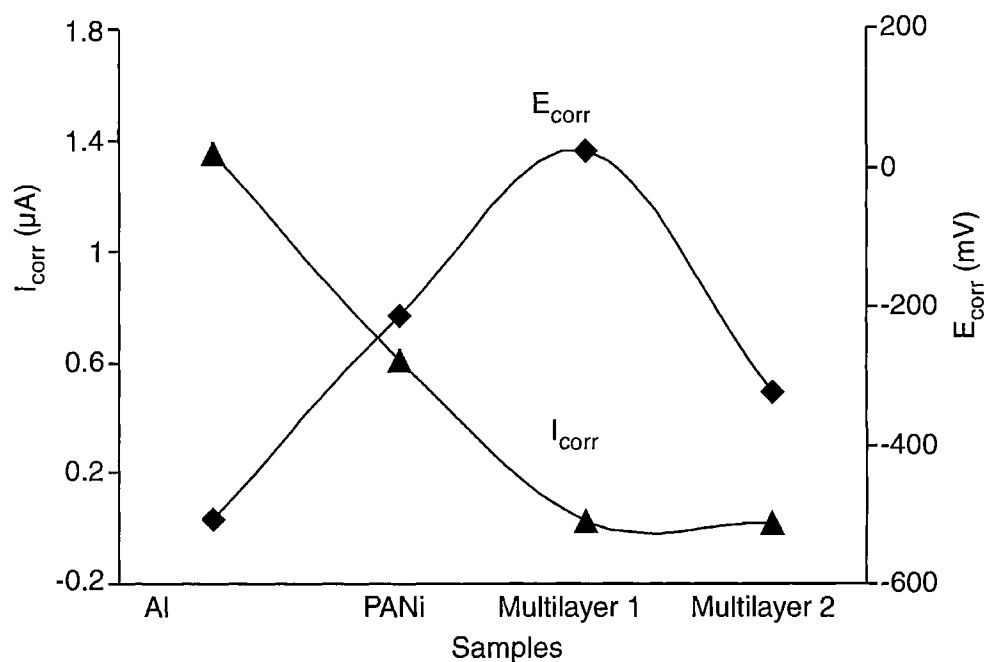


Fig. 5: Multilayer processing effect on I_{corr} and E_{corr} .

and the more noble OCP are indicative of better corrosion performance of the composite films. The quantitative corrosion test data are shown in Figure 5, which shows the performance of two excellent multilayered systems filled with clay and YSZ. It is shown that the corrosion

rate of Al substrate was lowered by two orders of magnitude by application of filled conducting polyaniline composites. The filled multilayer composite further decreased the corrosion rate by one order of magnitude compared with pure PANi.

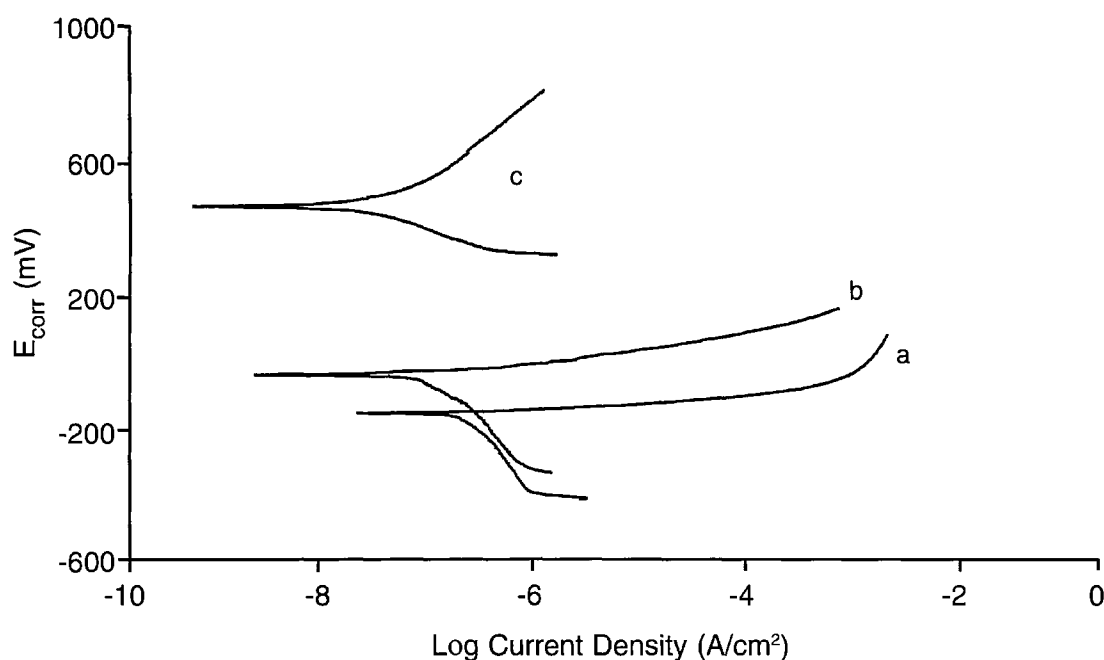


Fig. 6: TAFEL Plots (a) control (Bare Al-2024), (b) composite coating (10% pyrrole-90% aniline), and (c) multilayer coating.

Applying a PANi-PPy composite as the first layer in the multilayered system showed significant improvement in corrosion resistance. Shown in Figure 6 are the DC polarization curves for PPy-PANi composite and multilayered coatings. As shown in this figure, the multilayered coating reduces the corrosion rate of the aluminum substrate by 1.5 orders of magnitude. As compared to the first layer (the PANi-PPy composite coatings), the corrosion rate reduces by 0.5 orders of magnitude. Multilayered coatings give better corrosion protection because they are much thicker and cover the substrate more uniformly as compared to the single layered coatings. We believe that the presence of pyrrole in the first layer enhances the adhesion between the two layers. Therefore, the improved performance of the multilayer coatings probably results from a combination of barrier mechanism and better adhesion.

Figure 7 shows the change in corrosion current and corrosion potential with the variation of carbon fiber in the second layer. As seen from the figure, as the carbon fiber content is increased in the second layer, the corrosion current increases. The corrosion potential increases from 100 to 400 mV as the carbon fiber concentration is decreased from 2 to 0.75% by volume. This indicates that at lower carbon fiber concentration the surface of Al-2024 is more noble. We believe that, the increase in carbon fiber concentration may lead to increased film porosity and decreased uniformity and homogeneity of the coatings, resulting in a decrease in

the corrosion performance. Therefore, high concentration of the carbon fiber filler may decrease the corrosion resistance of the coating.

Figures 8 and 9 compares the corrosion current and corrosion potential for coatings formed under various conditions. As seen from the curves, the multilayer coatings show the least corrosion current, and thus give the best corrosion protection. The polymer composite and multilayer coatings (with and without carbon fibers) increase the corrosion potential of the substrate to more positive values, indicating that the surface of the system is more noble.

Table 1 shows the anodic and cathodic TAFEL slopes and the corrosion rates for various coating conditions. β_a is the anodic slope which gives us information about the anodic reaction occurring at the metal surface. β_c is the cathodic slope which tells us whether the corrosion is diffusion or activation controlled. The DC polarization tests were carried out in a 3.5 wt.% NaCl solution which has a pH of 6. As seen from Table 1, β_a for the bare Al-2024 is 0.022V/decade, suggesting that a passive film of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is formed on the substrate (from the Pourbaix diagram). The corrosion rate is high because this film is quite porous and has many defects. As we apply the coating on the substrate the anodic slope increases and we believe that the coating is stabilizing the passive film formed onto the substrate. The corresponding corrosion rate is also reduced drastically.

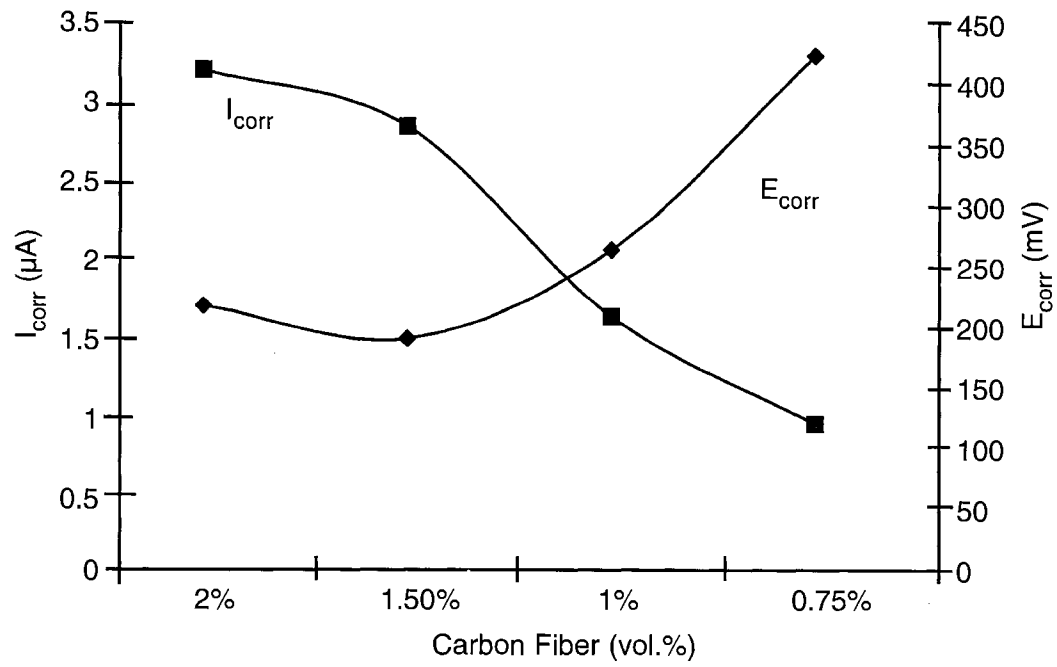


Fig. 7: Variation of I_{corr} and E_{corr} as a function of carbon fiber concentration.

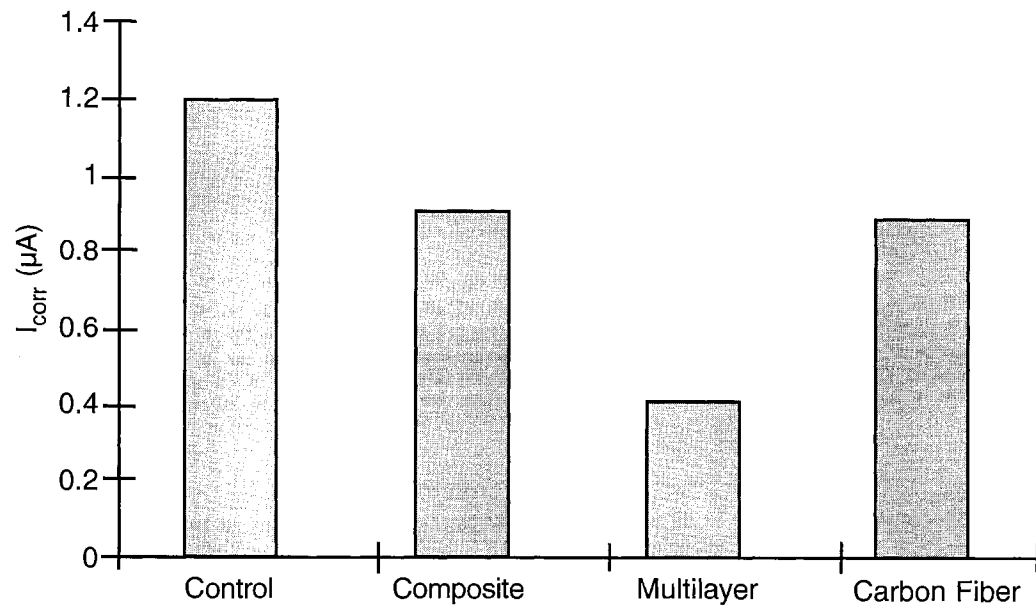


Fig. 8: Comparison of I_{corr} for various conditions.

Table 1. Comparison of β_a and β_c for Various Coating Conditions

Coating Conditions	β_a (V/Decade)	β_c (V/Decade)	Corrosion Rate (mmpy)
Control (Bare Al-2024)	0.022	-0.428	0.026
Composite (First Layer: 10% Pyrrole and 90% Aniline)	0.041	-0.331	0.012
Multilayer	0.249	-0.162	0.005
Multilayer + Carbon Fibers (0.75 vol.%)	0.389	-0.187	0.012

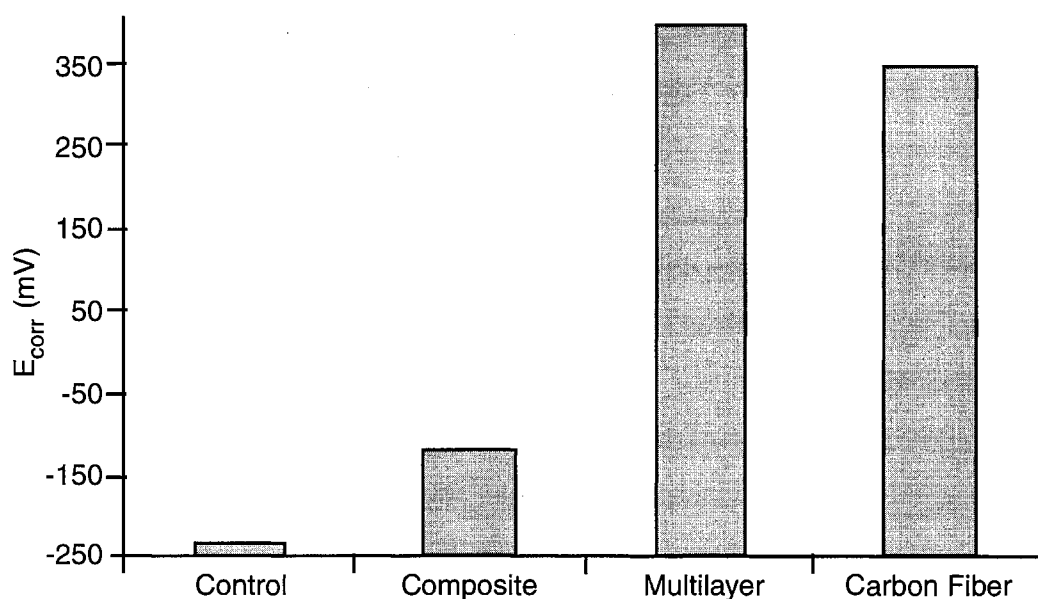


Fig. 9: Comparison of E_{corr} for various conditions.

5.0 Conclusion

Electrochemical deposition of PANi, PPy, PANi-PPy composites, inorganic particle-filled composites and multilayered conducting polymer coatings on aluminum substrates was successfully accomplished. DC polarization tests showed that the presence of fillers such as, YSZ, SiO_2 , and clay improved the corrosion resistant property of polyaniline and polypyrrole coatings deposited on aluminum. Formulating a multilayered system further improves the corrosion protection of the filled coating systems. Our results demonstrated a positive effect of fillers on corrosion resistance of polyaniline/polypyrrole coatings. The mechanism of corrosion resistance by filled conducting polymer coatings is currently under study in our laboratory.

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Experimental Determination of Interactions Between Molten Aluminum and Selected Die Coatings for Aluminum Pressure Die Casting

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1.0 Introduction

Aluminum die casting is a large and important industry in the modern manufacturing environment, and making this process more efficient and profitable is important to everyone involved. The H13 tool steel used for the die material has been optimized, and there is little room for improving this material further for the die casting process. For this reason coatings and surface modifications are now being considered as a way to continue to improve die casting dies. Preliminary

investigations show a two to three times improvement in the life of the H13. To date, some of the small pieces in the die have been coated but eventually it will be possible to coat all of the surfaces that come into contact with the molten aluminum.

The materials used for the die casting dies have been modified continuously in order to decrease down time, increase the life of the dies, and improve the surface finish of the cast products. The main modes of failure for the dies are soldering of the aluminum to the dies, heat checking or cracking, and washout of the die

materials. It is desirable to emulate these problems in the laboratory in order to reduce their occurrence during manufacturing. However, it is not possible to reproduce the actual conditions in the die casting dies, the speed at which the aluminum is injected into the dies and the pressures developed in the dies are hard to produce in a laboratory setting.

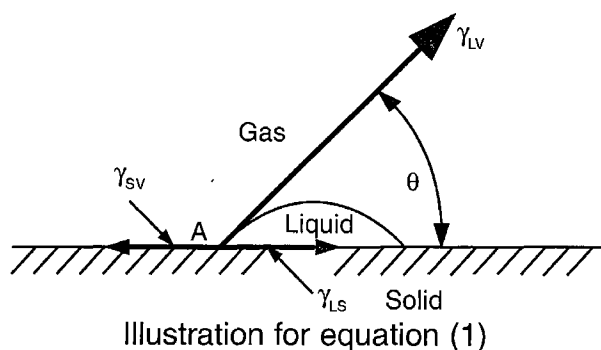
Die casting dies are very expensive. Increasing their useful production life is desirable, but of more importance is keeping the dies in operation. The time that a die is not in operation is very expensive; this is due to the high cost of keeping the aluminum above its melting temperature and the lost revenue due to the lower number of parts that are produced. The wasted energy is the most expensive aspect of down time, decreasing the amount of wasted energy by decreasing the down time is one of the main areas of focus of this research.

Determining the optimum surface modification and coating for each specific application is a complex problem. Aluminum is very reactive and easily alloyed. There are a variety of aluminum alloys used in die casting of pieces and parts, each one having properties that are desirable in the finished product. The problem is, there are properties for each of the alloys that can influence the behavior of the coatings that are applied to the die casting dies. In order to determine the interactions that occur, experiments are being developed that give rise to trends, which can be measured and evaluated.

2.0 Sessile Drop Tests

Whenever there are three phases in contact with each other, there are surface tensions between each of the phases that are related through the Young equation,^{2,4}

$$\gamma_{SV} \cos \theta = \gamma_{SV} - \gamma_{LS} \quad (1)$$



These surface tensions must be at equilibrium at any given time in order for the droplet to be stable. It is desirable for the thin films to be non reactive with the molten aluminum they are to be in contact with. If the molten aluminum has a large contact angle with the various coatings then there is a large interfacial energy between the liquid and solid and the surface is said to be

non-wetting. By having molten aluminum in contact with the various films and measuring the contact angle the molten aluminum makes with the film, it is possible to determine which films have the largest interfacial energy and are therefore likely to be the least reactive.

After the sessile drop test is complete, one can measure the amount of weight required to remove the solidified aluminum, and along with the contact area it is possible to determine the bond strength. Determining the mode of failure is also desirable, if the separation occurs exactly along the interface or above or below the interface. If the separation occurs below the interface then the film is no longer intact where it was in contact with the aluminum, and this film is not likely to perform well in the die casting of aluminum.

3.0 Experimental Setup

The system under investigation is complex in many ways, and it is desirable to simplify the number of variables as much as possible. The experiments must therefore be run in a self-consistent manner so that trends can be seen and measured which are related to the interactions that control the performance of the coatings. A preliminary experimental matrix was formed to find a set of conditions such that the aluminum was wetting on H13 tool steel. H13 tool steel is the main material most used for aluminum die casting dies, and so all of the films tested will be compared against it.

The experiments are performed by melting aluminum in contact with the surface coating and then measuring the contact angle and the spreading of the liquid aluminum as a function of time and temperature. The contact angle and the spreading change with respect to time due to gravity and the reaction layer that exists along the interface between the aluminum and the coating. The aluminum has an oxidized layer enveloping it and the films also tend to oxidize at temperatures lower than the experimental conditions.

It was found that the aluminum was more wetting upon the H13 tool steel when the partial pressure of oxygen was lowered, as can be seen in Figure 1. The partial pressure of oxygen is lowered by decreasing the pressure in the furnace to 60 mTorr and back filling with ultra high purity argon gas. This is done three times and then the argon is allowed to flow at 2.3 scfh for the duration of the experiment.

The four aluminum alloys chosen for these experiments are 360, 380, 383, and 390, which were cut into 1/4 inch cubes that were then melted in contact with the various coatings. Each of the candidate surface coatings was applied at 3-5 μm thick upon fully characterized H13 tool steel.

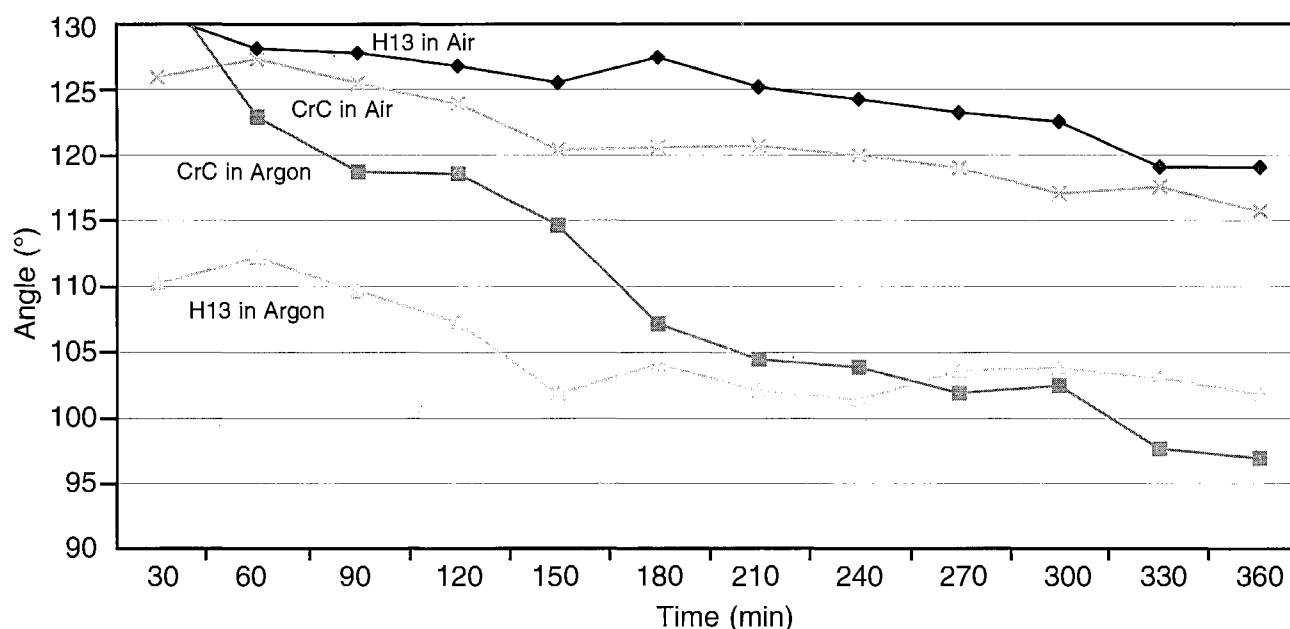


Fig. 1: 360 Aluminum melted upon CrN and H13 at 800°C in argon and air.

The experiments were run at 770°C for six hours under an argon atmosphere, in order to have a low partial pressure of oxygen. The samples were furnace cooled, and the aluminum was sheared off of the surface with an instron mechanical tester. The force that is required to shear the aluminum was recorded and by measuring the contact area that the aluminum had with the surface, a bond strength can be determined.

4.0 Results

The contact angle measurements for the experiments were found to vary for the alloy as well as for the coatings. For some of the film-alloy combinations the angle increased, and for some of the combinations the angle decreased. This is due to the interaction layer at the interface between the aluminum and the coating. If the contact area increased, the angle either decreased or stayed the same. If the contact area stayed the same and the droplet settled, the angle increased making it appear less wetting with time.

It was found that the H13 was more wetting than all of the films tested thus far. It was also found that more force was required to remove the aluminum from the H13 than for each of the coatings, as can be seen in Table 2. Some of the coatings had very low forces required to remove the aluminum and some had forces close to the H13. The reaction products have not been

determined, so the mechanisms for wetting or non wetting have not been determined.

A dunk tester is also being built which will have the actual aluminum in contact with the various coatings instead of an oxidized Al_2O_3 layer. The dunk tester will take a sample through a thermal cycling and corrosive environment. Many coatings fail due to the mismatch in coefficients of thermal expansion. A solution to the problem is to use multilayer films to help and reduce the stresses that are developed during changes in temperature. In order to test the ability of the film to remain attached to the substrate, it is necessary to take the sample through a thermal cycle.

A robotic arm was chosen to do the manipulating of the sample through the various stations. The robot is easily programmed to perform various tasks in a very consistent manner. Each of the experiments made for comparison will have been made in a consistent manner due to the computer control. The films will be tested in an industrial setting as well as by the experiment described in order to compare the results obtained in a laboratory setting to the real die casting environment.

Another sessile drop test is being developed that uses a molten droplet placed onto the surface coatings followed by contact angle measurement. The aluminum will solidify in a very short period of time and the solid castings can be compared in order to find which of the surfaces wet the least. The aluminum be cast in contact with each of the candidate working surfaces using the

Table 1. Contact Angles of Melted Al Alloys (360, 383, and 390) on H13 Selected and Selected Coatings

Coating or Material	360 Aluminum		383 Aluminum		390 Aluminum	
	Beginning Angle (°)	Finishing Angle (°)	Beginning Angle (°)	Finishing Angle (°)	Beginning Angle (°)	Finishing Angle (°)
H13	80	65	111	116	98	97
CrN (P)	126	124	126	95	122	123
CrN (IB)	113	123	104	111	113	120
CrC	119	109	95	107	106	114
TiAlN	111	113	120	118	121	122
ZrN	113	107	119	114	113	108
MoZrN	117	120	118	115	123	118
MoNx	110	114	111	112	120	111
Al ₂ O ₃	95	107	115	117	114	115
TiN-TiCN	98	114	118	115	111	121
Cr ₃ Si	112	112	90	102	111	101
Dynablue	102	103	111	111	113	110
TiB ₂ -TiC	102	118	103	109	118	121
TiBCN	110	116	116	118	118	122
MoSi ₂ -SiC	116	116	113	113	112	113
NiAl	< 90	< 90	< 90	< 90	< 90	< 90
NiAlN	< 90	< 90	< 90	< 90	< 90	< 90

Table 2. Force Required to Shear off Al Alloys (360, 383, and 390) on H13 and Selected Die Coatings

Coating or Material	360 Aluminum		383 Aluminum		390 Aluminum	
	Force to Remove Droplet (N)	Soldering Strength of Droplet (N/m ²)	Force to Remove Droplet (N)	Soldering Strength of Droplet (N/m ²)	Force to Remove Droplet (N)	Soldering Strength of Droplet (N/m ²)
H13	236	43,703	42	6,269	489	94,039
CrN (P)	178	247,222	0	0	396	99,000
CrN (IB)	258	78,181	10	83,333	98	23,902
CrC	0	0	49	7,903	36	5,714
TiAlN	0	0	7	2,058	0	7
ZrN	51	10,625	859	357,917	89	37,083
MoZrN	0	0	0	0	10	1,887
MoNx	0	0	0	0	0	0
Al ₂ O ₃	0	0	0	0	36	63,158
TiN-TiCN	0	0	0	0	0	0
Cr ₃ Si	311	47,498	18	3,473	622	61,002
Dynablue	578	147,017	27	8,631	889	161,616
TiB ₂ -TiC	0	0	0	0	0	0
TiBCN	667	456,623	0	0	222	54,200
MoSi ₂ -SiC	222	60,550			111	56,116

Table 3. Relative Roughness and Depth of the Surface Under the Sheared Al Alloys (360, 383, and 390) on H13 and Selected Die Coatings

Coating or Material	360 Aluminum		383 Aluminum		390 Aluminum	
	Relative Roughness of Fracture	(+) Above (-) Below Fracture Surface (μm)	Relative Roughness of Fracture	(+) Above (-) Below Fracture Surface (μm)	Relative Roughness of Fracture	(+) Above (-) Below Fracture Surface (μm)
H13	Very	-100	Very	-110	Very	-110
CrN (P)	Hills & Pitts	60	Hills & Pitts	-4.5	Hills & Pitts	-1
CrN (IB)	Hills & Pitts	-70 to +60	Hills & Pitts	15	Hills & Pitts	-125
CrC	Very	-120	Very	-130	Very	-150
TiAlN	Moderate	-190	Moderate	-190	Moderate	-200
ZrN	Moderate	-105	Pitted	-110	Pitted	-110
MoZrN	Very	-85	Moderate	-160	Very	-120
MoNx	Very	-85	Very	-95	Moderate	-135
Al ₂ O ₃	Smooth	0	Smooth	0	Pitted	-90
TiN-TiCN	Moderate	-95	Moderate	-120	Moderate	-130
Cr ₃ Si	Smooth	-135	Smooth	-180	Moderate	-140
Dynablu	Pitted	-150	Pitted	-145	Pitted	-200
TiB ₂ -TiC	Very	-160	Moderate	-200	Very	-170
TiBCN	Hills & Pitts	-210	Pitted	-200	Pitted	-215
MoSi ₂ -SiC	Pitted	-200	Pitted	-210	Pitted	-200

same robotic arm as is used for the dunk tester, this will be done in order to ensure that each casting will be made in the same way.

The various trends for each of the experiments will then be correlated in order to find what mechanisms are responsible for the performance of a coating and aluminum alloy combination and therefore it will be possible to optimize a coating for each specific application.

5.0 Conclusions

The contact angle measurements performed thus far are not sufficient to determine the best coating for a specific die casting operation. However in conjunction with other tests and experiments it should be possible to determine the major mechanisms that control the performance of a coating. The system is very complex and reactive, so it is necessary for the tests to be self-

consistent in order to find a set of markers for determining the behavior and the mechanisms that caused the behavior of the coating.

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Processing of Coatings

Laser Peening: Current Status and Future Outlook

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Abstract

Laser peening has been in existence for over 25 years, but within the last five years it has graduated from the laboratory into an industrial production process, as a viable surface enhancement process. Within the last ten years, the process has been receiving increasing attention world wide in university laboratories to further the understanding of the process and its effect on metal properties, and in corporate laboratories for evaluation and development as an industrial

process to enhance fatigue and corrosion resistance. This paper presents an overview of the current status of the process followed with a discussion on the future outlook of the process.

1.0 Introduction

The phenomena forming the basis of the laser peen process were first reported in the late 1960's and early 1970's.¹⁻⁵ In 1974, its use as a means to benefit material properties was patented by Malozzi and Fairand.⁶

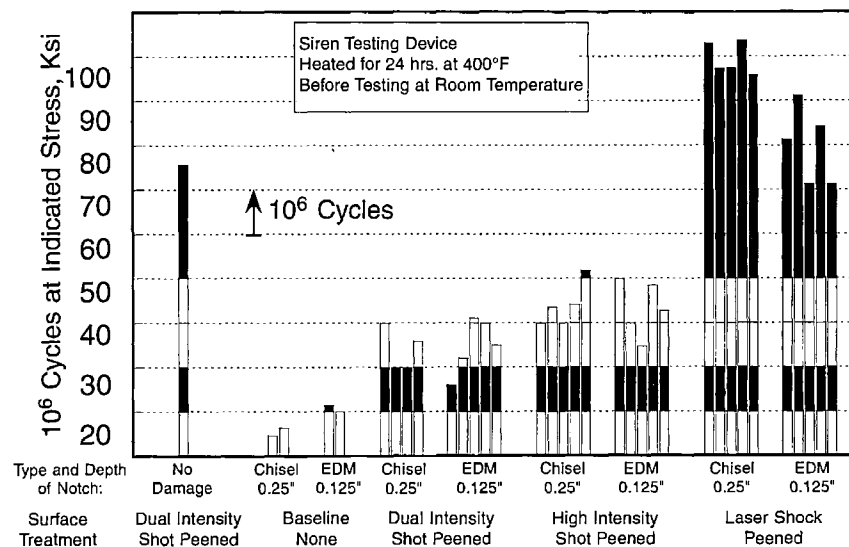


Fig. 1: Fatigue of Ti-6Al-4V alloy turbine engine fan blades showing a comparison of laser peening and shot peening for resistance to simulated FOD.¹⁵

Throughout the 1970's and early 1980's, the characteristics of the laser materials interaction and the material response to the induced shock waves were investigated.⁷⁻¹² This process is now known as laser peening.¹³

One of the current driving forces in using laser peening at this time is the dramatic increase in fatigue life and fatigue strength. The degree of improvement achievable with laser peening falls into two general categories. The most dramatic increases in fatigue strength are achievable in thin sections for through thickness cracks propagating into the structure from a stress riser associated with an edge, be it a hole, notch, corner, inclusion or other feature. Substantial increases in fatigue strength are also achieved in thicker structures laser peened on a single surface in the area of a stress riser or stress concentration. In thicker sections, the fatigue-critical regions laser peened for increased fatigue resistance are features which act as stress risers, such as holes in shafts or lugs, fillets in parts such as crankshafts, and teeth or roots in gears. Laser peening has been demonstrated to improve fatigue life, fatigue strength, and stress corrosion cracking resistance.¹⁴

The earliest investigation of the effect of laser peening on the fatigue behavior of thin sections was performed on F101 aircraft gas turbine engine fan blades.¹⁵ In this investigation, the effects of shot peening and laser peening surface treatments on increasing the resistance of the air-foils to foreign object damage (FOD) were compared. A patch near the bottom of the leading

edge of the blade was given one of three different surface treatments. One was a dual intensity shot peening representative of a typical process used on airfoils, another was a high intensity shot peening intended to drive residual stresses deep into the surfaces, and the third was laser peening. The location for treatment was selected as being an area of high tensile stress in the airfoil combined with having a high probability of being the location where FOD would occur. After treatment, the blades were notched to simulate FOD damage. Two types of notches were used: a 6 mm deep chisel notch having a plastic zone at the root of the notch and a 3 mm deep electro-discharge machined (EDM) notch having a recast layer at the root of the notch. After notching, the blades were fatigue tested in a siren testing device. The results of the fatigue testing are shown in Figure 1. The baseline, undamaged blade failed at 80 ksi. The notched, untreated blades failed at 20 to 30 ksi. The estimated average failure stress for the dual intensity shot peened blades was 35 ksi, and for the high intensity peened blades, 45 ksi. By comparison, the failure stress of the laser peened blades averaged about 100 ksi for the chisel notch, well above the failure stress of the undamaged blades, and at about the same level as the undamaged blades for the EDM notch. The laser peened blades had longer lives because the compressive residual stress in the leading edge of the laser peened blades slowed the growth rate of the crack to less than that for the undamaged blades. These results indicated that laser peening would enable a blade to continue to operate

safely, although damaged by FOD at some level above that previously viewed as cause for removal and repair of the blade. The laser peen process is being used in production on the first stage fan blades for the F101 and F110 engines for the US Air Force.

Since the mid 1980's, development of the laser peening process has taken two paths. One path has been the development of the process and hardware for industrial use to enhance the fatigue properties of metal parts. The other path has been academic pursuit of a deeper understanding of the physics of the process and broader investigation of its effect on material properties.^{16,17} The first path will be discussed here, first with a review of how the process works and what it does to the metal followed by a review of the current status and the future of the laser process.

2.0 Process Description

The lasers used for this process are Nd:Glass lasers capable of delivering up to 50 J per beam within 6 to 30 ns pulse. A laser beam produced is used to generate a high temperature plasma on the surface of the part. The part must be protected from this high temperature plasma with an overlay that is opaque to the laser beam, and the plasma must be confined to the surface of the part with a transparent overlay in order to generate a high-pressure shock wave that propagates into the metal.

2.1 Process Method

The process is performed by first applying the opaque overlay to the material surface to be treated, then covering the opaque overlay with the transparent overlay. The opaque overlay serves to protect the surface from direct thermal contact with the laser-induced plasma, and provides a consistent surface condition for interaction with the laser beam, independent of the actual material being treated. Direct contact of a metal surface with the plasma will, in most cases, form a thin melt layer on the surface of the metal, ranging from a surface discoloration to a surface melt layer up to 15 to 25 μm thick, depending on the laser irradiation conditions and metal properties. Opaque overlays can be of a variety of forms; paint, dry or wet, black tape, adhesive-backed metal foils, and metal foils have all been used with varying, but nominally equivalent, results in terms of the pressure pulses generated. The opaque overlay used in production is usually tape or paint and is currently applied by hand.

After placement of the opaque overlay, a transparent overlay, i.e., transparent to the laser beam, is placed over the opaque overlay. The transparent overlay serves to

confine the plasma generated at the surface of the opaque overlay against the surface being treated. The transparent overlay can be any material transparent to the laser beam, such as, mineral oil, water, quartz, glass, and clear plastics. The simplest and most cost-effective material and method of application is water flowing over the surface from an appropriately placed nozzle.

With the overlays in place, the laser pulse is directed through the transparent overlay and interacts with the opaque overlay as shown in Figure 2. The interaction consists of the laser energy being absorbed in the first few micrometers of the opaque overlay surface, vaporizing the material and forming a plasma. The plasma temperature rises rapidly through further heating from the incoming laser beam, but thermal expansion of the plasma is limited by the transparent overlay material. The pressure in the confined plasma increases rapidly, causing a shock wave to travel into the material through the opaque overlay, and outward through the transparent overlay material. The effective length of the pressure pulse will generally be two to five times the length of the laser pulse (10 to 40 ns), depending on the peak pressure of the pulse and the material properties. A nominal thickness of the transparent overlay is all that is required to maintain confinement of the plasma for a few hundred nanoseconds or less, until the process is over.

The shock wave traveling into the material being processed is the means for enhancing material properties. If the peak pressure of the shock wave is above the dynamic yield strength of the material, it will cause dynamic yielding as it travels into the material. The yielding of the material introduces tensile plastic strain in the plane of the surface, creating a residual compressive stress in the plane of the surface. As the peak pressure of the shock wave decreases with distance into the material, the total plastic strain associated with the shock wave decreases. This plastic strain gradient gives rise to the compressive stress gradient below the surface. Because the plastic strain produced by the shock wave extends much deeper than that produced by shot peening, the compressive residual stresses produced by laser peening also extend deeper into the material. The deeper residual stresses, in general, provide much more substantial property benefits.

The intensity of laser peening is related to two process parameters. One of these is the power density or irradiance, i.e., the power per unit area applied to the laser peened spot. As the power density is increased, the peak shock wave pressure increases, and this increases both the surface compressive stress and the depth of the compressive stress. The ability to continue to increase the power density to increase the magnitude and depth of the compressive stress is limited, however, by the onset of dielectric breakdown in the transparent overlay above

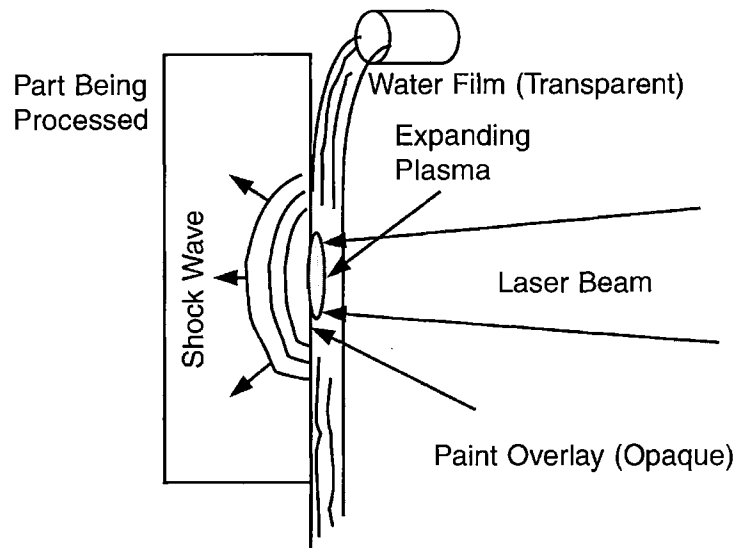


Fig. 2: Schematic of the laser peening process showing the overlays in place and the laser beam irradiating the material surface.

a certain power density. This limitation is overcome by applying more than one impact to a spot, i.e., laser peening the same spot more than once. These multiple impacts serve to drive the compressive residual stresses deeper into the material, and may also increase the surface residual stress somewhat depending on the laser peening conditions and material behavior.

Spot sizes for individual laser irradiated spots on a metal surface typically range from 3 to 10 mm or more in diameter, depending on the intensity of the treatment. An area larger than one spot is treated by a series of touching or overlapping spots to fill the area. Typically, this overlap of the spots is in the range of 10 to 30%. Higher laser peening intensities can be achieved by hitting a spot more than once, or by increasing the amount of overlap to effectively laser peen the same spot two or more times.

2.2 Process Effect on the Material

Laser peening produces residual compressive stresses in the surface of the part as does shot peening. However, the distribution of the residual compressive stresses below the surface is usually much deeper than it is for shot peening. Shot peening introduces residual stress by cold working the surface with metallic beads that impact the surface of the part. The cold working with this process typically extends to a depth of 0.1 mm below the surface. With laser peening, the residual stresses extend much deeper because as long as the peak pressure in the shock wave traveling through the material

is above the material's dynamic yield strength, it will cold work the material. The residual compressive stresses can extend up to 10 times deeper for laser peening depending upon the processing conditions chosen and the properties of the material, but in general the depths will range from 0.5 to 1.5 mm deep. In thin sections, up to nominally 3 to 5 mm thick, depending on the material, the residual compressive stresses can extend through the thickness under many conditions. By comparison, the depth of the residual stresses for shot peening will generally be 0.25 mm deep or less. In addition to the depth of the residual stresses, there is a notable difference in the shape of the residual stress profile observed between laser peening and shot peening. The maximum residual stress for laser peening is usually at the surface, and the residual stresses gradually decrease with increasing depth below the surface. For shot peening, the maximum residual stress is just below the surface because there is some relaxation due to high amount of cold work at the surface, thus creating a hook-shaped residual stress profile.

The magnitude and depth of the residual stresses can be varied by application of selected laser peening intensities. The effect of increasing power density is shown in Figure 3 for Ti-6Al-4V. Three different intensities, consisting of single impacts ranging from low to high power densities, were applied to one surface of a thick specimen (19 mm). The compressive stress on the surface increases with increasing laser peening intensity, from -100 MPa for the low intensity to -650 MPa for the high intensity. The total depth of the

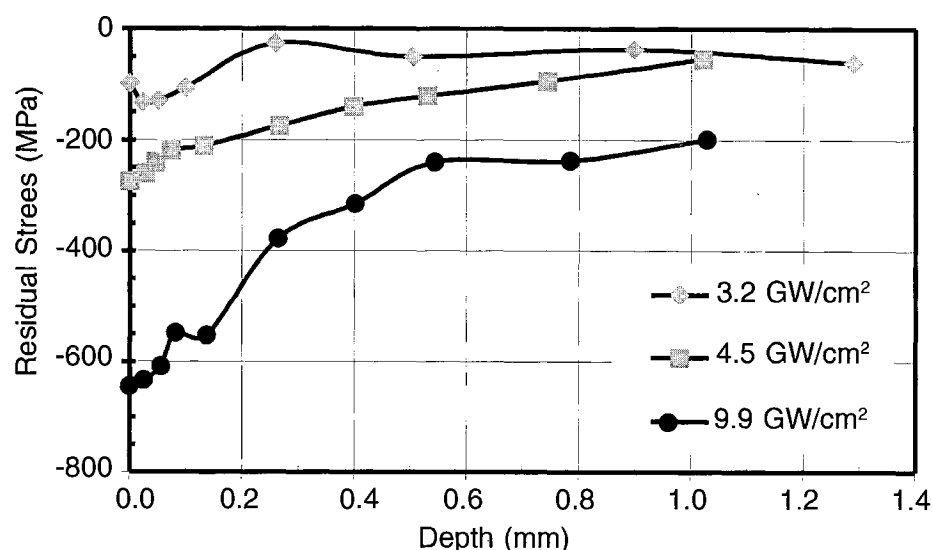


Fig. 3: Residual stress profiles for Ti-6Al-4V at increasing irradiances, one impact.

residual stresses also increases with increasing laser peening intensity. The lowest processing intensity produced compressive residual stresses near the surface only, the deeper compressive stresses for this intensity are probably close to baseline level. At the higher intensities, the residual stresses extend deeper below the surface and the magnitude of the stress increases. The deepest compressive stresses are achieved at the highest laser peening intensity. Here the compressive residual stress extends well beyond 1 mm, since the residual stresses are still in the range of -125 to -300 MPa at a depth of 1 mm. Steels, aluminum alloys, and nickel based alloys, for example, respond to laser peening in a similar manner to this alloy. However, the mechanical properties of the alloy, microstructure and laser beam processing conditions will influence the magnitude and depth of the residual stresses.

3.0 Current Status of the Laser Peening Process

The equipment to laser peen components in a production environment has been in use for over 4 years. Since that time, improvements have been made to the laser to include, for example, more robust laser components, increased repetition rates, improved diagnostics and the application of robotics to manipulate a part through the laser beam. The method for selecting the processing conditions for a component has not changed much during this time, requiring the application

of several processing conditions to a component and subsequent measurement of the residual stresses for each condition to select a final processing condition.

3.1 Equipment

The original development of laser peening and most of the current development and production processing has been performed using high energy pulsed Nd:glass lasers. This laser produces a wavelength of 1054 nm and provides a beam nominally 10 to 40 ns long having an energy of 50 to 200 J per pulse, depending on design. The repetition, or firing, rate of the laser depends on the laser design. Most current lasers used for laser peening are rod lasers having repetition rates from a shot every few minutes up to every few seconds, with a projected rate of 1.25 shots/second, or 1.25 Hz, in early 2002. Another laser concept under development, based on a combination of rods and slabs, has been projected to operate at up to 6 shots/second, or 6 Hz.¹⁸ However, the rate at which the laser can process parts is dependent on more than just the rate at which the laser pulses. Above about 1 Hz, there are numerous other issues that come into play. For example, the overlay material ejected into the beam path must be cleared away before the laser fires the next beam. Otherwise, the following beam will be seriously degraded by interacting with, and being blocked by, the debris from the previous shot. In addition to clearing the beam path, the overlay materials must be in place on the surface being processed, in exactly the same way each time, before the laser fires, to achieve

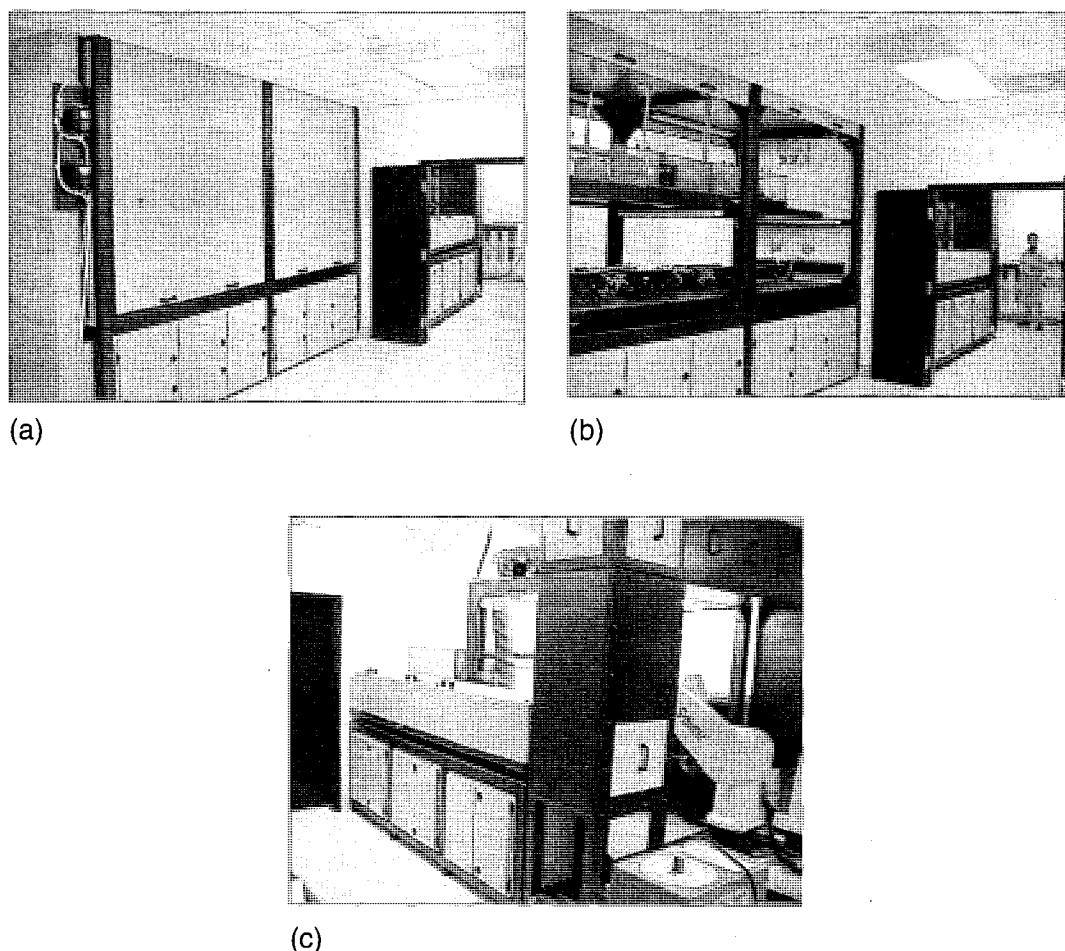


Fig. 4: Production development cell showing laser with (a) doors closed and (b) open, with the processing room and work cell in the background. Work cell (c) in the production development cell showing enclosed beam tables and the robot for manipulating parts inside the work cell during processing. The laser is on the far side of the back wall.

reproducible production processing. These issues must be resolved before higher laser repetition rates will be useful in production.

Figures 4a and b show a production prototype laser used for production development, and capable of small production runs. The beams go from the laser, through the wall, into the processing room visible through the doors in the background. The processing room contains the work cell. The laser can be configured for either two or four beams of 50 J each. The beams can be employed together, alternately in pairs, or separately in pairs, depending on the most efficient and effective way for processing a particular part. The work cell in the processing room is shown more clearly in Figure 4c. Here the laser beams are contained within the enclosures on the beam tables on three sides of the work cell. This gives great flexibility for directing the beams into the work cell in the desired direction. The beams are

stationary during processing, and the robot shown in the open side of the work cell manipulates the part being processed through the beam path during processing. A robot is used to provide the flexibility needed for developing laser peening for a variety of different parts, and for small production runs of different parts. With the robot, the work cell can process parts weighing up to 12 kg and a meter in maximum dimension. For production runs requiring high throughput, a parts handling machine tool specifically designed to minimize the time required to insert and remove a part for processing would replace the robot.

3.2 Selection of Process Conditions

Determination of the proper processing conditions for a particular component requires an evaluation of the component's service conditions, identification of the area

or areas that are prone to fatigue failure and then identification of potential processing conditions that may produce the desired residual stress profile. The number of potential processing conditions may be as high as 15 depending upon the alloy being evaluated. Titanium alloys, such as Ti-6Al-4V have received the most attention for laser peening, and there is a growing database of residual stress profiles for various processing conditions. Therefore, applications involving Ti-6Al-4V may not require the evaluation of as many potential processing conditions. Once the potential processing conditions are determined, they are applied to a component or representative coupons. The residual stress profiles are measured in each of these coupons by successive electropolishing to a specific depth and using x-ray diffraction techniques to measure the line broadening at each depth. The line broadening is representative of the residual stress. These residual stress data are used to down select to two or three candidate conditions. Each of these candidate conditions is applied to a sufficient number of components for component testing. In the component testing, service type loading conditions are applied to the component, and the data from these component tests are used to select a processing condition for production processing. Identifying a processing condition for an application is a very time intensive and costly process. Technology developments to reduce the time and cost involved in this step are being developed, but additional efforts are needed to help mature these technologies.

4.0 Future Outlook

The future of laser peening is promising. With each generation of laser systems, there are advancements, for example, in energy output, repetition rates, robust optics quality and process automation. Each of these advancements is increasing process efficiency and reducing production costs. In addition to the equipment developments, there are efforts to model the interaction of the laser beam with the processing overlays and to model the interaction of the shock wave as it travels through the material to predict the residual stress profiles.¹⁹ The emphasis of this effort is to get a component into production sooner by reducing the process selection cycle time.

4.1 Equipment

Significant technical advancements are being made to the laser peening equipment and process automation. In addition to increasing their power and repetition rate, they are being made more robust to allow them to operate

in a production environment, easier to maintain to minimize down time and automated to improve process consistency from part to part.

The first generation industrial production laser peening system is being designed and built on an Air Force Manufacturing Technology program. This factory floor ready, production Manufacturing Cell for laser peening will be operational near the end of 2001. The Manufacturing Cell will be housed in the module shown in Figure 5. In the far room, the module contains a production laser similar to that shown in Figures 4a and b having four beams of 50 J each operating at 1.25 Hz. The laser has a substantially modular design for all of its components to enable rapid replacement and minimum production downtime. In the middle processing room, there is a small parts work cell similar to that shown in Figure 4c. In the near processing room, there is a large parts cell containing a large robot for processing parts weighing up to 220 kg and having a maximum dimension of up to 2 meters.

As mentioned earlier, most areas to be processed require more than one laser shot, and these areas are built up by applying a series of successive overlapping shots. Also, with the manual application of the opaque overlay, every successive shot may not be applied since the opaque overlay surrounding the processed area may be damaged by the plasma or shock wave. One technology being developed to automate the application of the overlays is the Rapid Coater™ process, which applies and removes the opaque and transparent overlays during the processing. The apparatus shown in Figure 6 is for processing thin components such as airfoils. This apparatus, sequenced with the laser, applies a sufficient amount of opaque overlay to the surface for one laser pulse, covers this overlay with the transparent overlay, allows one laser pulse to be delivered, and then removes the spent overlays. The part being processed is then indexed to the next spot and the process is repeated until the desired area is processed. The unique feature of this process is that it allows the entire process area to be laser peened continuously eliminating the manual application and removal of the opaque overlay.

Other technologies being developed involve the application of different wavelengths of the laser beam. Frequency doubled Nd:YAG lasers have been used for laser peening under water.²⁰ Doubling the frequency decreases the wavelength by half, enabling the shorter wavelength beam to propagate longer distances through water with lower absorption of the beam energy. Currently, a copper vapor laser is also being evaluated for possible use for underwater laser peening, based on its high repetition rate and lower wavelength.²⁰ Excimer lasers have also been discussed because of their lower wavelength and higher repetition rate.¹⁶

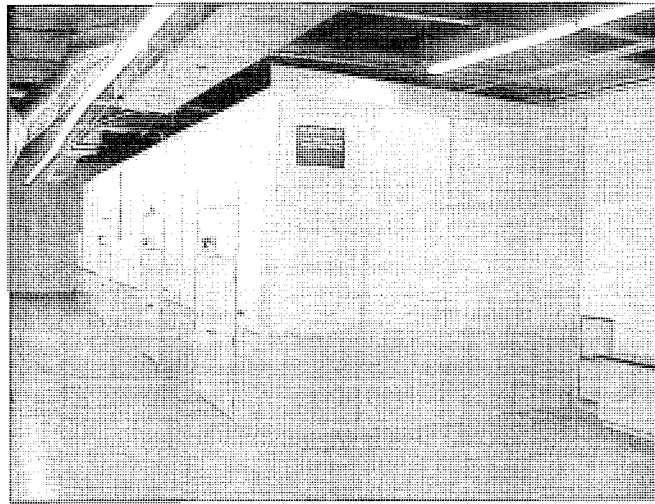


Fig. 5: Manufacturing production cell containing a laser, a small parts work cell, and a large parts work cell.

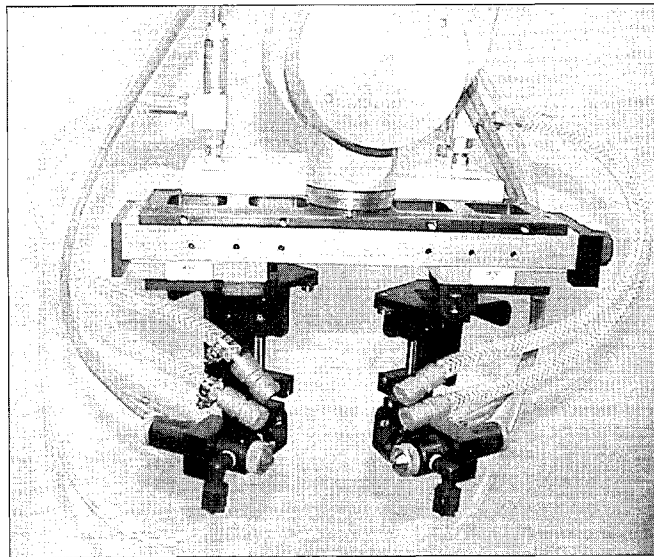


Fig. 6: Rapid Coater™ system for increasing through put and decreasing costs. The system is for processing thin components such as aircraft engine airfoils.

4.2 Selection of Process Condition

It would be beneficial from several points of view to be able to model laser peening. As with most processes, having a complete model of the process would save significant time and cost for developing new applications and for modifying and advancing the process. In addition, such a model would be invaluable in enabling close process control in production laser peening, saving time and cost of processing. To do this,

the ideal would be to have a complete model incorporating the laser beam parameters, overlay conditions and material properties, to enable the final outcome of the process in terms of material properties to be specified in terms of the laser beam and process conditions. This is obviously a long way from being realized. However, there are ongoing efforts to model accessible pieces of the process, the laser-materials interaction and the in-material effects, such as shock wave propagation and residual stresses.

4.2.1 Laser-Material Interaction Modeling

Much effort has been devoted to modeling the laser beam interaction with the surface of the material being laser peened, and by this means predict the peak pressure of the shock wave in terms of the laser beam characteristics.^{21,22} The general approach has been to use the “Piston Model” to predict the peak pressure and the pressure-time profile for a confined plasma. In this approach, the energy of the laser beam interacting with the plasma is partitioned into two parts, one of which is absorbed by the plasma and increases its temperature and thereby its pressure, and the other of which ionizes the plasma. The energy partitioning parameter is determined by calibrating the model with experiment. This model predicts $P_p \propto I^{1/2}$, in agreement with experiment, where P_p is the peak pressure and I is the peak irradiance of the laser beam. The energy absorbing partitioning parameter varies over a range of 0.2 to 0.5, and must be determined for changes in overlay and other processing conditions.

The laser material interaction is a complex phenomenon, made more complex for confined plasma conditions by the presence of the transparent overlay. For example, as the irradiance increases, a threshold for the onset of dielectric breakdown of the transparent overlay is reached. Dielectric breakdown of the transparent overlay begins with localized volumes within the overlay breaking down and absorbing the incoming laser energy, and ultimately reflecting the energy away from the material surface. As the irradiance level increases, this phenomenon becomes more severe, affecting larger volumes of the overlay and resulting in less and less of the beam energy reaching the material surface. The result is that with increasing irradiance, the peak pressure of the plasma steadily increases and the pressure pulse length remains nominally constant, until the nominal dielectric breakdown threshold of the overlay is reached. At irradiances above this threshold, the peak pressure no longer increases, but instead, scatters about a plateau level with increasing irradiance, while the pressure pulse length decreases.²³ Dielectric breakdown of the transparent overlay limits the peak pressure and pressure pulse length that can be achieved.

The dielectric breakdown threshold is not only irradiance dependent, but also time dependent. Hence, one way to partially circumvent the limiting effect of dielectric breakdown is to use a laser pulse with a very steep initial rise time, i.e., the irradiance rises very rapidly to its peak level. When this is done, a significant and useful amount of the beam energy will couple into the formation and expansion of the plasma before sufficient dielectric breakdown of the overlay occurs to limit the process. For current applications, laser pulses sliced on

the leading edge to produce a rise time of 1 to 5 ns are used for laser peening to enable higher peak shock wave pressures to be reached. At high irradiance levels, dielectric breakdown of the transparent overlay is a difficult process to control. It is a complex phenomenon, depending on the overlay material properties, and its quality, thickness, and surface characteristics.

As with most modeling efforts, the existing models for predicting the pressure pulse characteristics are useful, but significant modeling work and materials interaction characterization remain before the pressure profiles can be predicted on the basis of a complete modeling of all the physics and material characteristics involved in the laser-material interaction for confined plasmas.

4.2.2 Residual Stress Modeling

Modeling of the residual stress profiles is of significant interest because the residual stress profile developed by laser peening is dependent on the composition, microstructure and geometry of the part being evaluated, its surface condition and topology, and the pressure profile applied to the surface by the laser peening conditions used. Addressing all of these considerations when evaluating or optimizing the laser peening conditions for a new or modified application often adds time and cost to the evaluation unless there is closely allied experience available from a previous, similar application. Being able to make even a first order prediction of the residual stress profiles could substantially decrease the time and cost for evaluation and development of new applications.

Early modeling for residual stress prediction used an analytical model based on simple elastic-plastic material behavior and simplified pressure profiles.^{24,25} These efforts attempted to predict the magnitude of the surface residual stresses, the depth of the residual stresses, and the plastic strain gradient below the laser peened surface. The results were mixed due to the simplified material behavior models and pressure pulse shapes used.

More recent work utilized finite element modeling. It incorporated a more complex material model, including strain hardening and strain-rate sensitivity behavior. In addition, experimentally determined pressure profiles were applied to the model surface to represent different irradiances. A result for Ti-6Al-4V alloy is shown in Figure 7 for two peak pressures. The model was first calibrated to fit the residual stress profile measured (by x-ray diffraction) for 5.5 GPa peak pressure, then the stress profile for a peak pressure of 8.3 GPa was calculated independently, changing only the pressure profile for the higher pressure. The fit to the measured residual stress for 8.3 GPa peak pressure

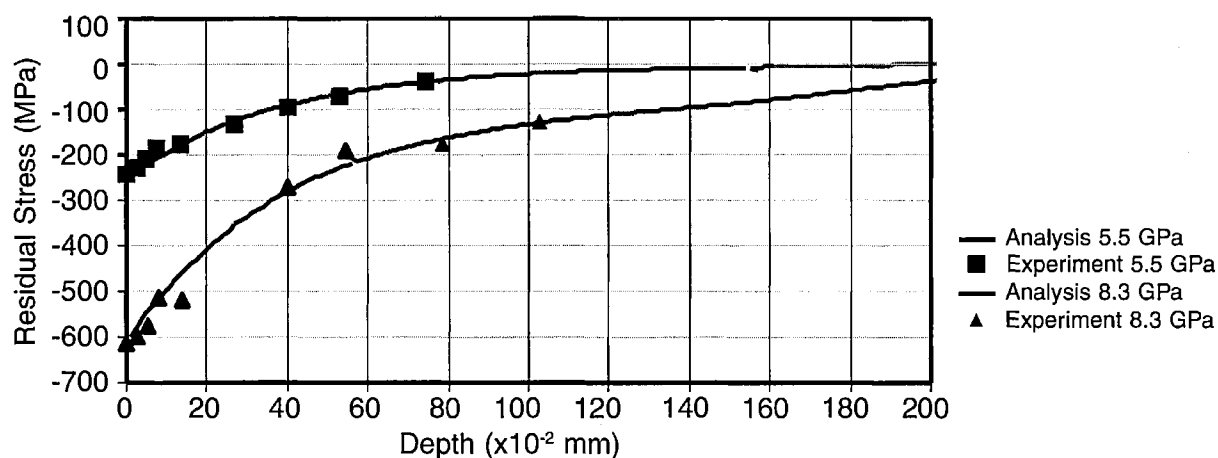


Fig. 7: Comparison of experimental and modeled residual stress profiles in Ti-6Al-4V alloy for two peak pressures.

was excellent. Calibration of the model to experimental results within the range of interest, and then using this model for predictions over the rest of the range is the most practical and probably most accurate means to achieve a useful model. This is because there is little or no actual material property data available in the strain rate range required for this type of modeling, i.e., 10^4 to $>10^6 \text{ sec}^{-1}$. Therefore, the approach adopted here was to modify the analytical material characteristics to make the predictions fit known experimental data, with the expectation that the model predictions would then be much better over the rest of the range. However, this approach does require that the model has to be independently modified for each alloy, and possibly for different heat treatments that change the alloy properties significantly.

Future efforts in to modeling the residual stress profile generated by a particular laser beam conditions will be to link the two models together, neither of which is complete and accurate. However, there has been some success in linking the confined plasma model to the prediction of the shock wave pressure profiles propagating within an aluminum target, using a simple elastic-perfectly plastic material model in a one-dimensional Lagrangian code.²³

5.0 Summary

The future of laser peening is one of continuing advancement in production applications, technology development and scientific research. The technology is being seriously pursued on these fronts in the U.S.A. and Europe, particularly in France, Japan, China, and Australia. The biggest barrier to wider application in

manufacturing has been the relatively high cost, and to a lesser extent, the slow throughput. This situation is rapidly changing with the advent of higher repetition rate lasers and advances in processing technology that can take advantage of the higher laser repetition rates. Much of this recent manufacturing oriented development for increasing throughput and decreasing cost has been supported by the Air Force's AFRL Materials and Manufacturing Technology Directorate. The variety of applications being evaluated for potential production continues to increase. From several production applications at present, this number is expected to triple or quadruple over the next five years.

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Iron Aluminide Based Coating Deposited by High Energy Density Processes

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Abstract

Iron aluminide based intermetallics such as Fe_3Al and FeAl are candidate materials for high temperature applications due to their excellent sulfidation and oxidation resistance, low density, good wear and erosion resistance and potentially lower cost. However, the usage of the Fe_3Al and FeAl based intermetallics for structural application has been restricted due to their inherent brittle behavior as they could not be fabricated into useful shapes. In the present work, it has been suggested

that a surface layer of Fe-Al intermetallic on steel components could address the fabrication problem. Fe-Al surface layers can be synthesized by driving the self-propagating exothermic reaction between aluminum and the underlying steel substrate using high energy density processes such as Pulsed Electrode Surfacing (PES) and Laser Surface Engineering (LSE). The preliminary results obtained from the experiments by these two techniques have been presented. An optimum control on process parameters could result in near net shape parts of plain carbon steel but with Fe-Al surface properties.

1.0 Introduction

Iron aluminide based intermetallics such as Fe_3Al and FeAl are candidate materials for high temperature applications due to their excellent sulfidation and oxidation resistance, low density, good wear and erosion resistance and potentially lower cost.¹ These unique properties of iron aluminides allow them to be used for several applications, which include high temperature structural material in fossil fuel energy plants, oxidation shields for tubes and incinerators in power plants, furnace fixtures and fasteners, hot gas filters, heating elements and components for molten salt application.¹ The potential success of iron aluminides would result in replacing several stainless steel components, which is beneficial for conserving strategic metals like Cr.

However, the usage of the Fe_3Al and FeAl based intermetallics for structural application has been restricted due to their inherent brittle behavior as they could not be fabricated into useful shapes such as plates and tubes.^{1,2} The lack of ductility in iron aluminides has been primarily attributed to *complex crystal structure* and *hydrogen embrittlement*¹⁻³. These intermetallic compounds possess a long range ordered superlattice structure, which reduces dislocation mobility. Consequently, the applied stress needed for deformation by dislocation slip is greater than that needed for cracking resulting in brittle fracture.¹ Secondly, moisture present in the environment reacts with iron aluminide to form high fugacity atomic hydrogen that rapidly penetrates to crack tips and causes significant embrittlement.³ Though several attempts have been made to improve the ductility of iron aluminides by alloying,⁴ thermomechanical treatments,^{1,2} coating and weld overlay⁵⁻⁶ and powder metallurgy route of processes,⁷ they are still far from being used as commercially available structural materials.

In the present work, it is proposed that high energy density processes such as Pulsed Electro Surfacing (PES) and Laser Surface Engineering (LSE) can be employed to synthesize iron aluminide-based intermetallic coatings on plain carbon steel surfaces. A surface layer of Fe-Al intermetallic is synthesized by driving the self-propagating exothermic reaction (SHS) between aluminum and the underlying steel substrate by using two surface engineering techniques mentioned above. Such high energy density surface engineering techniques can further be adopted to fabricate near net shape parts of plain carbon steel but with Fe-Al intermetallic surface properties. The preliminary results indicate that the Fe-Al based intermetallic layer can be successfully synthesized by these techniques. Precise control of the processing variables of these two

techniques can further tailor the properties of the surface Fe-Al intermetallic layer.

1.1 Pulsed Electro Surfacing

Pulsed Electro Surfacing (PES) utilizes high current electrical pulses of short duration to modify the metal surface. A high current, short duration pulse via discharge capacitance and voltage circuit results in melting the electrode and depositing the material on the substrate.⁸⁻¹² This process is very similar to an arc welding process with the exception of little total heat input. Hence, the PES process is also described as a micro welding process. The primary requirement for the electrode material is that it should be electrically conductive be melted in an electric arc. The consumable electrode having a positive polarity is brought close to the substrate, which has a negative polarity (Figure 1). This leads to generation of the spark and intense heat. The intensity of the spark is directly proportional to the voltage across the gap between the electrode and the substrate, the amount of current and the duration of current flow, which is known as pulse time.

$$\text{Energy of the Spark (E)} \propto \frac{\text{Voltage (V)} \times \text{Current (I)} \times \text{Time (t)}}{1}$$

The energy of the spark in turn decides the amount of electrode being deposited and the bond strength between the deposited material and the substrate. The dielectric medium which could be air, argon or any other environment provides a path for the discharge plasma and the region between the electrodes remains ionized, enabling continuous flow of current. The applied voltage should be higher than the discharge voltage which is dependent on the choice of the electrode-dielectric system. At present, most researchers assume that major erosion of the electrode in an arc discharge is thermal¹² and depends upon thermophysical properties of the electrodes. Thus, a suitable choice of processing parameters will lead to incipient melting of the electrode tip, and material transfer will occur through the discharge plasma. It has been successfully argued that material transfer from electrode tip to substrate occurs in the liquid state.^{9, 12} A molten droplet forms at the end of the consumable electrode and is accelerated towards the substrate by the discharge plasma. These droplets impact the surface with a splash appearance leading to a rough and thick coating surface.

The main advantage of the PES process is its ability to apply metallurgically bonded coatings with low heat input to the substrate at ambient temperature. Since the process requires very little total heat input, it reduces the heat affected zone (HAZ) and minimizes the chance

of thermal distortion.¹³ Substrate material acts as a huge heat sink leading to rapid solidification of the molten pool. This results in an extremely fine-grained coating of high density, hardness and strength. Coatings deposited using the PES process are used for several applications in the nuclear, fossil and geothermal energy environments, high temperature turbine coatings, industrial cutting tools such as milling cutters and drills, wear resistant surfaces on large agricultural and textile and pharmaceutical equipment and for modern sport equipment.¹⁰⁻¹⁴ In the earlier studies of PES process, ultrahard ceramic coatings have been deposited using an electrode of the same material as that of coating.¹⁰⁻¹⁶ However, in the present study an attempt has been made to synthesize intermetallic coating using self propagating reactive synthesis (SHS) during the PES process.

1.2 Laser Surface Engineering (LSE)

Laser surface engineering (LSE) is a non-equilibrium synthesis involving techniques such as surface alloying, heat treatment, composite layer formation and texturing (Figure 1). In this process, a preplaced powder precursor or simultaneously injected powder is melted along with a thin layer of the substrate to produce a laser melt zone of desired composition. High cooling rates of 10^3 to 10^8 K/sec associated with the process results in formation of novel, metastable phases and a variety of microstructures by exceeding the solid solubility limit beyond the equilibrium phase diagram.¹⁷ In contrast with the PES technique, a laser beam is a coherent energy source with low divergence and high energy density.¹⁵ Most of the laser beam energy is consumed in interacting “directly” with the precursor and the substrate resulting in an intense rise in temperature and heat. A very small amount of laser beam energy is used in the interaction with the environment above the substrate. Hence, energy transfer in the LSE process is much more efficient than the PES process resulting in formation of a large melt zone and significant heat affected zone. Energy transfer from the laser beam to the substrate also depends upon the material properties such as absorptivity and thermal conductivity.¹⁸ The interaction of the laser and metal substrate is explained by the free electron model of materials. Materials such as metals have free electrons which oscillate with high energy leading to a plume/plasma formation. A suitable choice of laser and material system decides the frequency of such plasma which in turn is associated with the absorption coefficient of that irradiated metal. In the present case, the AISI 1010 steel surface has good absorption for Nd: YAG laser radiation which assists in formation of a melt zone.¹⁹ Figure 1 and Table 1 provide

a direct comparison between the PES and LSE processes. In the present study, a FeAl based intermetallic coating has been synthesized on 1010 steel substrate with self propagating reaction synthesis approach.

2.0 Experimental Procedure

2.1 Pulsed Electrode Surfacing (PES) Process

Coupons of AISI 1018 steel of dimensions $25 \times 10 \times 3$ mm were mechanically polished on emery paper of grit 240 and then rinsed with acetone. An aluminum electrode (99.9% purity) was used to deposit a coating on these steel coupons. Deposition was done using a hand held electrode gun in localized nitrogen (N_2) environment provided around the region of deposition at room temperature. Pulsed electrode deposition was carried out at 100 volts and a spark time of 10 μ s. The discharge capacitance used for the PES process was 300 μ F with a current of 50 amperes.

2.2 Laser Surface Engineering (LSE)

Commercially available A 359 aluminum powder (containing ~12 wt.% Si) obtained from CERAC, Milwaukee, WI was used as the precursor for this study. The average particle size range was 10 ± 5 μ m. Thin plates of AISI 1010 steel of size $75 \times 150 \times 3$ mm were cleaned using sand blasting. The precursor of aluminum powder was sprayed on these coupons using a spray gun. The preplaced powder bed had an average thickness of 100 ± 10 μ m. Sprayed coupons were dried at 70°C for 1 hour prior to laser processing. A 2.5 kW Rofin Sinar CW 020 continuous wave Nd:YAG laser (1.06 μ m wavelength) equipped with a fiber optic beam delivery system was employed for reaction synthesis of an FeAl based intermetallic coating. In the present study, the laser beam power and traverse speed were kept constant at 1.5 kW and 33 mm/sec respectively. Thus, the approximate energy density input for LSE is 10 MW.m^{-2} which is about two orders of magnitude higher than PES (0.1 MW.m^{-2}) process.

2.3 Characterization

Microstructural characterization was performed using a Nikon EPIPHOT 200 optical microscope and a JEOL model 5800LV scanning electron microscope (SEM). Metallographic samples were prepared by polishing on a Buehler TEXMET 2000 cloth during initial stages of polishing. The scanning electron microscope coupled with EDAX was employed for

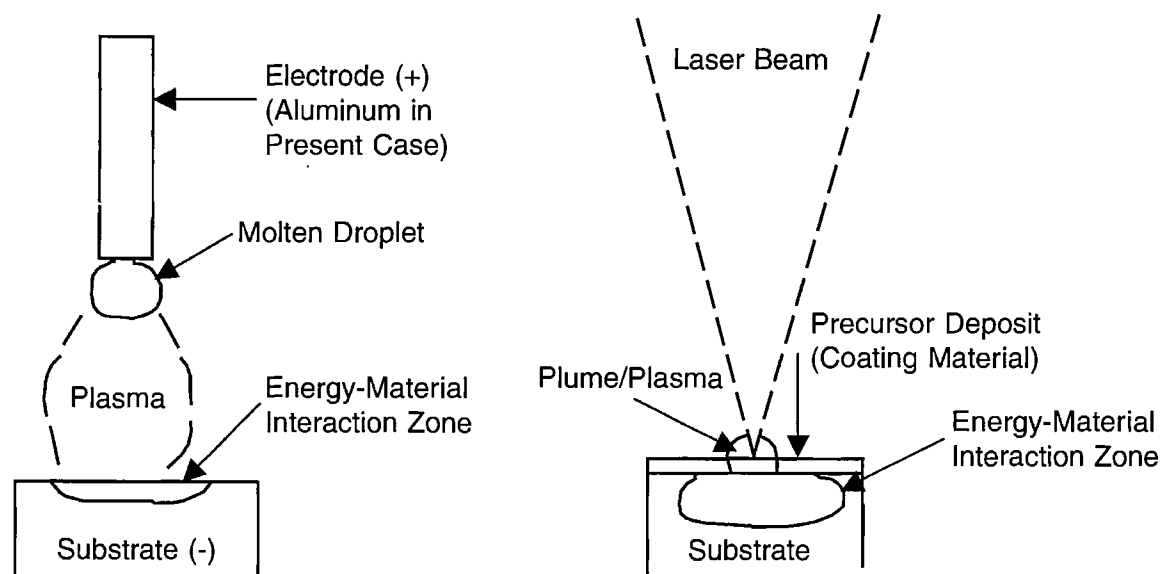


Fig. 1: A schematic drawing illustrating the “physical process” of Pulsed Electrode Surfacing (PES) and Laser Surface Engineering (LSE).

Table 1. Physical Characteristics of the PES and LSE Techniques

Features	PES Process	LSE Process
Energy/Beam Source	Incoherent	Coherent Beam with Less Divergence
Interaction with Medium	Significant Interaction with Dielectric Atoms Present Between the Electrode and the Substrate	Minimal Interaction with the Dielectric Atoms Present Above the Substrate
Energy Transfer to the Substrate	Indirect Transfer Through Molten Electrode Droplet and Radiation from the Dielectric Atoms	Direct Interaction with the Substrate Forming a Plume/Plasma
Approximate Energy Density Input (MW.m^{-2})	0.10	10

chemical characterization of the coating and interface. Structural characterization for phase(s) identification was carried out on a Philips Norelco x-ray diffractometer with CuK_α radiation operating at 30 kV and 40 mA. Microhardness measurements were performed on a Buehler Micromet II microhardness unit with a load applied for 15 seconds. The normal load applied was varied to obtain the microhardness from various microstructural features.

3.0 Results and Discussion

3.1 Mechanism of Fe-Al Intermetallic Coating Synthesis

Self-propagating high temperature reaction synthesis (SHS) is the basis of Fe-Al intermetallic

coating formation by PES and LSE. These techniques utilize an exothermic reaction between the different elemental species to synthesize desired compounds. Such a process comprises of has two steps:

- Ignition of reaction and
- Propagation of the reaction.

An external heating source, which could be a laser beam, electric arc, radiant flux, resistance heating etc. ignites the reactants and then induces the chemical reaction inside them. During this process, the reaction is initiated by heating the reactants (Al and Fe) from ambient temperature (T_0) to ignition temperature (T_{ig}) and reaching a maximum or combustion temperature (T_c). Figure 2 shows the enthalpy of formation of Al containing intermetallics. Formation of Fe_3Al and FeAl is exothermic in nature^{1, 20} as shown in Figure 2 and equations (1) and (2).

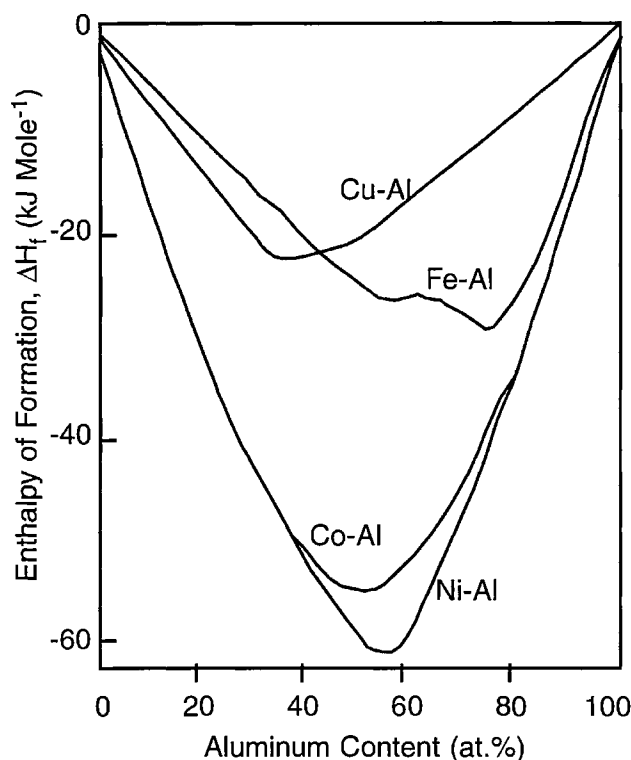
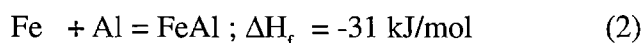
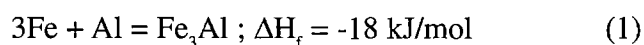


Fig. 2: Enthalpy of formation of various Al-based intermetallic systems.¹



In such techniques, the exothermicity of the combustion synthesis plays an important part in the stability of the reaction and the combustion temperature achieved, which consequently affects both the microstructure and the properties of the synthesized product. In the present work, high energy density sources (electric arc in the case of PES and laser beam in the case of LSE) ignite the exothermic reaction between the aluminum electrode or precursor layer and the underlying steel substrate to form an Fe-Al intermetallic based coating.

3.2 Fe-Al Synthesis by PES

Figure 3 shows the x-ray diffraction spectrum of the coated surface. Fe_3Al is the major phase present in the coating. However, few peaks of non-stoichiometric phase(s) such as Fe_xAl_y are also indicated. During the PES process, the consumable Al electrode with positive polarity is brought close to the substrate having negative polarity, which results in arc formation of microsecond duration. Though temperature measurement during arc formation is a debatable issue, it has been successfully

argued that material transfer from electrode tip to substrate occurs in the liquid state.^{9, 12} Hence, it is reasonable to assume that arc temperature is higher than melting point of Al. Liquid Al drops impinge on the 1018 steel substrate and forms the Fe-Al based intermetallic. Formation of Fe_3Al (equation 1) is an exothermic reaction, which occurs after the melting point of Al is achieved.²⁰ Several researchers have indicated that combustion starts as soon as liquid appears, usually close to the melting point of Al (660°C) or the lowest eutectic temperature (640°C).²⁰⁻²¹ Once a small amount of liquid Al is formed, it causes a rapid increase in the reaction rate resulting in heat evolution, which further increases reaction rate leading to synthesis of Fe_3Al within a few seconds.²⁰ A similar reaction mechanism occurs during the PES process where the liquid Al droplet reacts exothermically with the steel substrate to form an Fe_3Al based intermetallic coating. EDS analysis suggests 23-28 at.% Al within the coating region. Such composition is further indicative of Fe_3Al formation within the coating.²⁰ Microhardness values within the coating, interface and substrate are shown in Figure 4. The coating has a higher hardness (594 Kg.mm^{-2}) which is attributed to the presence of the Fe_3Al intermetallic. FeAl based intermetallics have a hardness¹ in the range of 380-620 Kg.mm^{-2} . Figure 5 shows a SEM micrograph

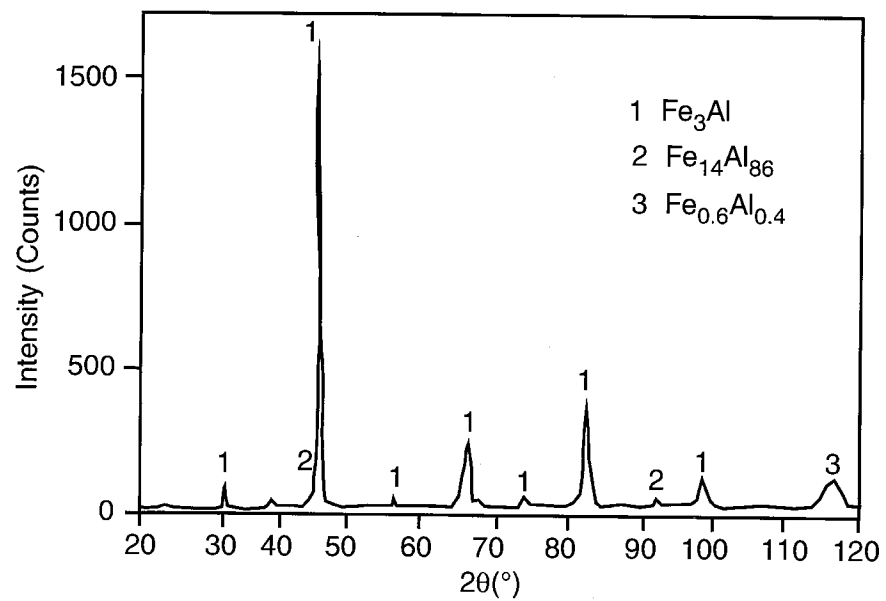


Fig. 3: X-ray diffraction spectrum of PES coated Fe-Al surface.

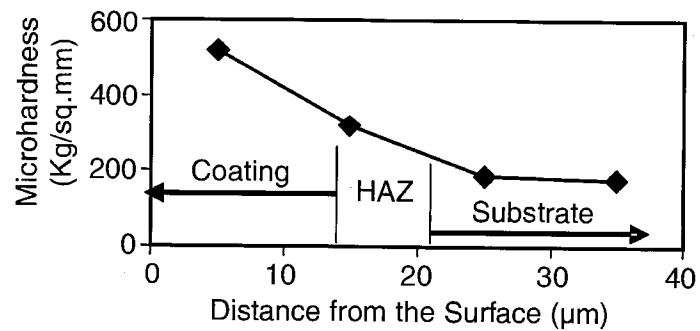


Fig. 4: Microhardness variation within the PES coating, interface and substrate.

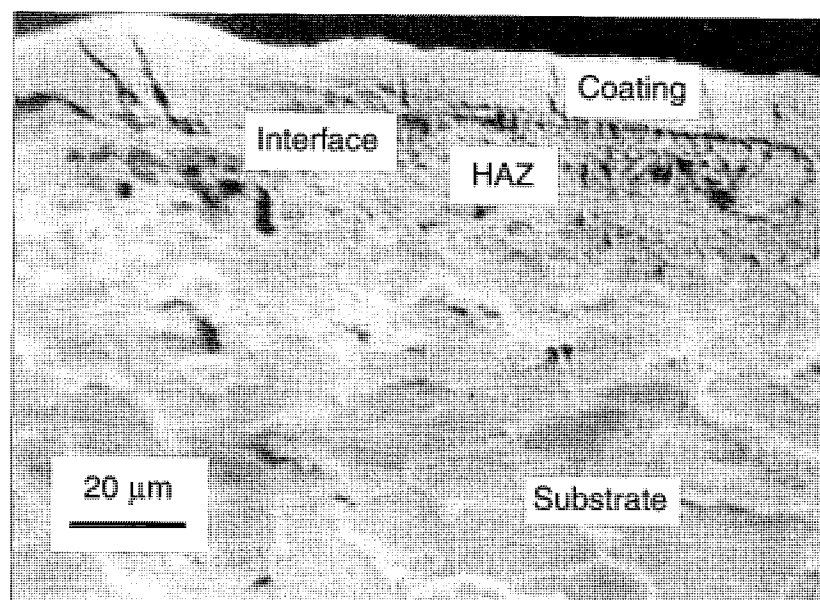


Fig. 5: Cross-sectional view of the PES coated surface.

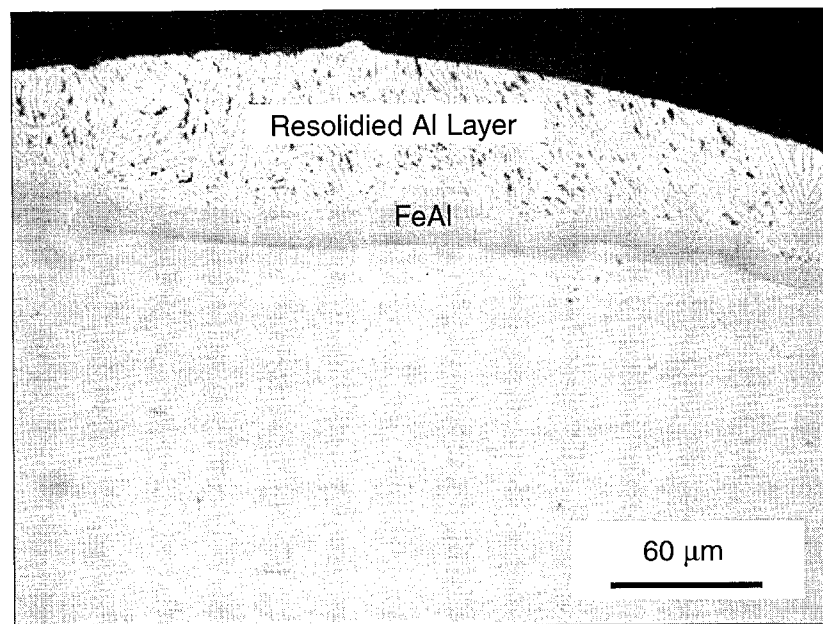


Fig. 6: Optical micrograph of the cross-section of the LSE surface.

of the cross section of the coating produced by the PES process. The coating is metallurgically bonded and adherent to the substrate. There are few vertical cracks within the coating, which could be due to shock waves experienced during the self propagating reaction synthesis. Cracking can be minimized by controlling the process variables such as arc frequency and current.

3.3 Fe-Al Synthesis by LSE

Figure 6 shows an optical micrograph of the laser surface engineered layer on the 1010 steel substrate. It appears that the 100 μm precursor layer was too thick for the desired SHS reaction. Two layers with the topmost layer having a thickness of $\sim 80 \mu\text{m}$ and the lower layer of 15-20 μm thickness are distinctly shown in Figure 6. The unreacted and excess aluminum (top 80 μm) has been melted and resolidified. The incident laser beam hits the aluminum precursor layer and ignites the reaction by melting the aluminum and underlying steel. The topmost layer of resolidified Al layer contains fine Si dendrites. In LSE, the rapid solidification process results in considerable supercooling which caused realignment of Si as fine and elongated dendrites. These dendrites are oriented upwards toward the surface which is in accordance with the cooling direction. The lower 15-20 μm thick layer is FeAl with some vertically aligned fine cracks. Figure 7 is a higher magnification SEM micrograph of the same region, which distinctly shows Si dendrites in the

topmost layer and FeAl layer below. EDS spot analysis from the lower layer indicates 47% Fe, 48% Al, and 5% Si (all percentages are atomic). Such stoichiometry indicates synthesis of the FeAl phase. Solubility of Al in Fe is higher ($\sim 48 \text{ at.}\%$) for LSE than for PES ($\sim 28 \text{ at.}\%$). This behavior is attributed to the higher energy density input of the laser beam compared to pulsed electrode surfacing.¹⁵ Moreover, the mode of energy transfer is more efficient for laser beam in comparison to pulsed electrode surfacing.¹⁵ Figure 8 shows the microhardness variation in the top layer of resolidified Al, FeAl layer and the substrate material. There is a gradual change in the microhardness values across the coating to the substrate. Microhardness values in the top layer are low with an average value of 150 Kg mm^{-2} , while it sharply increases to 482 Kg mm^{-2} in the FeAl layer. Microhardness at the interface of the FeAl and steel substrate is 284 Kg mm^{-2} due to the presence of the heat affected zone, whereas it decreases to 208 Kg mm^{-2} in the unaffected 1010 steel substrate region. In addition, the relative difference in the size of microhardness indentations in Figure 7 shows the hardness variation in FeAl layer and the substrate. A high hardness value in the thin layer corroborates synthesis of FeAl. As mentioned earlier, FeAl based intermetallics have hardness in the range of 380-620 Kg mm^{-2} .

Synthesis of FeAl based intermetallic coating by the LSE technique can be further optimized by controlling the several processing variables which

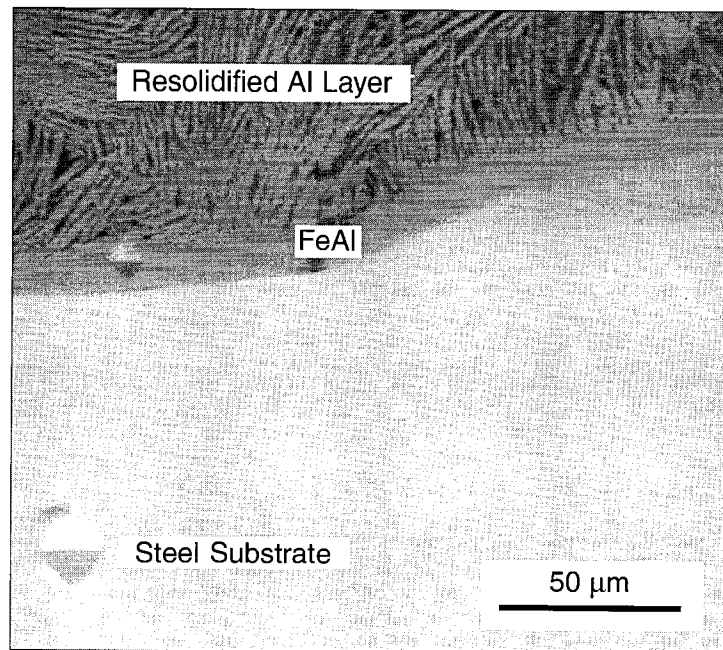


Fig. 7: Scanning electron microscope (SEM) micrograph of the cross-section of the LSE surface. Microhardness indentations of various sizes in FeAl layer and 1010 steel substrate indicate relative hardness.

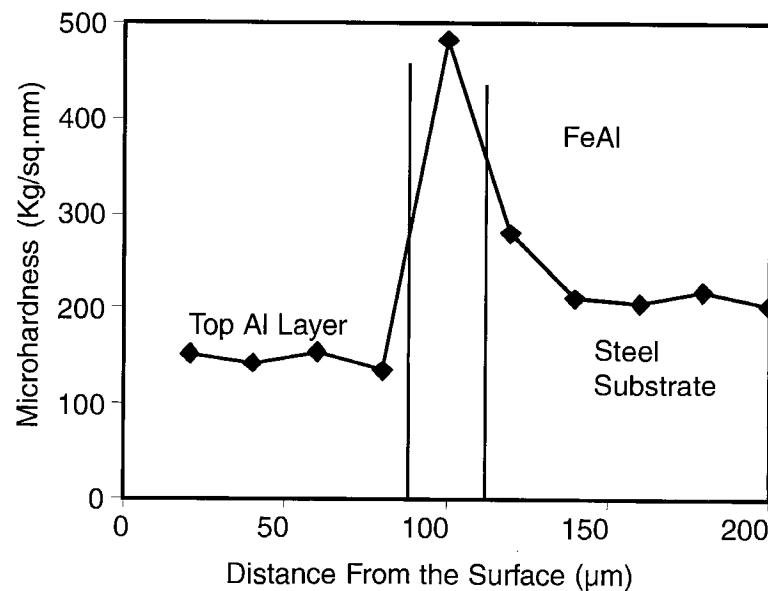


Fig. 8: Microhardness variation within the LSE coated surface, interface and substrate.

include thickness of the precursor layer, laser power and traverse speed. Shen et al. have studied the synthesis of a NiAl intermetallic by laser ignition.²⁶ In their study, it has been postulated that ignition delay time, t to start the exothermic reaction can be controlled by varying the material and processing parameters shown in equation (3).²¹

$$t = \frac{\pi \lambda \rho C (T_{ig} - T_0)^2 S^2}{4 A^2 P^2} \quad (3)$$

It indicates that ignition will be easily initiated when the raw material (aluminum in this case) has a low thermal conductivity (λ), low specific heat (C), low density (ρ) and a high absorptivity (A) for the laser beam.

A high flux density laser beam (P/S) should be used. T_{ig} indicates ignition temperature, which is the melting point of Al whereas T_0 is the ambient temperature. It can be easily inferred from equation (3) that by controlling the laser processing variables (laser flux density) and the ignition time, the self propagating reaction synthesis can be controlled for several material combinations. Many microstructures of the Fe-Al intermetallic coating could be synthesized by varying the ignition delay time. Such an approach in future research could provide correlation between the processing variables on the evolved Fe-Al microstructure.

4.0 Conclusions

It has been successfully shown that FeAl based intermetallic coatings could be synthesized by high energy density processes such as Pulsed Electrode Surfacing (PES) and Laser Surface Engineering (LSE). The exothermic nature of the reaction has been utilized for self propagating reaction synthesis of Fe-Al based intermetallics. Fe_3Al phase formation occurs in the PES process whereas the FeAl phase is obtained during the LSE process. However, a precise control of processing variables is required to synthesize a homogeneous, adherent and crack-free iron aluminide coating on steel surface.

5.0 Acknowledgments

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Interfacial Adhesion of Laser Clad Functionally Graded Materials

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Abstract

Specially designed samples of laser clad AlSi40 functionally graded materials (FGM) are made for evaluating the interfacial adhesion. To obtain the interfacial bond strength notches are made right at the interface of the FGMs. *In-situ* microstructural observations during straining in an FEG-ESEM (field emission gun - environmental scanning electron microscopy) reveal different failure modes of the FGMs and substrate. Mapping of strain fields using digital imaging correlation shows a gradual transition of deformation over the

interface region and softening effects in the heat-affected zones of the FGM tracks. The strengthening of the FGM is dominated by the size of the Al-halos around the particles, in accordance with a dislocation pile-up model.

1.0 Introduction

The term 'functionally graded materials' (FGMs) is now widely used by the materials community for a class of materials exhibiting spatially inhomogeneous microstructures and properties. Graded materials in

themselves are not something new, but what is exciting about them is the realization that gradients can be designed at a microstructural level to tailor specific materials for their functional performance in particular applications. Therefore, a possible approach for eliminating the sharp interface present in laser surface cladding (LSC) is to introduce the concept of FGMs into the design of coating structure. In general, the performance of a coating depends in many applications on the bond strength between coating and substrate material. Consequently, it is essential to quantify the adhesive strength of a coating so as to guarantee the functionality of the material system. The actual strength of a coating/substrate interface is governed by a number of variables such as, the elastic mismatch between dissimilar materials, the possible plastic flow, the residual stresses and defects introduced into the coating, the substrate and near the interface. Actually, it is already difficult to find a generally accepted definition of adhesion between coating and substrate that takes into account the complexity of the effects of the microstructure, external loading and the environment. Several methods exist to determine the interfacial bond strength of coatings, such as the direct pull test, bend test, scratch and indentation tests, impact test, cavitation test and Rockwell imprint test. However, none of these tests is accurate enough to provide detailed information about adhesion properties in various types of coatings. Indeed, they even show contradictory results on the same type of coatings, as reported by Ollendorf and Schneider.¹ Nevertheless, among these various tests direct pull and bending tests are frequently used. In the direct pull test as defined in the ASTM D4541 and ASTM C633-79, failure often occurs at the location of the polymeric adhesive that is applied on top of the coating. Further, although four-point flexure test is suitable to evaluate the adhesive strength between the ceramic/metal interfaces ($\text{Cr}_2\text{O}_3/\text{steel}$) produced by laser processing,² this method may not work on systems with a very strong interface. With such an interface the pre-crack propagates directly across the interface, and no delamination occurs between the coating and the substrate.

It is well known that laser surface engineering may form a strong bond between a coating and the substrate material.³⁻⁵ In particular, we have recently produced functionally graded materials (FGMs) by laser cladding,⁶ in which a progressive change in both microstructure and related properties is achieved as a function of depth. The strength of such an interface in FGMs cannot be measured by a direct pull test on the specimen with a clamp attached to it because the interface is stronger than available adhesives. This paper concentrates on a specially designed specimen so as to allow a direct pull

test on the as-coated samples without the necessity of any attachment. Furthermore, Digital Image Correlation (DIC) technique is used to study the deformation behavior of both the FGM and the substrate near the interface during tensile tests. It is applied to examine whether or not a gradual transition in mechanical properties is realized between the laser-clad FGMs and the substrate.

2.0 Experimental Details

The specimens are fabricated by a one-step laser cladding technique, in which AlSi-based FGMs of 1.5–2.5 mm thickness are coated on an Al-alloy substrate.⁶ The laser-clad samples are (see Figure 1a), such that the FGM track just fills in the grooved substrate as a whole. Tensile specimens are then cut from the clad samples by spark erosion (see Figure 1a). After finishing a tensile specimen, the FGM track looks like a weld located at the center of the specimen and perpendicular to the tensile loading direction, as illustrated in Figure 1b. This configuration ensures that the interfaces between the FGM track and the substrates on both sides are under an applied load during the tensile test. After further machining of the test specimens, a notch can be made right at the interface. The notches have a hyperbolic cross section.

In this work a Rofin CW020-type 2 kW Nd:YAG laser is applied to produce the FGM coating tracks. The focal length of the lens is 100 mm, but the lens is operated at a defocusing distance of +9 mm with a $\varnothing$ 2.5 mm spot on the surface of the substrate. A numerically controlled x-y table executes the movement of the specimen. The powder feeder apparatus is a Metco 9 MP instrument. The details of the setup for laser cladding are given in reference.⁶ The processing parameters are 2000 W laser power, 7 mm/s scanning speed and 10–30 g/min powder feeding rate. The shielding gas is helium with a flow rate of 0.167 l/s.

Aluminum-based substrates are cut from a cast piston of a commercial AlSi-alloy with a nominal composition (wt.%): 11.94 Si, 1.19 Mg, 1.08 Cu, 0.89 Ni, 0.62 Fe, 0.27 Mn and the balance being Al. Two grooves with 2.2 mm open width and 1.5 mm depth are made by electric discharge cutting on the flat substrates 100 × 50 × 10 mm³ in size. The coating material is Al-40 wt.% Si alloy powder with a particle size of 50 to 125 μm .

According to the ASTM standard A370, the tensile specimen dimensions are modified in order to fit the tensile stage inside the chamber of a scanning electron microscope (SEM). Specimen dimensions are length 20 mm and width 6.25 mm. The thickness of the specimens varied from 0.9–1.0 mm. All the FGM specimens are naturally aged for one month before tensile tests.

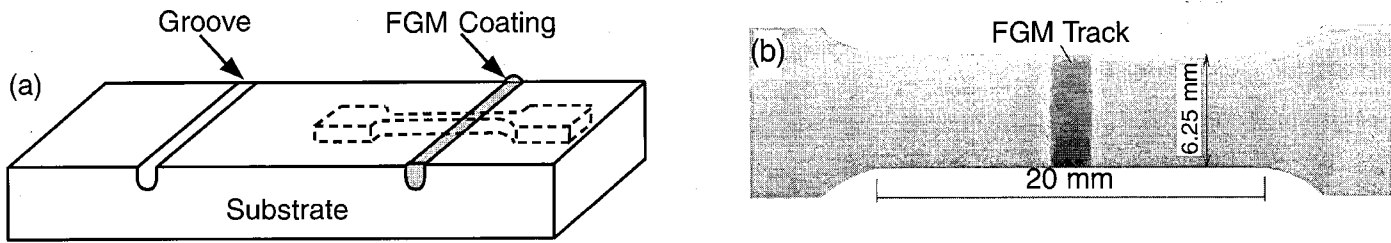


Fig. 1: (a) Sketch of sample preparation and (b) top view of a prepared tensile specimen without notches.

The specimens are loaded using the special stage (Kammrath & Weiss GmbH) mounted inside a Philips E-SEM XL30 FEG environmental SEM or under an optical microscope (OM). A fixed speed of 0.5 $\mu\text{m/s}$ is used in all the tensile tests. A series of digitized optical micrographs are stored at constant time intervals and are fed into the DIC software (so-called Aramis) of GOM GMBH, where the displacements and the strain fields are computed. For an overview of the strain field over the whole gauge area, very fine dots of black paint are sprayed onto the specimen surface, the image of which is captured by a CCD camera for optimized contrast images during deformation.

The principle of DIC is based on the correlation between micro-features in a *source* image taken prior to deformation and the corresponding displaced markers in a so-called *destination* image.^{7, 8} For the sake of comparison, a commercial video extensometer of MESSPHYSIK ME46 is used to examine the axial strain distribution over the whole gauge length of the specimens. The extensometer could simultaneously monitor the elongation of nine segments, which makes it possible to study the overall deformation behavior of both the clad FGMs and the substrate materials under tensile stress.

3.0 Results

The typical microstructure over the interface region of the proposed samples is shown in Figure 2a. The transition from the substrate to the AlSi40 FGM is smooth and gradual: fine α -Al dendrites nucleate and grow on the original coarse Al dendrites in the substrate; primary Si particles appear at a distance of about 50 μm from the molten boundary, which covers a particle free zone. In the FGM the discrete Si crystals surrounded by α -Al dendritic halos increase continuously in size and volume fraction as a function of the distance from the boundary, from 5 μm and 21 vol.% near the boundary to 48 μm and 35 vol.% at the center of the FGM track,

respectively. In contrast, the α -Al halos exhibit less change in size over the same distance. The width of the particle-free zone, ranging from 20 to 50 μm , is mainly controlled by the temperature gradient and the scan velocity of the laser beam.

Due to the difference between the melting temperature of the α -Al phase and the AlSi eutectic temperature, the molten boundary is rough at a micro-scale and the roughness is governed by the geometry and size of the coarse Al dendrites in the substrate. The secondary arm spacing of the coarse Al dendrites is found to be 40 μm and the melt depth between the secondary arms may reach 25 μm , depending on the inclined angle of the arms with respect to the molten boundary. Figure 2b exhibits the microstructure of the normal FGM clad on the top surface of a substrate. A very similar transition over the molten boundary and the graded microstructure can be seen as observed in Figure 2a.

Tensile tests of all ten specimens without a notch exhibit fracture in the substrate material, i.e. outside the laser clad AlSi40 FGM tracks. It means that both the strength of the FGM tracks and their interfacial adhesion are higher than the ultimate tensile strength (UTS) of the substrate. Seven specimens fractured approximately 1.5 mm away from the FGM track, as shown in Figure 3a. The rest exhibit fracture at random positions far away from the track. During tensile tests the strain-stress curves keep the linear character until a uniaxial deformation of 0.14% at the tensile stress of approximately 125 MPa. Then plastic deformation appears and the final fracture occurs suddenly at a strain of 0.4-0.5%.

Although the experiments with unnotched specimens have demonstrated the rather strong adhesion of the FGM tracks to the substrate, it still remains uncertain how far the adhesive strength lies above the UTS value of the substrate. No failure could be observed directly at the interfaces during these tensile tests. Therefore, V-notches are made right at the interface. Eight tensile tests are performed with the notched and

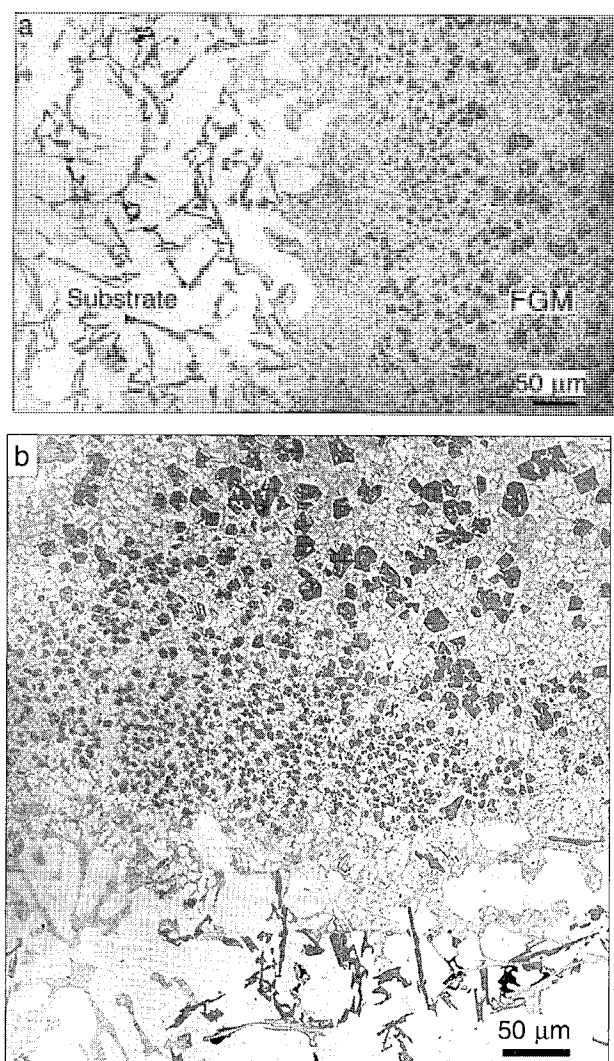


Fig. 2: (a) Microstructure of AlSi40 FGM and (b) the longitudinal cross-section of an AlSi40 FGM track clad on the surface of the substrate (3000 W laser power, 25 mm/s beam speed).

unnotched specimens, respectively, of the same substrate material in order to determine experimentally the stress concentration factor, which is found to be 1.26. The interfacial strength of the FGM tracks of the notched samples is given in Table 1. The global failure initiates at the notch tip and follows the interface, as seen in Figure 3b. However, the main crack is often deflected into the heat-affected zone (HAZ) of the substrate, which is obviously related to the difference in strength. To provide insight into the different levels of UTS, tensile tests are also performed on the specimens of both the original cast substrate materials and the pure AlSi40 FGM layer produced by 25 overlapping laser tracks on the substrate. The specimens of the pure AlSi40 FGM layer are cut out by spark erosion from the substrate in such a way that all the laser tracks are perpendicular to the loading direction, and no notches are employed. The results are

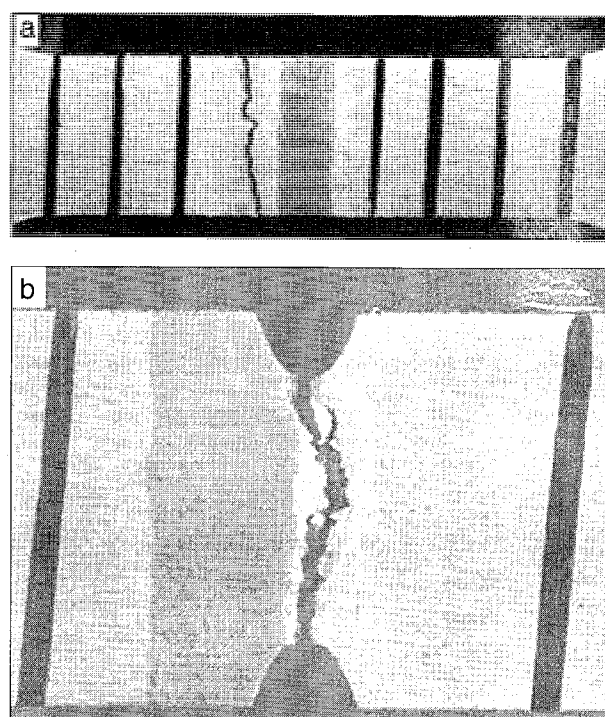


Fig. 3: (a) Fracture near the boundary of HAZ in an unnotched sample and (b) fracture at the interface near the notches. The black straight lines are markers for the video extensometer set-up.

Table 1. Bond Strength of FGM and Substrate

	Strength (MPa)	Standard Deviation (MPa)
AlSi ₄₀ FGMs	272.8	16.2
Interface	258.5	17.4
Substrate	212.6	13.8

also listed in Table 1. It is clear that the interfacial strength of the FGM tracks is 22% above the UTS of the substrates and is very close to the UTS of the FGMs.

In order to study the deformation behavior of the FGM tracks with respect to the substrate, DIC measurements are applied. A typical axial strain field over the gauge without a notch is presented in Figure 4. The FGM track shows homogenous strain fields and a gradual strain transition over the interface. In contrast, the substrate exhibits rather inhomogeneous strain fields that consist of locally deformed areas, which may develop as potential sites of failure. In particular, softening effects are clearly observed in the heat-affected

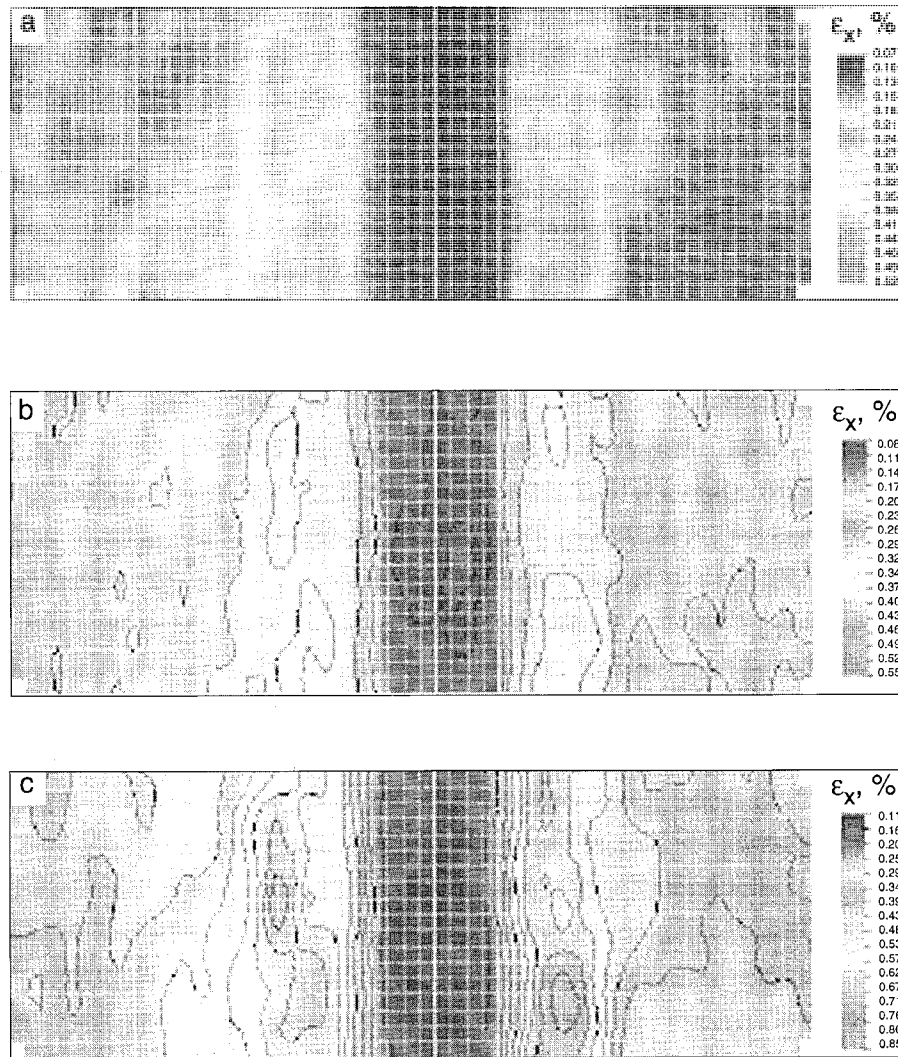


Fig. 4: Evolution of the axial strain field measured by DIC on a laser clad FGM specimen at different applied tensile stresses: (a) 117.5 MPa, (b) 166.3 MPa, and (c) 190.4 MPa. The cell size of the grid is 0.28 mm.

zones (HAZs) of the substrate even at the early stages of deformation. The outer regions of the HAZs, which are adjacent to the thermally undisturbed substrates, exhibit the highest strain levels during tensile tests and may initiate the final fracture in most cases. About 70% of the tensile samples fracture at the outer region of the HAZs, where the UTS value of the substrate material is reached.

A detailed field of elastic strain over the interface region of an FGM track is shown in Figure 6a. The strain field is measured at a tensile stress of 116.7 MPa, which is still lower than the macro yield stress of the sample. Dense iso-strain lines are seen in the interfacial region which run parallel to the interface. For overall patterns of the lines see also Figures 4c and 5a. These parallel iso-strain lines show an almost constant interval in the vicinity of the bond region of the FGM track and become less dense towards the interior of the track. By extracting the strain values at a certain section, one may estimate

the variation of the stiffness of the FGMs across the interface (see Figure 6b). Figure 7 presents the axial strain distribution over the whole gauge length, which is measured with the video-extensometer. On the inset, the black markers divide the gauge length into nine segments. Segment No.5 covers the FGM track and, segments No. 4 and 6 correspond to the HAZs on both side of the track. Because the extensometer measures the elongations by scanning 50 to 70 horizontal lines, the measured values are just the average strain of a segment. From Figure 7, it can be seen that the HAZs are heavily deformed and that the FGM track shows an extremely low strain value. The final fracture initiates in segment No.4, where the highest strain value is measured. This result corresponds to the DIC measurements of the strain field.

SEM *in-situ* observations during tensile tests revealed the same mechanism of crack initiation and

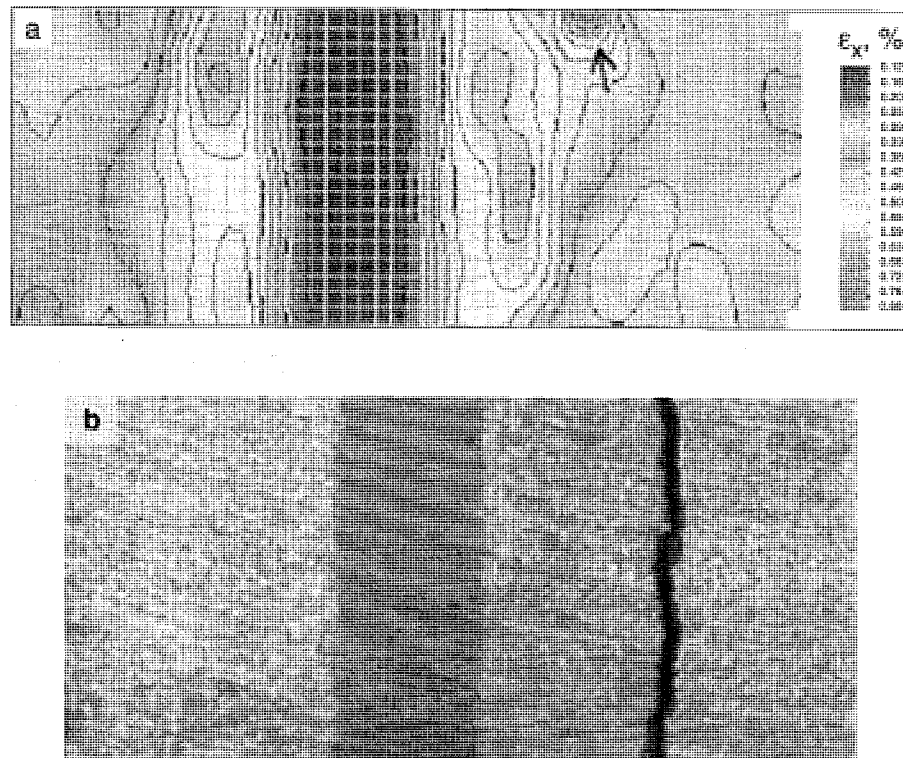


Fig. 5: Strain field (a) showing crack initiation, indicated by an arrow, far away from the FGM track. The destination image for obtaining this figure was recorded just prior to the fracture and (b) fractured sample.

propagation at both cases where the fracture occurred at the HAZ outer boundary and far away from the HAZ, respectively. Cracks mainly resulted from decohesion of the large Si or AlCu_2 plates from the Al matrix, as seen in Figure 8a. These plate-like precipitates have a maximum size of about $100\text{ }\mu\text{m}$ in length and a few micrometers in width. In order to distinguish the different failure mode of the laser clad AlSi40 FGMs, SEM *in-situ* observations during tensile tests are performed on the unnotched samples of the pure AlSi40 FGM produced by the laser cladding technique. These observations revealed that failure initiation in the FGMs is dominated by cracking of Si particles. Figure 9 shows typical cracked Si particles after the onset of the plastic deformation of the coating. The opening of the crack surfaces leads to voids nucleation in the adjacent Al-halos, see Figure 9b. Most of the cracked particles tend to align their fracture plane perpendicular to the loading direction. On the other hand, the cracked Si particles are randomly distributed and can be found anywhere from the edge to the center of the gauge. It is often observed that the surrounding particles of a cracked particle might not crack until a much higher deformation level is reached, during which new cracked particles appear somewhere else. It is almost impossible to predict

the position where fracture occurs in the unnotched samples. Although it is impossible to observe directly the actual size of the particles on 2D projections, the particle size seems not to be a strong factor for cracking because both small and large broken particles often co-exist. Nevertheless, it is considered that the final fracture results from the growth and linkage of voids that initiate at the cracked particles.

The fractography present in Figure 10 shows both flat fracture planes of the particles and dense micro-dimples in the Al-halos around the Si particles. The tip corners of the Si_p stay undamaged. In contrast, the fracture surface of the substrate exhibits large smooth areas due to decohesion of the hard plate-like phases from the matrix, see Figure 8b.

4.0 Discussion

One may argue that the adhesion of an FGM coating to the substrate may not be the same as the adhesion in our specially designed samples, when the FGM fills a groove as shown in Figure 1a. However, the consistency of the microstructure over the transition areas between the FGM and the substrate in both cases mentioned above is clearly documented in Figures 2a and b.

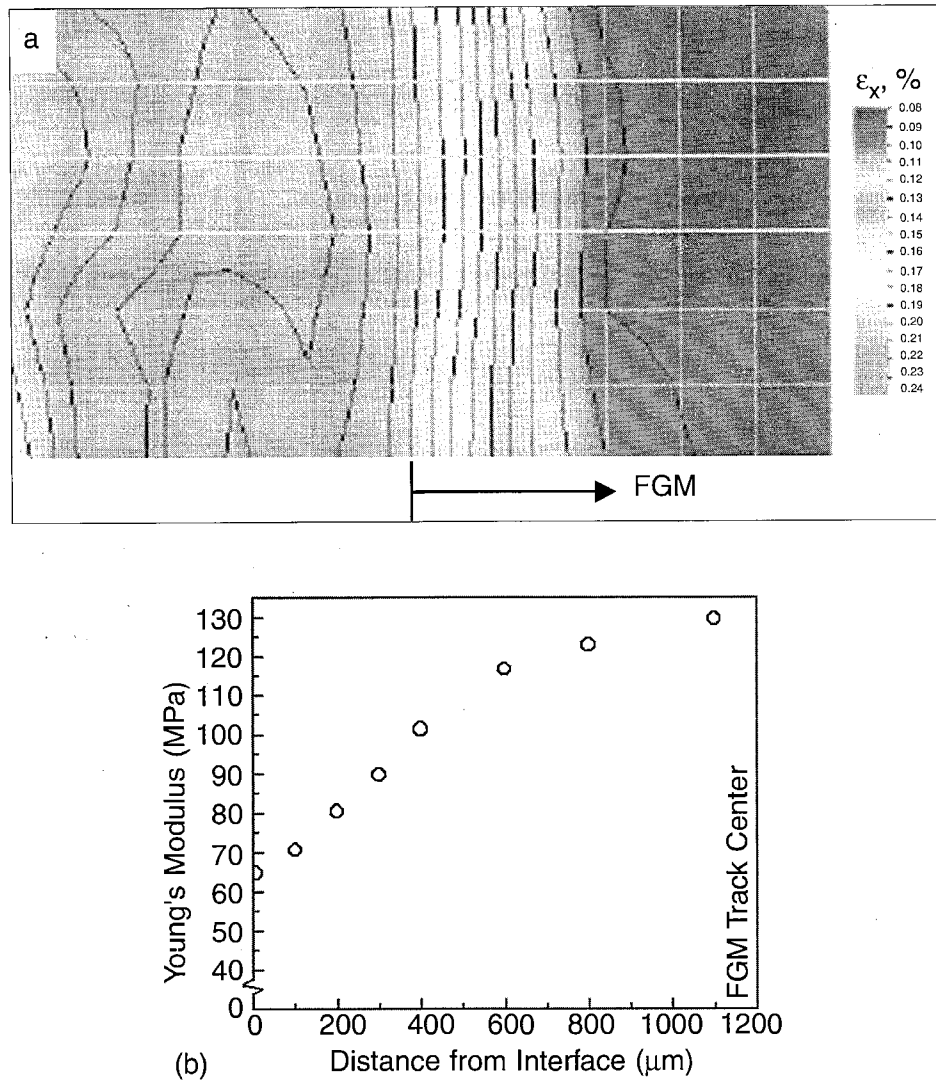


Fig. 6: (a) Detailed strain field over the interface region of an FGM track under an applied tensile stress of 116.7 MPa and (b) the corresponding profile of the stiffness.

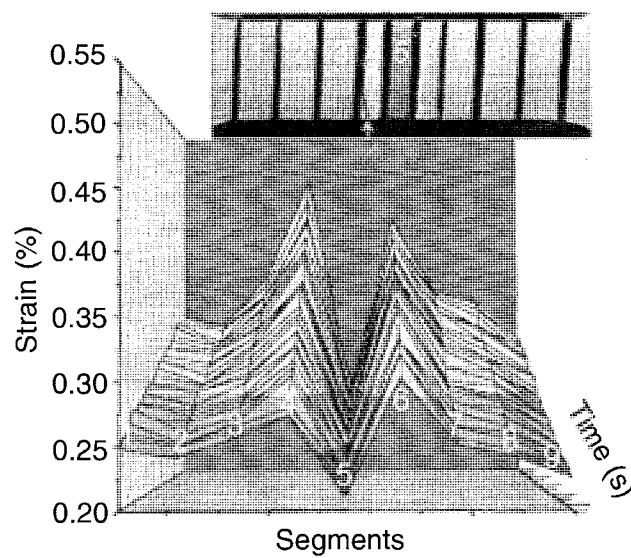


Fig. 7: Strain-time curves of the various segments over the gauge length measured by the video-extensometer. The optical micrograph indicates the segments on the specimen and an arrow indicates the main crack in segment No.4.

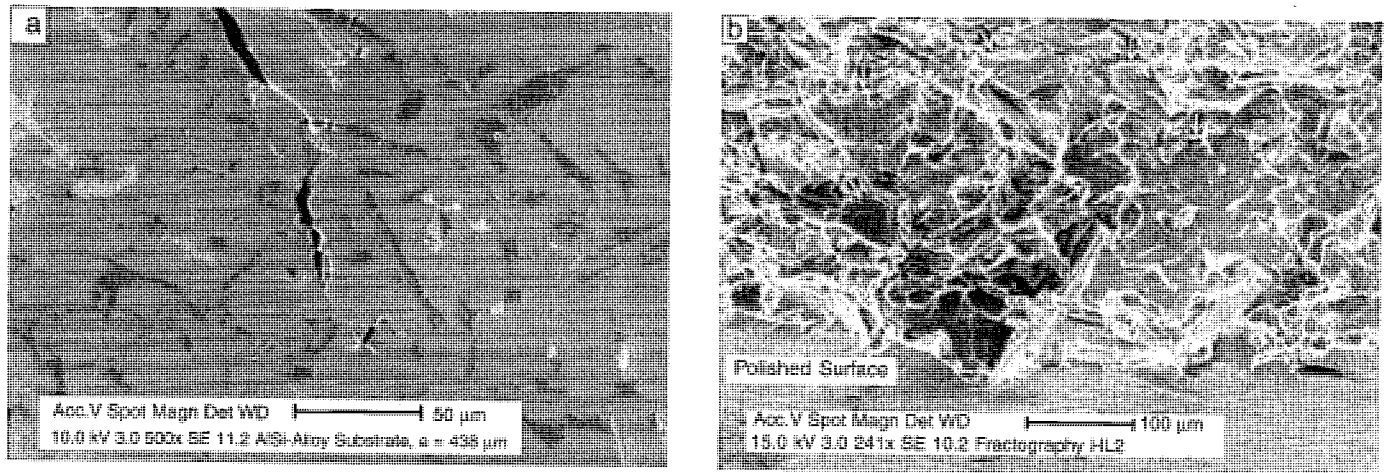


Fig. 8: (a) In-situ SEM observation showing crack initiation and propagation along the plates in the substrate under a tensile load in the horizontal direction and (b) fractography showing smooth areas on the fracture surface due to decohesion of plates.

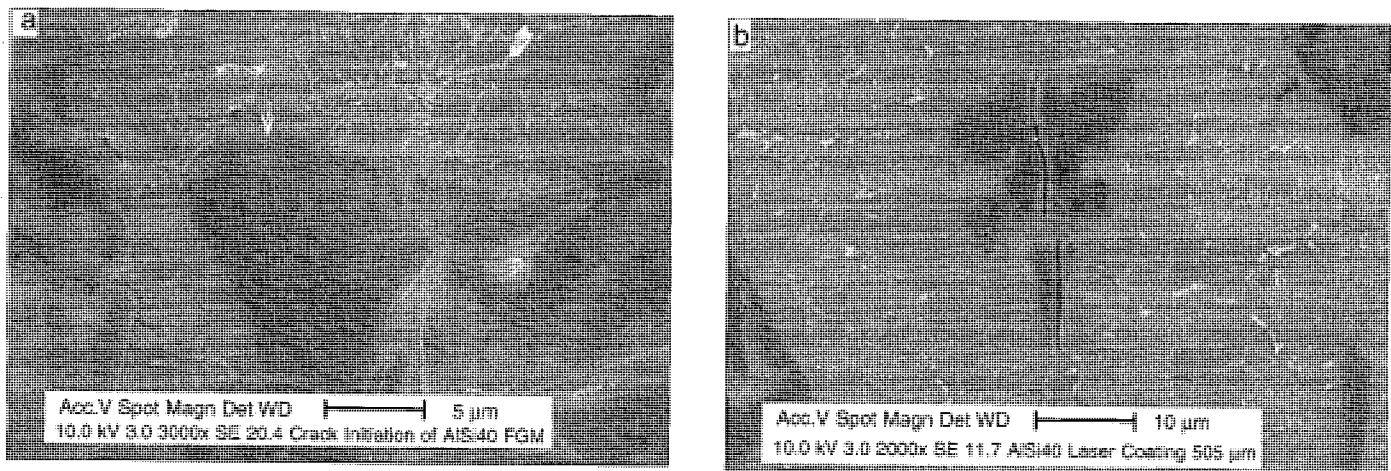


Fig. 9: (a) In situ observations of crack initiation in a Si particle, indicated by an arrow and (b) cracked Si particles in the AISi40 FGMs.

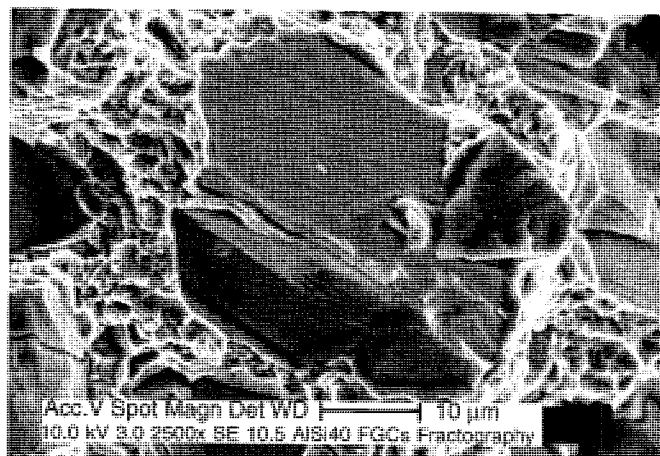


Fig. 10: Fractography of AISi40 FGM showing the cleaved Si particles and micro-dimples in the surrounding Al-halos.

Microstructural similarity between the proposed samples and the FGM coating tracks⁶ supports the validity of the method for the FGMs in this particular case.

Rough interfaces are formed in laser clad AlSi40 FGMs by inhomogeneous remelting a surface layer of the substrate materials due to the different melting temperatures of the α -Al dendrites and AlSi eutectics. Such interfacial roughness promotes a good mechanical locking of the coating to the substrate. Unlike the situations in sprayed thermal barrier coatings (TBCs),^{9, 10} the alternating stresses at the peaks and valleys along the interface are restricted after cooling due to two main reasons. The particle-free zone has the same chemical composition and thermal expansion coefficient. The elastic modulus is equal to the elastic modulus of the bulk substrate. This is because the thin layer of the substrate does not mix with the melt of the coating material. Secondly, the gradual changes in volume fraction of Si particles suggest a graded thermal expansion coefficient and elastic modulus. It results in a low level of residual stress in the coating. On the other hand, the roughness increases the total area of the interface by a factor of 1.68, assuming a half-period sinusoidal profile with amplitude of 25 μm and half-wavelength of 40 μm . Such an increase is expected to contribute to the interfacial bond strength compared to a straight interface.

In particle reinforced metal matrix composites fracture initiation is mainly associated with particle fracture and particle-matrix interfacial failure, depending on the particular composite and matrix conditions.²⁰⁻²⁴ There are numerous models proposed to describe the crack initiation of the particles, mainly based on three different criteria, i.e. stress criterion, strain criterion and energy criterion.¹¹⁻¹⁴ These models also have different mechanism, that is to say, some of them are derived from continuum mechanics and some are based on dislocation theory. With respect to the general behavior of particle cracking, several features may be summarized here:

1. The number of cracked particles increases as the stress or strain increases,
2. Lenticular particles crack more easily than spherical particles, and
3. The stress required for particle cracking decreases as particle size increases.

In addition, Lloyd¹⁵ observed that fracture initiates more easily in clusters of particles that are ineluctable in the fabrication with the molten metal route. Initiated by particle cracking and/or decohesion of the matrix between the particles within the clusters, final fracture is achieved by fracture through the matrix. Because of localization of damage and very limited void growth, the reason of failure is the intensification of a large

triaxial stress state exerted on the matrix. Such clustering factor does not play an important role in our case, because the Si particles in the FGMs are well separated by the Al-halos and the adjacent eutectics. This is controlled by the nucleation events and growth process of Si_p in the laser pool.⁶ What is important for Si_p cracking appears to be the size of the Al-halos.

In plastically heterogeneous materials such as the AlSi40 FGMs, the activity of dislocation sources generates dislocation pile-ups in the ductile phase. The pile-up of dislocations will continue until a critical stress is reached at the spearhead of the pile-up. The stress may generate either plastic flow or fracture in the particles. The equivalent normal stress, σ_{eff} , acting on the particle by the pile-up is proportional to the length of the pile-up and the applied tensile stress squared.¹³ In AlSi40 FGMs, the length of the pile-up is limited to the sizes of Al-halos because the eutectics are considered to be transparent for slip. As shown in⁶ the α -Al halos surrounding the Si_p in the lower part of a FGM coating are thinner than those in the upper part. Another notable feature is that the dendritic nature of the α -Al halos is more fully developed further from the bottom of the track. This is considered to be additional evidence that their growth rate increases with decreasing depth in the melt pool. These observed characteristics suggest that the size of the halos is limited by both their growth rate and by the time necessary to reach the temperature at which the eutectic finally forms.

The average size of the Al-halos in AlSi40 FGMs is between 3 and 10 μm , i.e. one or two orders of magnitude smaller than the size of Al dendrites in the substrate materials. It suggests that a much higher tensile stress is necessary to generate cracks in the particle. However, to know the real stress in the particles under an applied load, it is necessary to also consider the misfit stress that is due to the difference in the thermal expansion coefficient between Si particles and Al matrix.¹⁸ The particles are actually under a hydrostatical compressive stress of the order of the yield stress of the matrix, even when no external stress is applied to the materials. At an applied tensile stress just above the yield stress of the matrix, the net normal stress acting on the particles in the loading direction is approximately zero. This leaves the particles under the sole effect of the stresses arising from the plastic deformation, which may explain the fact that Si particles start to crack immediately after the onset of plastic deformation.

Softening of HAZs is often reported as an accompanying effect of welds in age hardened or strain hardened Al-alloys due to the microstructural change of the areas exposed to the heat input. Commonly, the softening effect is examined with hardness measurements where the hardness profile exhibits a drop

in HAZs.¹⁹ For Al-alloys with a high concentration of alloying elements, however, it may be questionable to detect softening effects with hardness measurements because of inhomogeneities. The softening phenomenon in the HAZs of laser clad FGMs can be observed by strain mapping with the DIC technique, which reveals directly the different deformation resistance of the FGMs, HAZs and the undistorted substrate materials subjected to the applied tensile stress.

In the study of welds, the properties of the HAZs are usually expressed either as a function of exposed peak temperature or as a function of distance from the fusion boundary. It has been shown that the maximum loss in hardness of the HAZs corresponds to a relatively low peak temperature at which over-aging occurs, rather than the higher peak temperatures that result in the dissolution of precipitates in the HAZs of 6xxx and 7xxx Al-alloys.¹⁹ In other words, the minimum hardness level in the HAZs always appears at a distance away from the fusion boundary. Natural aging may only recover a part of the reduced hardness/strength of the HAZs. It is the same situation in our case that the maximum strain levels most likely appear at the outer region of the HAZs during deformation, as seen in Figure 4. The reason for softening here is considered to be the same as in the welds of 6xxx alloys. The Al dendrites in the substrate possess a similar composition to that of the 6xxx alloys and are consequently subjected to similar microstructure changes during the thermal cycle of laser cladding. Another fact that is noteworthy is that the softening of the HAZs is not homogeneous because of the inhomogeneous distribution of particles in the substrate.

5.0 Conclusions

The specially designed samples of laser clad AlSi40 functionally graded materials (FGMs) in a grooved substrate have been examined as a potential configuration for the evaluation of interfacial adhesion of FGMs. Both the UTS and the interfacial bond strength of the AlSi40 FGMs are studied, and both appear to be higher than the UTS of the substrate material. With the application of digital imaging correlation techniques, the deformation behavior of both the FGM and the substrate near the interface is clearly revealed. Strain field mapping demonstrates the gradual transition in strain of the FGMs over the interface region and the softening effects in the heat-affected zones of the FGM tracks. In-situ microstructure observations during tensile tests reveal the different failure modes of the FGMs and the substrates, respectively. The strengthening of the FGM is dominated by the size of the Al-halos around the particles, in accordance with a dislocation pile-up model.

6.0 Acknowledgments

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Characterization of Coatings

Stability and Oxidation Resistance of Novel Metallic Fibers

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Abstract

Fine advanced alloy fibers are emerging as excellent candidates in hot gas-gas separation. High temperature oxidation behavior of Fe-Cr-Al alloy fiber media consisted of random nonwoven felt like structure was investigated at temperatures of 1073 and 1255 K in dry air. Two types of Fe-Cr-Al alloy, Hoskins 875 and Fe-Cr-Al-Mo were used in the present study. It was observed that the oxidation kinetics obeys the parabolic law. The scale morphology was studied by scanning auger microscopy. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES)

studies confirm that alumina scale forms on the surface of the Fe-Cr-Al alloy fibers comprising the media. Hoskins 875 was found to be more oxidation resistant than Fe-Cr-Al-Mo at 1073 and 1255 K. The oxidation rate of Fe-Cr-Al alloy media was found to increase with increasing fiber diameters at 1073 and 1255 K in dry air.

1.0 Introduction

Increasingly stringent demands are being placed on materials used for gas-gas separation membranes as

technological processes change. These membranes require gas selectivity, high permeation and corrosion resistance at temperatures approaching 1273 K. Most membranes are produced by sintering material processed via the powder metallurgy route, which results in low permeability. An alternative to the powder metallurgy route is to fabricate membranes in the form of felted-wire of small diameter. Current alloys for the felted-wire membranes are of the 18-8 austenitic stainless steel variety and do not possess adequate oxidation resistance at elevated temperatures. The bundle method for making 18-8 wire of 0.5 to 50 μm diameter has been altered to fabricate wires of advanced high temperature alloys such as Fe-Cr-Al and intermetallic alloys.

Fe-Cr-Al alloys form a continuous, adherent and protective alumina scale on the surface at high temperatures in dry air. These alloys exhibit superior oxidation resistance mainly due to slow growth of the alumina scale. Fe-Cr-Al alloys are primarily used as materials for heating elements, fire grid, honeycomb catalytic converters for automotive exhaust, gas-gas separation, gas burners, hot gas blow back filters and catalyst support substrate for their excellent high temperature oxidation resistance. Numerous studies have been performed to investigate the growth mechanism of the alumina scale during high temperature oxidation of the Fe-Cr-Al alloys.¹⁻¹⁵ The mechanism of alumina scale growth on Fe-Cr-Al alloy is yet to be firmly established. Growth by diffusion of aluminum from the inner alloy/scale interface to the outer scale/air interface was proposed by some researchers.^{4-6, 10} In contrast, others^{2, 3, 7, 15-17} have argued that the alumina scale growth on Fe-Cr-Al alloy takes place predominantly by the inward diffusion of oxygen. The grain boundary diffusion of oxygen for the growth of the alumina scale was investigated by Clemens and coworkers⁹ in order to study the mechanism of scale growth on Fe-Cr-Al alloy. Jedlinski and Borchardt⁸ have reported that growth takes place by both outward migration of aluminum and inward diffusion of oxygen across the oxide scale. Surprisingly, high temperature oxidation studies of metallic-media made of thin fibers of Fe-Cr-Al alloys are largely absent. Srinivasan and Lannutti¹⁸ attempted to study the oxidation resistance of metal fiber made of Fe-Cr alloy for burner applications in the temperature range of 923-1423 K. However, the study was based on Fe-Cr alloy fibers into which Al was diffused by pack cementation to have an Fe-Cr-Al composition on the surface. Such an experiment usually does not reflect the actual oxidation behavior of the Fe-Cr-Al alloy fibers. Scale morphology of the alumina scale grown on the Fe-Cr-Al alloy was reported to be influenced by the oxidation temperature.¹³ Badini and Laurella¹³ observed

that the scale surface was distinctively flat at an oxidation temperature of 1473 K, whereas the surface contained alumina whiskers at 1173 K. It was suggested by them¹³ that the change in scale morphology might be attributed to the change in diffusion mechanism of aluminum and oxygen at various temperatures. Nevertheless, a mechanism for high temperature oxidation of the Fe-Cr-Al alloy, especially in the form of fibers, is yet to be established with a sound basis of kinetic and diffusion data.

The primary objective of the present investigation is to study the oxidation kinetics of two types of Fe-Cr-Al alloy fiber media with varying fiber size in dry static air in order to assess their performance as a heat resistant material for high temperature applications. Additionally, we characterized the scale/alloy interface and scale morphology on the surface of the oxidized fibers using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning Auger microscopy (SAM) techniques.

2.0 Experimental

Fe-Cr-Al alloy fiber media with diameter 8, 12, 25, and 38 μm were obtained from US Filter (Deland, FL). The chemical compositions of the two Fe-Cr-Al alloys used in the present study are shown in Table 1. Rectangular specimens of dimensions (30 $\times$ 20 $\times$ 0.7 mm) were used for the oxidation study. Specimens were thoroughly cleaned in acetone using an ultrasonic cleaner. The oxidation set-up used in the present study is described elsewhere.^{19, 20} An electronic microbalance (Sartorius MP 8: precision of ± 0.1 mg) attached to a computer was used to record the continuous mass change of the specimen as a function of time. Isothermal oxidation studies were conducted at temperatures of 1255 and 1073 K in dry air for a period of about 50 hours.

Post-oxidation studies were carried out by using scanning Auger microscopy (SAM) and XPS techniques not only to characterize the scale morphology but also to identify the various oxides present on the surface. For surface analysis, the oxidized samples were kept under a vacuum of about 10^{-9} Torr inside the chamber of a PHI 5400 ESCA system. Non-monochromatic Mg-K α X-rays ($h\nu = 1253.6$ eV) at a power of 350 watt were used for the analysis. In order to achieve the maximum resolution, survey and individual high-resolution spectra were recorded with pass energies of 35.7 and 17.9 eV, respectively. The spectrometer was calibrated using a metallic gold standard ($\text{Au } 4f_{7/2} = 84.0 \pm 0.1$ eV). Charging shifts produced by the sample were removed by using a binding energy scale referenced²¹ with respect to the C(1s) binding energy of the hydrocarbon part of

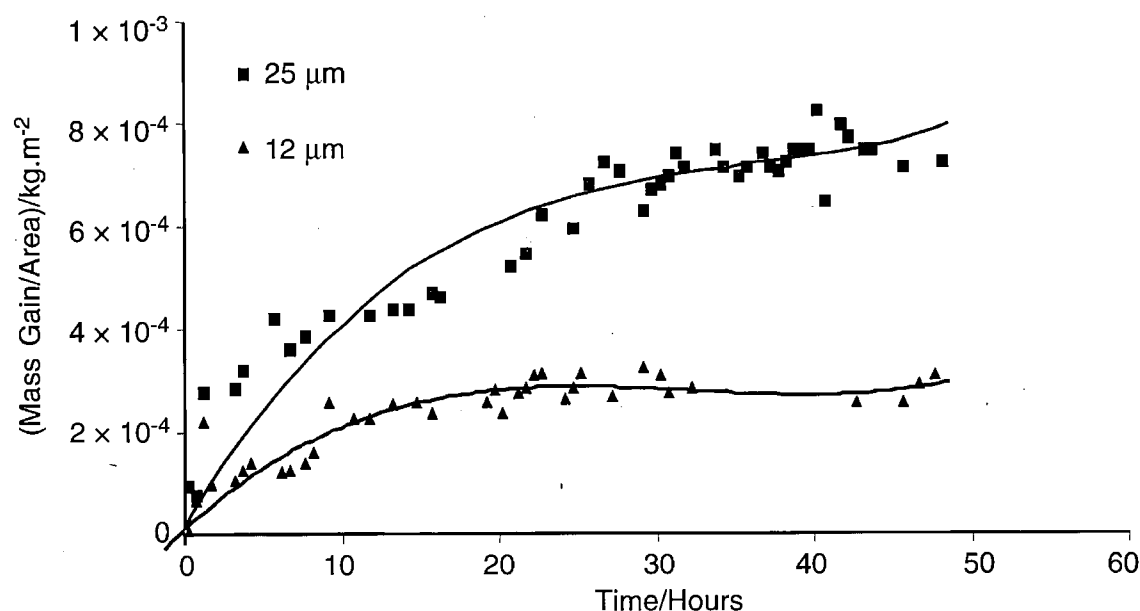


Fig. 1: Mass gain per unit area vs. time plots for isothermal oxidation of Hoskins 875 media with fibers of 12 and 25 μm diameter at 1073 K in dry air.

Table 1. Chemical Compositions of Fe-Cr-Al Alloys Used

Alloy	Composition in wt. %						
	Al	Cr	Mo	Si	C	Y	Fe
Hoskins 875	5.5	22.5	-	0.5	0.10	0.01	Balance
Fe-Cr-Al-Mo	7.0	27.0	2.0	-	0.03	0.15	Balance

the adventitious carbon line at 284.6 eV. Non-linear background was removed from the spectra using a method described by others.²² Subsequently, nonlinear least-squares curve fitting was performed using a Gaussian-Lorentzian distribution. The peak height and peak areas were used to calculate the relative atomic concentrations. The elemental concentrations shown in the profiles were determined by using the calibrated sensitivity factors.²²

A PHI 600 scanning Auger microprobe (SAM) with a probe size of 30 nm and an analytical depth of 2 nm makes this instrument to be a highly surface-sensitive technique for a site-specific study. The electron beam is thermionically produced from a LaB_6 crystal. The beam can be scanned as in scanning electron microscopy (SEM), and compositional maps of the surface can be obtained. For typical AES analysis, primary excitation (E) was used between 5 and 15 keV.

3.0 Results and Discussion

Mass gain per unit area vs. time plots for oxidation of Hoskins 875 media with different fiber sizes at 1073 in dry static air are shown in Figure 1. The oxidation plots for Fe-Cr-Al-Mo media in various fiber sizes at 1073 and 1255 K in dry air are presented in Figures 2 and 3, respectively. The oxidation kinetics of fiber media of Hoskins 875 (Figure 1) and Fe-Cr-Al-M (Figure 2) alloys follow a parabolic law. Such parabolic oxidation kinetic behavior of Fe-Cr-Al alloy was also reported by earlier researchers.^{1, 12, 13} At a temperature of 1255 K, the Fe-Cr-Al-Mo alloy fiber media exhibited parabolic kinetics. The isothermal parabolic rate constants were estimated from the kinetic data and are presented in Table 2. Fe-Cr-Al-Mo fiber media exhibited a higher oxidation rate at 1255 K than at 1073 K. Such behavior might be attributed to the increase in diffusivity of the

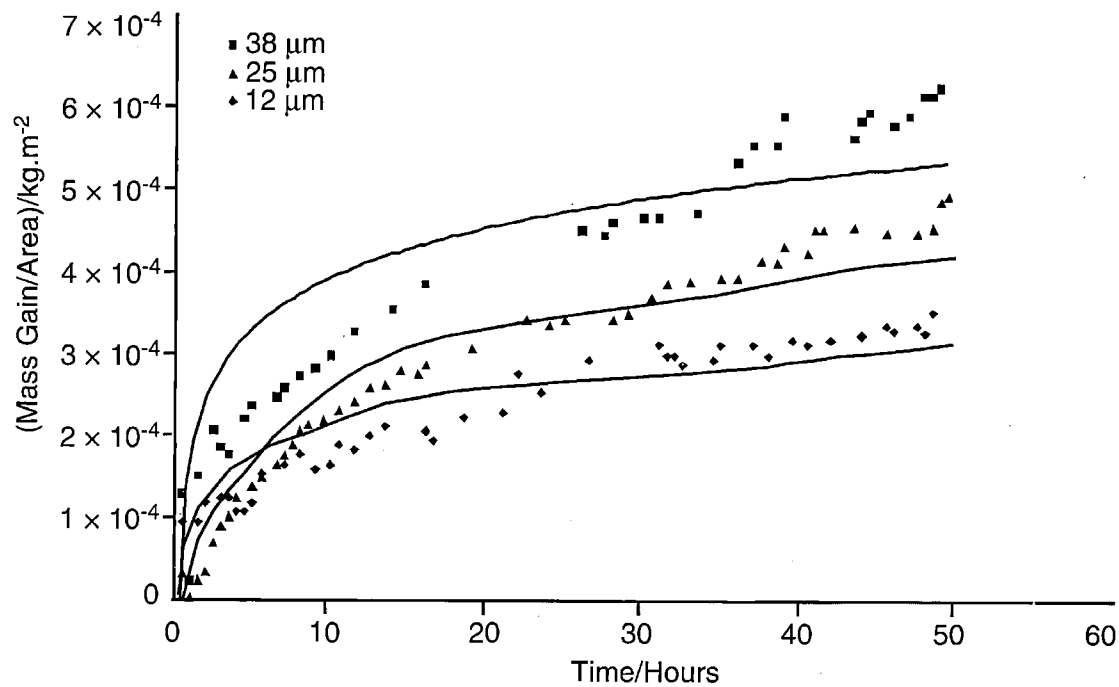


Fig. 2: Mass gain per unit area vs. time plots for isothermal oxidation of Fe-Cr-Al-Mo media with fibers of 12, 25, and 38 μm diameter at 1073 K in dry air.

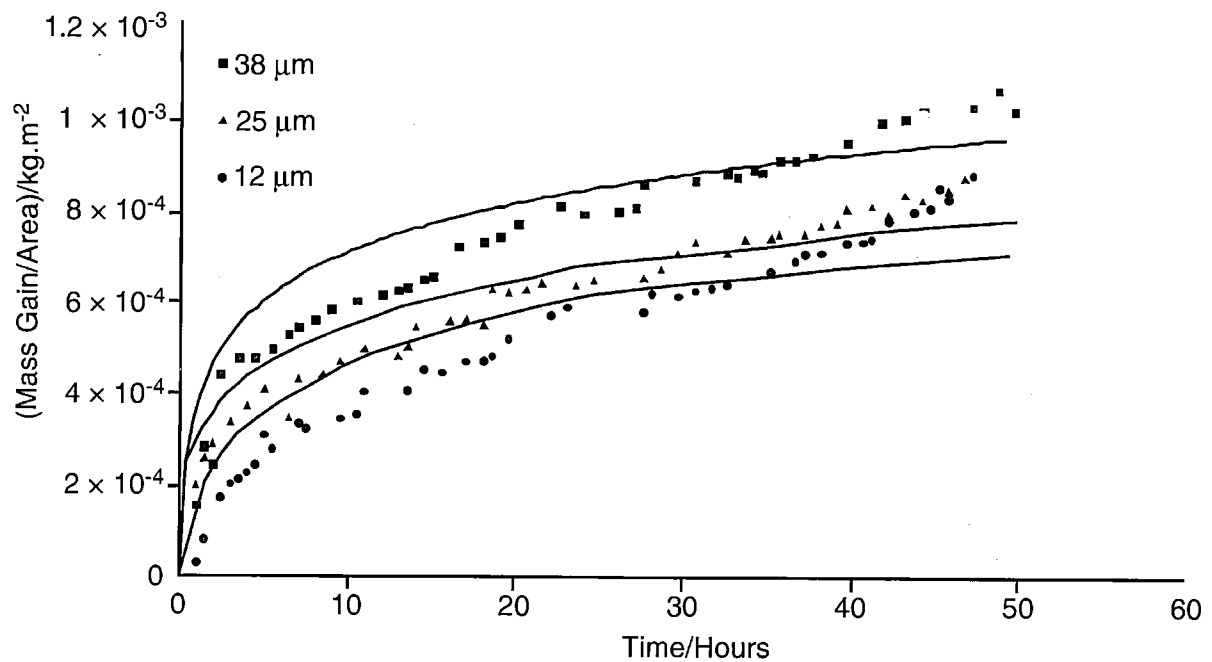


Fig. 3: Mass gain per unit area vs. time plots for isothermal oxidation of Fe-Cr-Al-Mo media with fibers of 12, 25, and 38 μm diameter at 1255 K in dry air.

Table 2. Isothermal Parabolic Rate Constants for Oxidation of Various Fe-Cr-Al Alloy Fiber Mediaes at 1073 and 1255 K in Dry Air

Temperature, K	Isothermal Parabolic Rate Constant ($k_p/10^{-13} \text{ kg}^2\text{m}^{-4}\text{s}^{-1}$)				
	Hoskins 875 Fiber		Fe-Cr-Al-Mo Alloy Fiber		
	12 μm	25 μm	12 μm	25 μm	38 μm
1073	3.30	3.92	5.44	11.17	18.53
1255	-	36.10	35.50	41.70	62.50

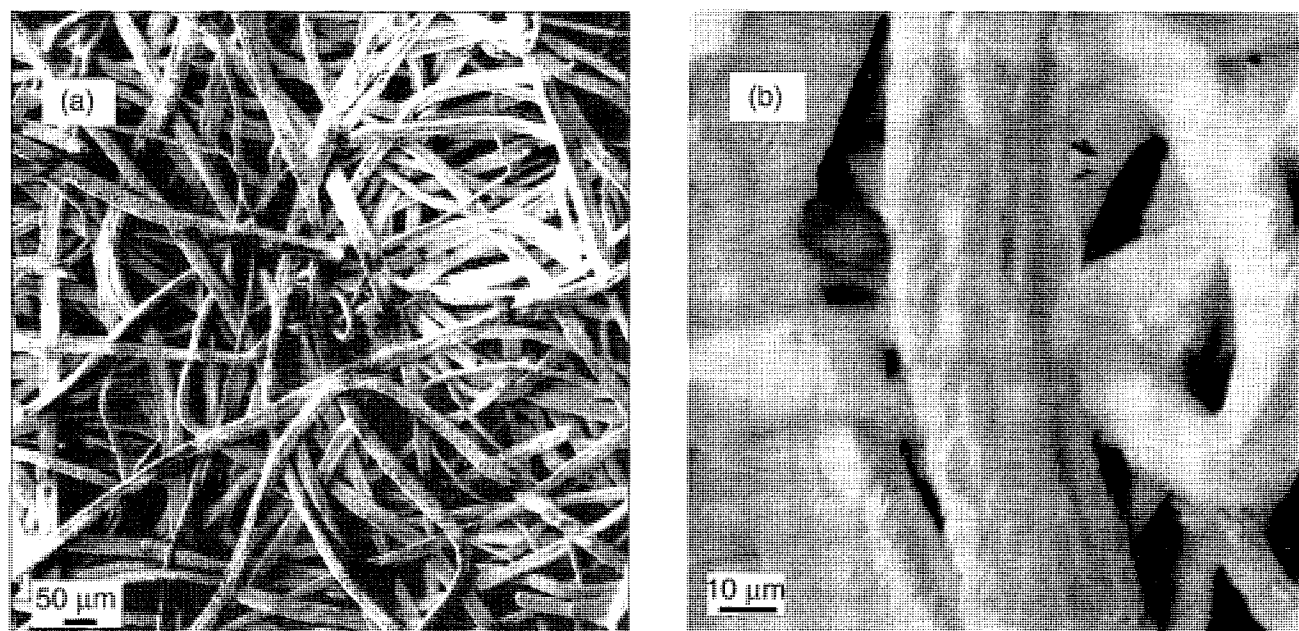


Fig. 4: Scanning Auger micrograph of oxide surface of Fe-Cr-Al-Mo alloy media with fibers of 38 μm diameter oxidized at 1255 K in dry air for 50 hours at (a) low and (b) high magnifications.

rate limiting species with increase of temperature from 1073 to 1255 K. Hoskins 875 was found to have a lower isothermal parabolic rate constant than Fe-Cr-Al-Mo at temperatures of 1073 and 1255 K in dry static air. It is interesting to note that there exists a relationship between fiber size and the parabolic rate constant value at constant temperature for both the alloys. It was observed that the isothermal parabolic rate constant increased with increasing fiber size. The reason is probably that the scale spallation behavior varies with fiber size. Further study is needed concerning this point.

Scanning Auger micrographs of the surface of 38 μm Fe-Cr-Al-Mo alloy media fibers at 1255 K in dry air for 50 hours at low and at high magnification are shown in Figures 4a and b, respectively. It can be observed from Figure 4a that the fibers did not have a circular cross section. These fibers were produced by a repetitive bundle drawing process. At high magnification the surface of the oxidized fibers shows formation of scale ridges at many locations (Figure 4b). The ridges are oriented along the longitudinal axes of the fibers. An AES spectrum of the top surface of the Fe-Cr-Al-Mo alloy media of 38 μm fibers at 1255 K in dry air for 50 hours is shown in Figure 5. The AES spectrum confirms the presence of alumina scale on the surface

of the fibers. Besides the peaks of alumina, the AES spectrum also revealed the presence of titanium oxide. A small amount of titanium is usually added to this Fe-Cr-Al alloy in order to enhance the formation of $\alpha\text{-Al}_2\text{O}_3$ scale on the surface which renders more protection to the alloy underneath. The XPS spectrum of the surface of 38 μm Fe-Cr-Al-Mo alloy media oxidized at 1255 K in dry static air for 50 hours is shown in Figure 6. It confirms the presence of a protective alumina scale on the top surface of the fiber media oxidized at 1255 K.

4.0 Conclusions

Oxidation kinetics of the media made of Fe-Cr-Al alloy fibers obeys a parabolic law. Hoskins 875 was found to be more oxidation resistant than Fe-Cr-Al-Mo at 1073 and 1255 K in dry air. The oxidation rate of the Fe-Cr-Al alloy media was found to increase with increasing fiber size at 1073 and 1255 K in dry static air.

5.0 Acknowledgments

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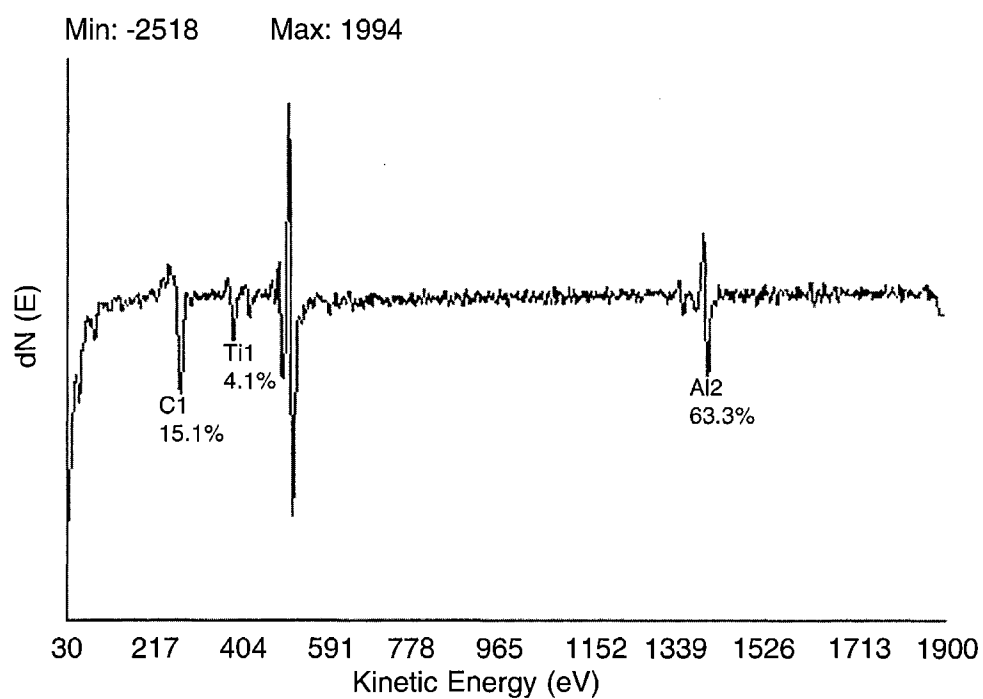


Fig. 5: AES spectrum of the oxide surface of Fe-Cr-Al-Mo alloy media with fibers of 38 μm diameter oxidized at 1255 K in dry air for 50 hours.

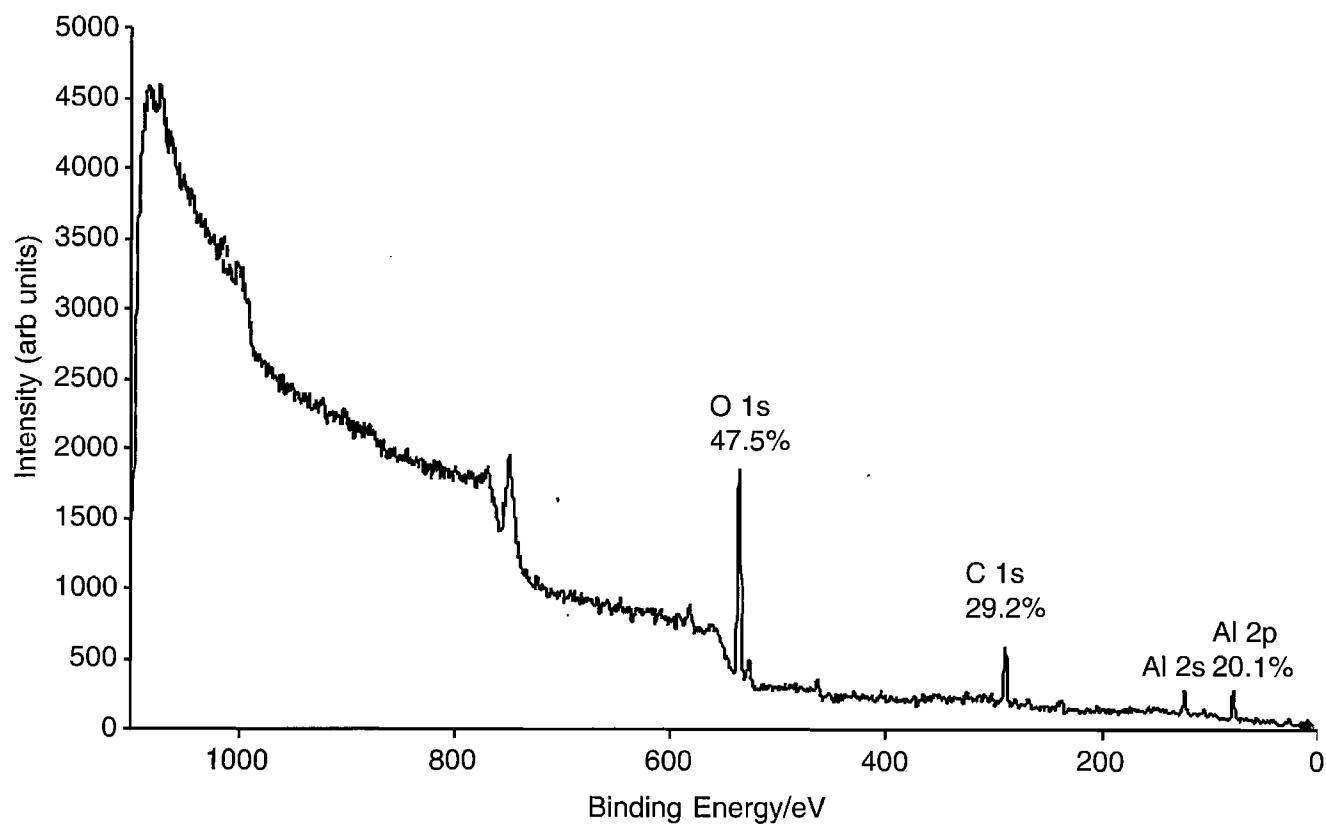


Fig. 6: XPS spectrum of the oxide surface of Fe-Cr-Al-Mo alloy media with fibers of 38 μm diameter oxidized at 1255 K in dry air for 50 hours.

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Controlled Superficial Cracking of the Substrate to Enhance Adhesion of Plasma Sprayed Coatings

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Abstract

Deliberate cracking of the substrate surface was shown to be beneficial for improving the coating adhesion of thermally sprayed coatings. This results from a better mechanical anchoring of the coating from cracks which act as efficient pegging sites.

Controlled cracking was obtained through heat treatment of the surface prior or simultaneously to spraying. Cracking process and effects on adhesion were studied for two coating/substrate systems, i.e. stainless steel onto an acrylate resin

and tin onto lithium fluoride, for which adhesion is known to be conventionally very limited. Coatings were achieved using a CAPS-ATC ("Controlled Atmosphere/Temperature Plasma Spraying") unit. SEM, EDS, EPMA, FTIR, QIA, and confocal microscopy were particularly employed to study microstructures and interfaces, coupled with a finite element analysis of adhesion due to cracks.

One of the prominent advantages of the cracking process, e.g. compared to conventional sand blasting, is that substrate roughness can be kept (except for crack sites) very low (up to a mirror-like polished surface). This corresponds

to a quasi flat coating/substrate interface except for the pinning cracks.

Due to this unique adhesion process (patented for some bonding applications), thermal spray could be successfully applied to a new route for rapid prototyping of molds and to new materials for optical pyrometric measurements.

The superficial substrate cracking concept can be extended to coatings other than thermally sprayed coatings, primarily to those of polymers and minerals as in the two examples which are discussed in this contribution.

1.0 Introduction

Thermal spraying is conventionally claimed to be a sort of universal process for the coating of any material substrate, i.e. a metal, a ceramic, a composite or a polymer, with any material, i.e., a metal, a ceramic. This high flexibility and versatility result from the process principle basically and from the high number of spraying variants, including some, with newest technologies such as those in this work (for details, one may refer to the recent “*Quo Vadis Thermal Spraying*” paper, by P. Fauchais et al.¹ However, some restrictions in applications still remain, especially because of a limited coating substrate adhesion for a certain number of materials couples.

This work deals with an innovative adhesion process to expand the range of material substrate material to be coated by thermal spraying. It was expected in particular to cover polymers and inert materials with flat surfaces or surfaces which could not undergo conventional surface preparation such as grit blasting or bond coating.

Nothing is less original than stating that three major phenomena can govern adhesion, i.e. in order of decreasing importance : mechanical anchoring, diffusional (metallurgical) bonding and atomic force attraction.

The above mentioned innovative process relates to mechanical anchoring which can be promoted through specific heat treating of the substrate prior to spraying. Heat treating results in Controlled microcracking of the substrate surface which allows subsequent efficient interlocking of the sprayed material. This shows that cracking is not always detrimental to material systems. However, few examples were given up to now, which, moreover, deals with stress relaxation quasi-exclusively. Regarding sprayed materials, one may refer to deliberate laser craze cracking of plasma sprayed zirconia to achieve more strain tolerant thermal barrier coatings.²

In early works from the bibliography, many substrate surface preparations were developed to improve

mechanical anchoring of sprayed coatings. However, they are not intrinsic to the substrate material in so far as they all require either material addition or material removal. This results in two classes of processes, i.e., respectively those using a bond-coat between the substrate and the top layer and those without any bond coat. In the first family of processes, the bond-coat may be a high performance thermoplastic,³ a fiber ply,⁴ a metallic grid,⁵ a rough and porous electrophoretic deposit,⁶ or a composite layer.⁷ In the second family, the process generally consists in grit blasting⁸ or machining.⁹

In contrast, this work deals with a process which can be said to be inherent to the substrate since it is based on crack self generating materials under heat effect. In this contribution, the process is discussed in the light of two examples of plasma spraying involving rather incompatible coating-substrate systems for which adhesion is a key issue : first, plasma spray of stainless steel onto a polymeric resin and, second, plasma spray of tin onto lithium fluoride. Process parameters were determined to optimize the anchoring effect due to superficial microcracks. Cracking and adhesion mechanisms were identified. Modeling of adhesion was carried out to confirm experimental observations and testing. For the latter, the newly-developed **LA**ser **SH**ock **A**dhesion **T**esting, namely **LASAT**, was performed as a flexible and relevant test for thermally sprayed materials. Deliberate substrate microcracking is discussed in the last part as a process to open promising applications for plasma spraying for rapid prototyping and the manufacturing of sensors.

2.0 Materials and Processes

2.1 Substrates

The first type of substrate was commercial MVA200 stereolithography resin (from LASER 3D, Villers-les-Nancy, France) made of a thermoset matrix (diethoxylated bisphenol-A dimethacrylate) with glass particle addition. Spraying experiments were applied to parallelepiped specimens of $15 \times 35 \times 10$, $30 \times 35 \times 10$ or $50 \times 35 \times 10$ mm³ in size.

The second type of substrate was monocrystalline lithium fluoride (LiF) supplied by O.P.A., Villepinte, France. The specimens to be coated were semi discs of 35 mm in diameter (Figure 1) with an optical surface finish of less than 0.0025 μ m (Ra).

2.2 Powders

The sprayed powders were “225NS602” AISI 316 from S.N.M.I., Avignon, France., and “PT-H-50-31” tin

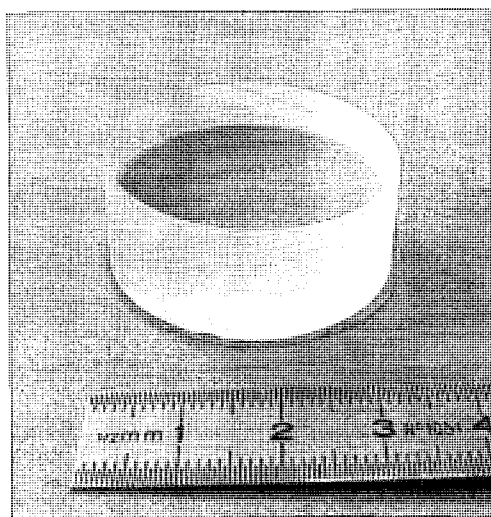


Fig. 1: Lithium fluoride substrate.

from PLASMATEC, Montreal, Canada with a 45 -106 μm and + 60 - 140 μm distribution range respectively.

2.3 Spraying

All spraying experiments were performed in the SULZER-METCO CAPS ("Controlled Atmosphere Plasma Spraying") unit of the C2P ("Center for Plasma Processing") in Evry. These were carried out in the APS ("Air Plasma Spraying") mode for both powders. However, for the spraying of AISI 316 onto MVA200, APS was coupled with the ATC ("Atmosphere and Temperature Controlled") system, which consists of a cooling device using gaseous and/or liquid argon. All spraying tests were duplicated three times at least to study reproducibility.

2.4 Characterization

Substrate temperature prior to spraying (at the pre-treatment stage) and during spraying was real time monitored through thermocouples connected to a computed acquisition system (AX 5232 card by AXIOM and WINATS software by SYSMA) with a sampling rate of 5 s^{-1} . Thermocouples were inserted at a depth of 0.5 mm below the surface when testing MVA200 and located close to the specimen when testing LiF.

Specimen surfaces and cross sections were observed using conventional optical microscopy (ZEISS Axiovert 405 M), confocal microscopy (TRACOR NORTHERN TSM), SEM (PHILIPS PSEM 501), and

high resolution SEM (Gemini field effect LEO982). In addition, a CAMECA SX 50 microprobe and a HOMMEL T 500 tester were employed for microanalysis and roughness measurements.

3.0 Results and Discussion

3.1 Substrate Cracking Process

Controlled cracking can result from heat treatment of the substrate surface prior or simultaneously to spraying.

When applied to MVA200 polymer, heat treating consisted in either plasma torch application on the substrate before powder injection in the spraying operation or pre-treating in an oven outside the spraying chamber. Typical experimental conditions for this process, namely "PINPRO" (i.e. for **P**INning **P**ROcess, see section 1.0), are given in Table 1 and related aspects discussed more thoroughly.¹⁰ For applications, the selection of one of the two processes rather than the other would mainly depend on practical criteria (e.g., size and shape of the part to be coated, time to operate).

When applied to LiF, the most suitable heat treating for cracking was shown to be that due to the impingement of the first sprayed droplets on the substrate. Heat treatment resulted from droplet-to-substrate heat transfer, which led to the solidification of the first coating layer.

3.1.1 Cracking Characteristics

Superficial cracking of MVA200 due to PINPRO is characterized by more or less hexagonal cells (Figure 2), which were the sign of a sort of craze cracking. Crack density and crack depth were optimized as for coating/substrate adhesion (see section 3.2). The optimal vertical crack segmentation of the substrate surface (Figure 3) corresponds to a linear crack density of about 40 cm^{-1} , i.e. one microcrack every 250 μm , combined to a crack depth of about 20 μm (mean value). These values were obtained from a systematic study of cracks as a function of PINPRO conditions.¹¹

Cracking of the LiF surface could occur due to sprayed particle impinging. The number of cracks was Controlled by preheating of the substrate prior to spraying. In contrast with the previously mentioned heat treatment for surface cracking of polymers, this pre-treating of LiF, as in a symmetric role, limits the cracking which is subsequently achieved in the first stages of spraying. This results in an indirect process, the basic mechanisms of which section 3.2 will elaborate. Preheating temperature was determined (near 200°C) to optimize the crack number and distribution for suitable coating substrate adhesion (see section 3.2).

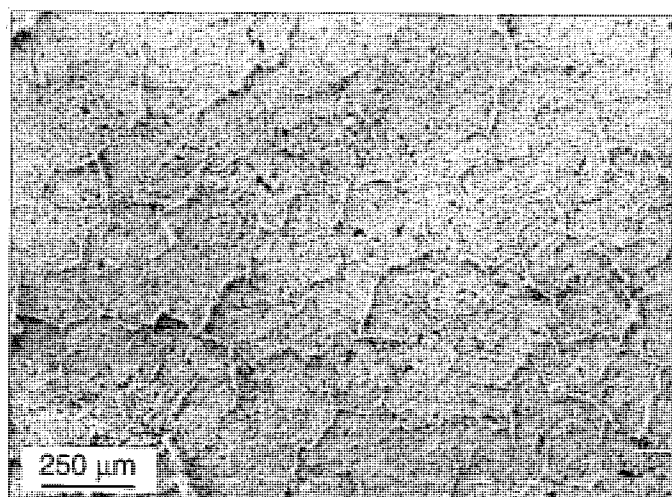


Fig. 2: SEM image of a replica of the optimal network of microcracks at the substrate surface.

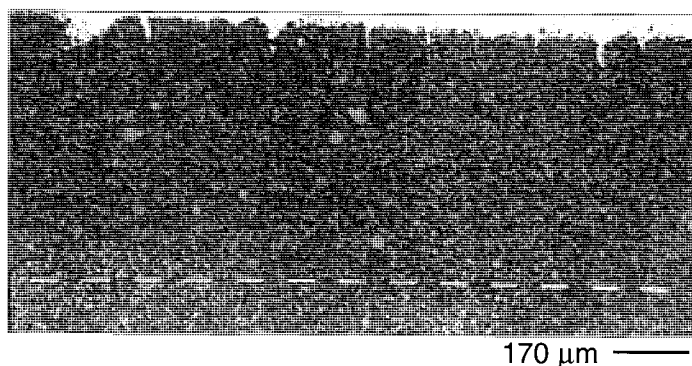


Fig. 3: Cross-section back-scattered SEM image of microcracked MVA200 (with infiltrated metal to reveal the microcracks).

Table 1. Typical PINPRO Pre-Treatment Conditions for MVA200 Using the Plasma Torch

Plasma Gas Flow Rate, $\text{L} \cdot \text{min}^{-1}$	Ar20H ₂ 3He30
Arc Current, A	500
Plasma Flaming Distance, mm	d_{opt}
Number of Torch Passes	20

Cracking could be observed from underneath through the substrate adequately due to LiF transparency (Figure 1). Cracks were shown to be straight and of a length limited to that of the overlaying tin “splat” (Figure 4a). They were uniformly distributed and all the

more numerous because the preheating temperature was low (Figure 4b). When above a certain number, they formed a typical network made of triangles to be related to LiF crystallographic features (see sections 3.1.2 and 3.2.3).

3.1.2 Cracking Mechanisms

Superficial microcracking in MVA200 was a consequence of stresses induced by heating of the heterogeneous structure. The MVA200 substrate was obtained by stereolithography, i.e. from curing a photopolymer resin with a scanning laser beam. This process resulted in a typical structure made of an outer skin (of about 150 μm in thickness) over a bulk of incompletely polymerized resin.

When heated (by an energy source to be more precise) from the plasma torch or in an oven, polymerization took place in the partially cured regions which led to shrinkage of the substrate. On the other hand, there was a conventional thermal expansion in the fully-polymerized skin. These coupled effects led to tensile stresses at the substrate surface and compressive stresses in the bulk. Uniform superficial microcracking formed to relax the tensile stresses.

The cracking mechanism in LiF was quite different from that in polymers (e.g. MVA200) because of quite different properties. Cracking was due to cleavage initiated by a thermal shock at the droplet impact onto the LiF surface. LiF is a thermal shock sensitive material which cleaves along the [001] plane in an f.c.c. lattice. This is consistent with the observation of straight and thin cracks exhibiting preferential orientations (see previous section 3.1.1). Thermal shock was all the more limited as pre-heating was at a higher temperature, which was ascertained by the presence of fewer corresponding cracks.

3.2 Coating/Substrate Adhesion

3.2.1 Adhesion Mechanisms

Adhesion depended on anchoring mechanisms from sprayed material (i.e. AISI 316 or tin)/substrate interlocking through the surface cracks. Anchoring was very efficient and definitely enough to allow for building-up thick coatings (in the [0.5-1 mm] range) (Figures 4b, 5, and 6). Incidentally, one may note that underneath and external views of tin coated LiF are more significant than cross section images to show adhesion. This is because cross section metallographical preparation could not reveal the actual interface due to smearing of LiF by the very ductile tin.

Except for the pinning effect due to microcracks, there was (almost) no adhesion. No additional pegging due to roughness could be achieved because the substrate was smooth (outside the microcracks). The wetting of

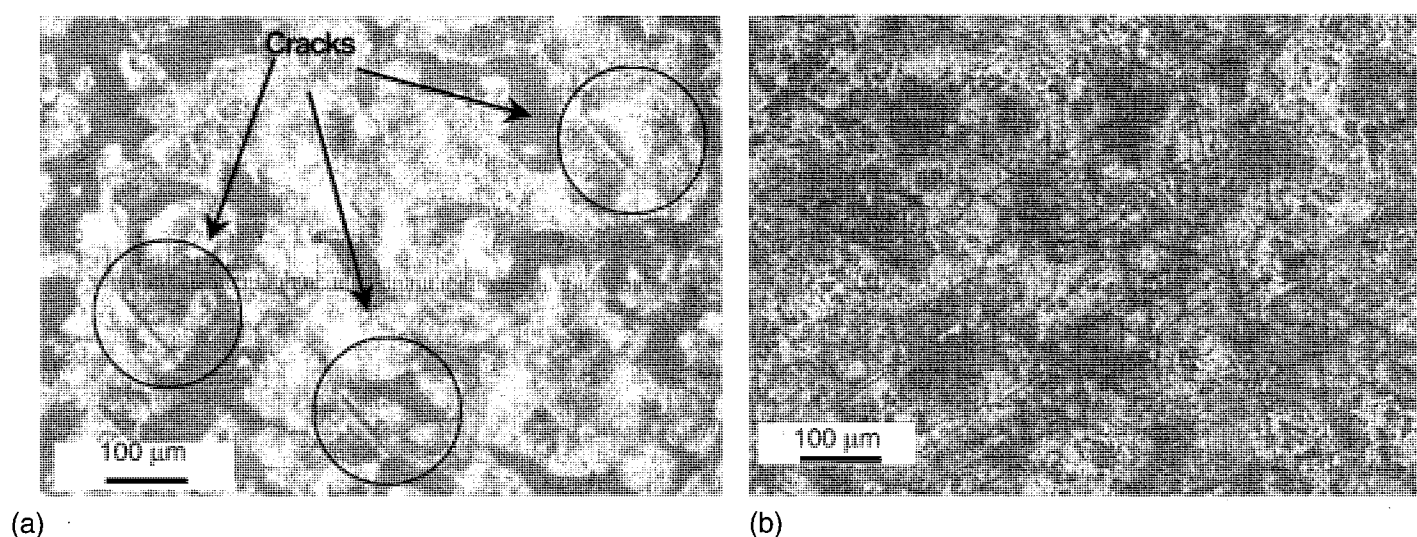


Fig. 4: Optical views of the interface (from underneath) through the LiF substrate exhibiting cracks for two thermal shock conditions, (a) low density of cracks and (b) higher density of cracks.

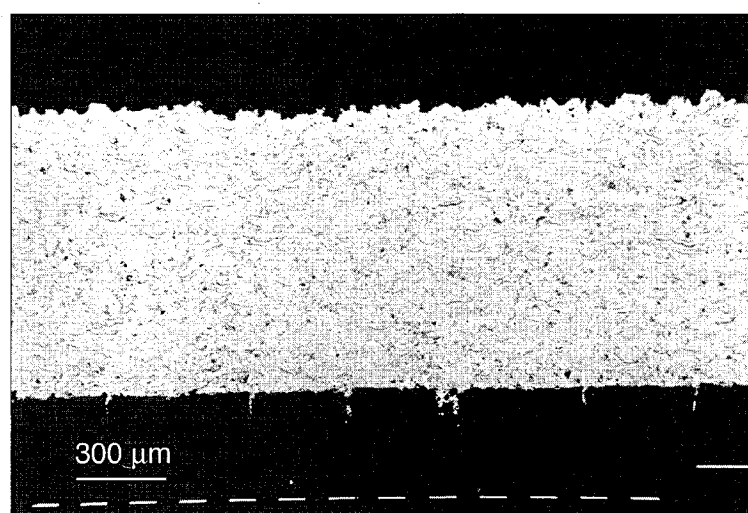


Fig. 5: Cross-section SEM image of plasma-sprayed AISI 316 onto microcracked MVA200.

the substrate by the sprayed droplets (in both examples) was extremely poor, which did not promote any physico chemical bonding. No metallurgical/diffusional adhesion could be achieved due to the non-metallic nature of the substrate. Only the increase in the number of polar links such as C–O, C=O, or C–O–C, due to plasma torch pre-treatment (see section 3.1) could increase adhesion. This was determined in a parallel study,¹⁰ which will not be discussed in this article, using Fourier Transform Infrared Spectrometry (FTIR). However, this effect can be assumed to be negligible compared to anchoring from microcracks.

Anchoring resulted from liquid metal penetration within the substrate through the microcracks. Molten metal could fill the microcracks and solidify to conform closely to the microcrack wall. This phenomenon is due to the high velocity of the sprayed droplet when penetrating the microcrack.

One may assume that for MVA200, glass particles (i.e. the filler in the base resin) contributed to pegging since they might give the microcrack wall some waviness (Figure 7).

For the LiF/tin coating system, the adhesion mechanism was similar to that for AISI 316 onto

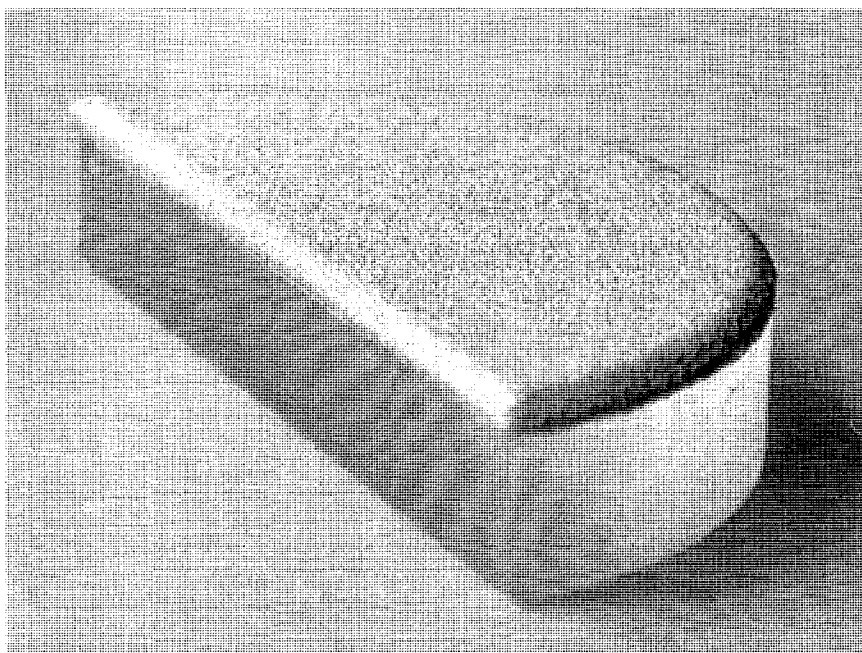


Fig. 6: Typical Sn-coated LiF sample ($\varnothing$ 35 mm).

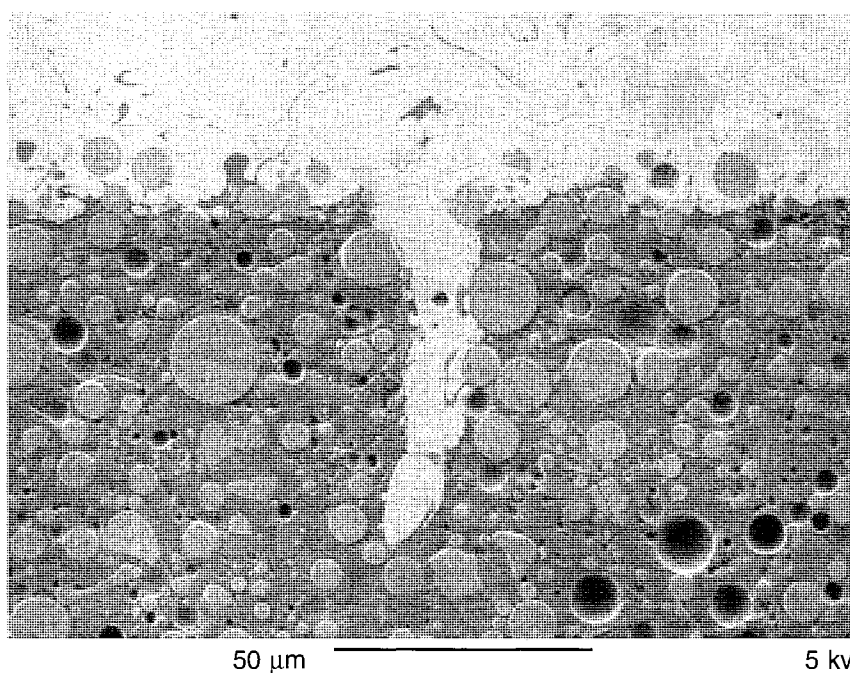


Fig. 7: Cross-section back-scattered SEM image of anchoring microcrack filled by sprayed AISI 316.

MVA200, i.e. anchoring due to microcracks filled with tin from the first impinging particles. Tin coating removal by deliberate (manual) mechanical pulling left typical triangle-shaped LiF fragments stuck to tin (Figure 8). Adhesion of tin was therefore shown to be fairly high.

LiF spalling resulted from some lamellar (brittle) fracture, one may assume, along [111] planes in the LiF f.c.c. lattice. Fragment thickness ranged from 10 to 30 μm , as measured by confocal microscopy, which corresponded to the microcrack depth range.

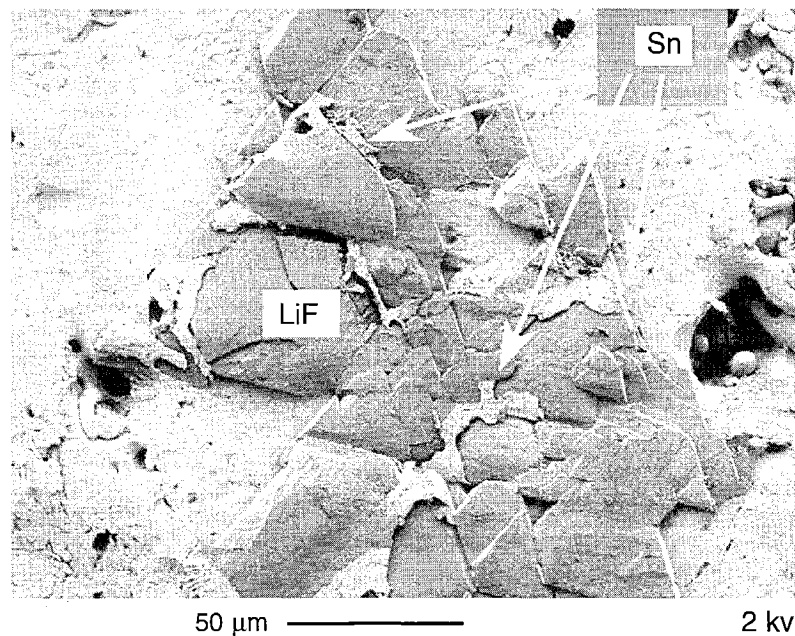


Fig. 8: SEM image of plasma-sprayed Sn coating from underneath.

3.2.2 Modeling of Crack-Pinning Adhesion

Finite element calculations using the ABAQUS® code were applied to an elementary edge of the hexagonal pattern (Figure 9) which simulated the craze cracking microcrack network (Figure 2).

The main assumptions for modeling were :

- The use of elastic calculations,
- No specific role for the triple points of the hexagonal cell,
- A uniform tensile loading (i.e. at a level of 4 MPa) at the material surface, and
- A coating material made of AISI 316 within and topping the cracks and of a low-modulus and low Poisson's ratio material for the remainder, since adhesion was due almost entirely to mechanical interlocking from cracks.

The mechanical properties data for calculations (Table 2) came from the bibliography and from the supplier, except for the coating (for which they were arbitrary).

The size, shape and typical features (e.g. the number of glass particles) of the elementary cell for calculations resulted from thorough experimental observation of numerous coating-substrate interface cross sections coupled with quantitative measurements.

Among the series of results which were obtained for tensile (S_{22}) and shear (S_{12}) stress distributions, this section will focus on the shear stress field in the vicinity of

a given microcrack. The maximum shear stress field was shown to be located near glass particles and at the crack tip (Figure 10). The MVA200 resin shear strength (≈ 10 MPa) outline in the calculated field diagram (Figure 10) corresponded well to the volume of debonded resin after tearing the coating from the substrate. This could be shown by back-scattered SEM imaging of the organic resin (dark phase in Figure 11) stuck to the metal pin and of glass particles which further improved the pegging effect.

3.2.3 Adhesion Tests

Adhesion was measured using LASAT, i.e. **LA**ser **S**hock **A**dhesion **T**esting. LASAT, which was recently developed for thermally sprayed coating adhesion, is based on dynamic loading (strain rate of 10^7 - 10^8 s⁻¹ typically) from a laser shock.¹⁵

Because of the limited number (and cost) of available LiF substrates and to complement the modeling adequately, LASAT was applied to AISI 316-coated MVA200 only. LASAT was carried out at the "Ecole Polytechnique/LULI" Palaiseau, France, using a beam spot 3 mm in diameter, for a 2.6 ns pulse in the confined mode.

LASAT was shown to be suitable for testing with satisfactory reproducibility. The surface after spalling exhibited an adhesive rupture at the coating substrate interface and a cohesive rupture within the substrate at

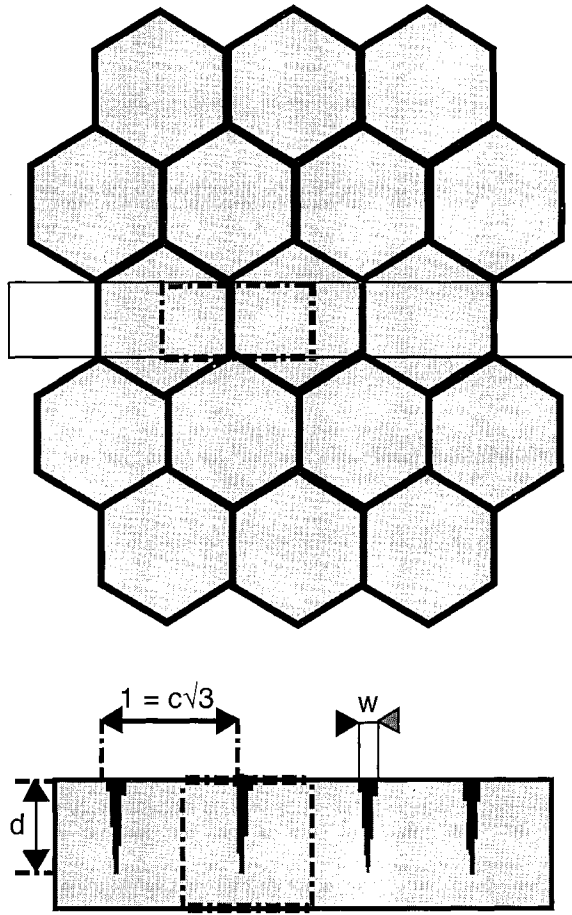


Fig. 9: Schematic illustration of the microcrack network used for the modeling of anchoring. Top view and cross-section of the pattern exhibiting an elementary cell.

Table 2. Mechanical Properties Data for Calculations

	Young's Modulus (E, GPa)	Poisson's Ratio (ν)
Stereolithography Resin Matrix ¹²	2.0	0.35
Glass Particles	69.0	0.17
Thermally-Sprayed AISI 316 ^{13, 14}	75.0	0.25
Low E, ν Coating Material	0.1	0.005

the crack sites. This confirmed the previously discussed adhesion mechanism.

Actual calculations of the adhesion strength could not be achieved since shock wave propagation

characteristics in MVA200 were not known at the time of the tests (additional calibration tests remained to be done). This is required to calculate pressure, thus stress vs. time from the state equation. However, a good semi-quantitative approach to adhesion strength could be performed. It was based on the comparison of the threshold laser fluence, i.e. that above which the coating started to debond, from these tests with that from others carried out in similar conditions (by the same team) for another metal polymer system also, i.e. plasma sprayed Al/PET.¹⁶ The comparison showed that adhesion ranged from 5.0 to 8.0 MPa. This is in keeping with the results of analytical modeling of adhesion strength, key points of which are given below.

With basic assumptions similar to those used in the finite element analysis discussed in section 3.2 (i.e. elasticity conditions, homogeneous and isotropic materials, an hexagonal elementary cell,) and assuming a dihedral shape for the crack, calculations led to the expression of the adhesion strength, $\sigma_o^{\max}$, as:

$$\sigma_o^{\max} = \frac{2}{\sqrt{3}} \cdot \frac{w}{c} \left(1 + \frac{4d^2}{w^2} \right) \cdot \sigma_n^{\max}$$

$$= \frac{1}{\sqrt{3}} \cdot \frac{1}{d \cdot c} (w^2 + 4d^2) \cdot \sigma_T^{\max}$$

with

- $\sigma_n^{\max}$ is the maximum normal stress at the substrate coating interface in the crack,
- $\sigma_T^{\max}$ is the maximum tangential stress at the substrate-coating interface in the crack,
- d is the crack depth,
- w is the crack width, and
- c is the edge length of the hexagonal cell.

Using the following rather conventional rupture criterion,

$$\left(\frac{\sigma_n^{\max}}{\sigma_T} \right)^2 + \left(\frac{\sigma_T^{\max}}{\sigma_s} \right)^2 = 1$$

with

- σ_T is the tensile rupture strength and
- σ_s is the shear rupture strength

one can express $\sigma_n^{\max}$ and $\sigma_T^{\max}$ (therefore $\sigma_o^{\max}$) as:

$$\sigma_n^{\max} = \frac{36}{\sqrt{1 + \frac{144d^2}{w^2}}}$$

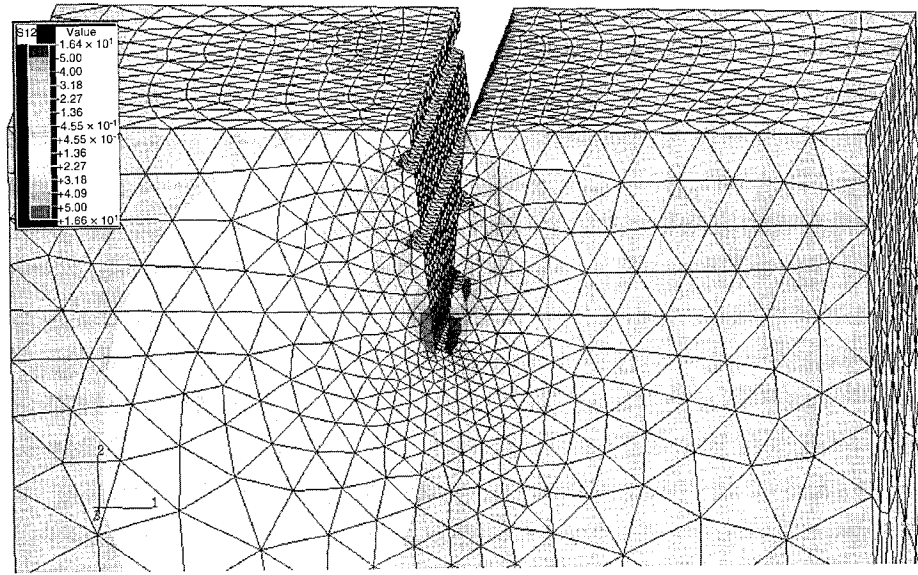


Fig. 10: Shear stress field at the vicinity of an anchoring superficial crack in MVA200.

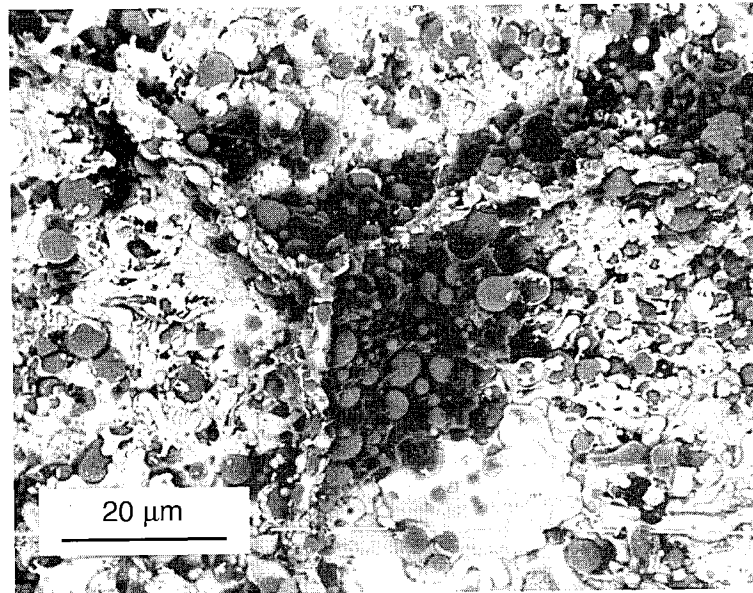


Fig. 11: Back-scattered SEM image (from underneath) of plasma-sprayed AISI 316 after de-bonding at a triple point.

$$\sigma_T^{\max} = \frac{2d}{w} \cdot \frac{36}{\sqrt{1 + \frac{144d^2}{w^2}}}$$

taking (from the bibliography) 36 and 6 MPa as respective values for σ_T and σ_S .

Numerical application led to $\sigma_n^{\max} = 0.75$ MPa, $\sigma_T^{\max} = 6.00$ MPa, and $\sigma_o^{\max} = 6.36$ MPa: the latter in keeping with experimental measurements.

4.0 Conclusion

This study demonstrated that deliberate superficial microcracking of the substrate can promote mechanical anchoring of a thermally sprayed coating to the substrate surface. This establishes an innovative substrate treatment prior to spraying, which exhibits significant advantages compared to conventional sand blasting or bond-coating. These advantages rest on the fact

that neither removal nor addition of any material is needed.

Controlled microcracking was shown to be feasible by heat treating when applied to acrylate MVA200 resin and LiF. However, from the study of the basic mechanisms in both crack formation and resulting anchoring capabilities, the process can lend itself to a large range of materials, primarily polymers, ceramics and other crack-generating materials.

Modeling of coating substrate adhesion due to anchoring/pinning from cracks was developed using a finite element analysis. The results from modeling were in keeping with experimental observation and measurements of adhesion. The latter was determined using newly developed LASAT (LAsER Shock Adhesion Testing) which is very promising for application to thermally-sprayed coating systems.

Microcracking was shown to be a fairly flexible process which can result from different heat treatments such as plasma flaming, conventional furnace/oven treatment or local thermal shock treatment due to sprayed droplet impinging. This flexibility allows for controlling the type, level and distribution of microcracking and adhesion. When applied to a stereolithography resin, this (patented) process, namely "PINPRO" (for PINning PROcess), opens the road for plasma spraying in advanced rapid prototyping / tooling. This exploits the above-mentioned capability in controlling adhesion (including that of thick deposits) and in retaining substrate soundness and morphology (except for the cracks).

Further development are also expected in the field of coated systems in physics research. Optical pyrometric measurements (OPM) were tested successfully from the above results on tin coating of LiF.

5.0 Acknowledgments

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Residual Stresses in MoN and Mo₂N Coatings Deposited by Arc PVD on High Speed Steel Substrate

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Abstract

Polycrystalline MoN and Mo₂N films have been deposited by chemical vapor deposition (CVD), magnetron sputtering and arc PVD techniques. They have interesting physical and mechanical properties, which made them candidates for wear and corrosion resistant coatings and diffusion barriers in microelectronics. The residual stresses in MoN and Mo₂N films consist of thermal stress and growth stress or intrinsic stress generated during deposition. The magnitude of measured residual stress in the film depends on

process parameters such as temperature, bias voltage, gas pressure, substrate, deposition time, and film thickness. It is important to measure residual stresses in the MoN and Mo₂N coating to estimate and interpret the adhesion, wear and hardness correctly. Residual stresses in these coatings were measured by XRD using the Rocking and the Fixed Incident Multiplane techniques. Residual stresses in Mo₂N (f.c.c) and in MoN (hexagonal) films were about 5 and 10 GPa (compressive) respectively. These results were discussed with respect to the elastic constant, crystal structure and deposition condition of MoN and Mo₂N films.

Table 1. Residual Stresses in (Ti, Al, and Cr) N Coatings and Elastic Constants Used for Residual Stress Calculation

Materials	Residual Stresses (GPa)	Elastic Constants of Films Used in Stress Calculation (GPa)
TiN on Stainless Steel	-10 to -2 (0 to -400V)	640 (Ref.8 cited in Ref.5)
TiAlCrN on A2 Steel	-3.8	410 (Nanoindentation) ⁸
TiN on HSS Substrate	-4.6	425 (Tensile Testing) ⁶
TiN on Stainless Steel	-10	640 (Bulk Elastic Constant) ⁸

1.0 Introduction

Polycrystalline MoN and Mo₂N films have been grown by chemical vapor deposition (CVD), (rf) magnetron sputtering and arc PVD.¹⁻³ They have interesting physical and mechanical properties, which made them candidates for wear and corrosion resistant coatings and diffusion barriers in microelectronics. The transition metal nitrides such as ZrN, HfN, and TiN have been extensively studied for these applications. On the other hand, there have been a few researches on Mo-N system.¹⁻³ The Mo-N system was reported to have several stable bulk phases, γ -Mo₂N (face center cubic (f.c.c) and tetragonal) and δ -MoN (hexagonal) phases.¹⁻³ The γ -Mo₂N (f.c.c) and δ -MoN (hexagonal) films, and mixed films were successfully grown by CVD, arc PVD and (rf) magnetron sputtering techniques on several substrates such as Ti, HSS, silicon wafers and glass.^{1, 2, 4}

Their mechanical and physical properties promise some advantages compared to other hard coatings such as TiN and (Ti, Al) N. For example, the hardness of δ -MoN (hexagonal) film (5000 HV) is greater than the hardness of TiN and TiAlN (2200-3500 HV).^{3, 5, 6} The wear resistance of Mo-N system is 14 times greater than that of the TiN films.³

Hardness, adhesion and wear properties of the hard coatings are influenced by residual stress in a film resulted from a deposition process.^{5, 7} The residual stress consists of thermal stress resulted from cooling after deposition due to differences in the thermal expansion coefficient of the film and substrate, and growth stress or intrinsic stress generated during deposition. The magnitude of measured residual stress in the film depends on process parameters such as temperature, bias voltage, gas pressure, substrate, deposition time, and film thickness.^{5, 7} It is important to measure residual stresses in the coatings such as TiN and MoN to estimate and interpret the adhesion, wear and hardness correctly.

In the literature, reported residual stress data for the same coating such as TiN differed significantly.⁶⁻⁸

The differences are believed to be due to differences in bias voltage, temperature, gas pressure, deposition process and elastic constant of films used for stress calculations, Table 1.

There are a number of ways to obtain an elastic modulus of the film or coating. These are

1. Indentation technique,
2. Tensile testing,
3. Beam bending, and
4. Method based on elastic wave generation.^{6, 9}

The bulk elastic constant of TiN was quite different from the thin film elastic constant obtained by the indentation technique and tensile testing, Table 1. The indentation and tensile testing techniques gave similar results as about 400 GPa for the TiN coatings. One reason for differences in the calculated residual stress in Table 1 is certainly due to using different elastic constant for TiN film. In this paper, the elastic constants of MoN (450 GPa) and Mo₂N (370 GPa) calculated by indentation technique were used in the residual stress calculations.³

Residual stresses in MoN (hexagonal) and Mo₂N (f.c.c) coatings deposited on HSS substrate were measured using XRD techniques; Rocking and Fixed Incidence Multi-Plane Technique (FIM).

1.1 X-ray Stress Measurement Techniques

In XRD strain measurement, the strain, $\epsilon_{\phi\psi}$ is defined as differences in a “d” spacing for unstressed and stressed lattice, as shown in eqn. 1. After assuming that the film is isotropic and the stress-state is biaxial, and inserting Hooke’s law, residual stress in the film is calculated using the eqn. 1.¹⁰

$$\epsilon_{\phi\psi} = \frac{d_{\phi\psi} - d_0}{d_0} = \frac{1+\nu}{E} \cdot \sigma_{\phi} \sin^2 \psi - \frac{\nu}{E} (\sigma_{11} + \sigma_{22})$$

$$\sigma_{\phi} = \sigma_{11} \cos^2 \phi + \sigma_{12} \sin 2\phi + \sigma_{22} \sin^2 \phi$$
(1)

The strain in eqn. 1 is associated with a particular set of (hkl) plane in a laboratory coordinate system,

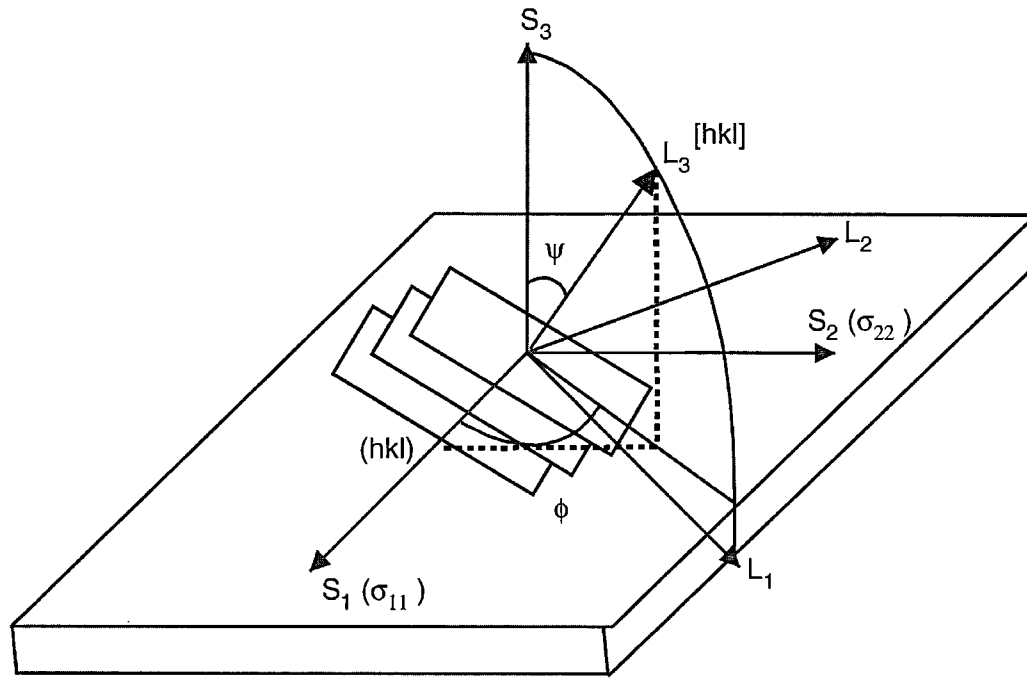


Fig. 1: Definition of the laboratory coordinate system (L_i) and surface coordinate system (S_i).

Figure 1. d_{ψ} is the lattice spacing of (hkl) planes tilted by ψ and rotated by ϕ within the plane of film with respect to axes S_i and d_0 is the strain-free lattice spacing. The stress in the volume of interest (film) is defined in the surface coordinate system (Figure 1). The terms E , ν , σ_0 are the elastic constant, Poisson ratio and normal stress in the ϕ direction. In “Sin² ψ ” technique, the stresses are calculated from the slope of the $\epsilon_{\phi\psi}$ or d_{ψ} vs. Sin² ψ plot.

The “Sin² ψ ” technique is commonly used to measure residual stresses in films.¹⁰⁻¹³ Classical technique for determination of the d vs. Sin² ψ plot is the “Rocking” technique. In this technique, the only one selected set of (hkl) plane is used for the measurement, Figure 2. In the FIM technique, the low incidence limits the diffraction within a thin layer, Figure 3. Fixed low incidence can be used for diffraction with different sets of (hkl) planes and the result can be analyzed with the “Sin² ψ ” technique using eqn. 1.^{8, 10-13} The FIM technique makes use of the multiple (hkl) planes as the ψ tilt. The angle ψ in the fixed incidence geometry in Figure 3 is defined as $\theta_b - \alpha$. The α is the angle of incidence. If one uses the “Sin² ψ ” technique to plot data as $\epsilon_{\phi\psi}$ vs. Sin² ψ for the (hkl) planes, the stress is obtained from the slope of the line as described previously (eqn. 1). The intercept values of the “ d ” and “ a ” were used in the place of d_0 and a_0 , the terms in eqn. 1, since this did not introduce significant error in the stress calculations.¹⁰⁻¹⁴

2.0 Experimental Details

The MoN and Mo₂N films were prepared using the arc PVD process described in detail in Ref. 3. The thickness of the MoN and Mo₂N films were 1.7 and 2.7 μm respectively. The process parameters were listed in Table 2. The XRD patterns of MoN (hexagonal) and MoN (f.c.c) were analyzed and shown in Figures 4 and 5.

Residual stresses in both Mo₂N and MoN films deposited by arc PVD process were measured by XRD using the Rocking and FIM techniques. The Rocking and FIM techniques were performed in a Philip’s diffractometer with a CuK α line source. In all cases, parallel beam optics with a flat graphite monochromator and a proportional counter were used. The diffractometer was aligned using silicon sample.

In the Rocking technique, the specimen was offset to obtain data at different “ ψ ” angle. A Bragg peak from a particular (hkl) plane was obtained for each “ ψ ” angle, Figure 2. The (hkl) planes selected, considering overlaps and higher two theta angles, were (420) plane for MoN and (422) plane for Mo₂N. After applying the absorption and Lorenz Polarization Factor corrections to data, the position of the Bragg peak ($2\theta_b$) was determined using curve fitting program. During curve fitting, the $2\theta_b$ of the K α 1 was determined by this program and then converted to “ d ”-spacing. The data were plotted as “ d ” vs. Sin² ψ . Residual stress was calculated from the slope

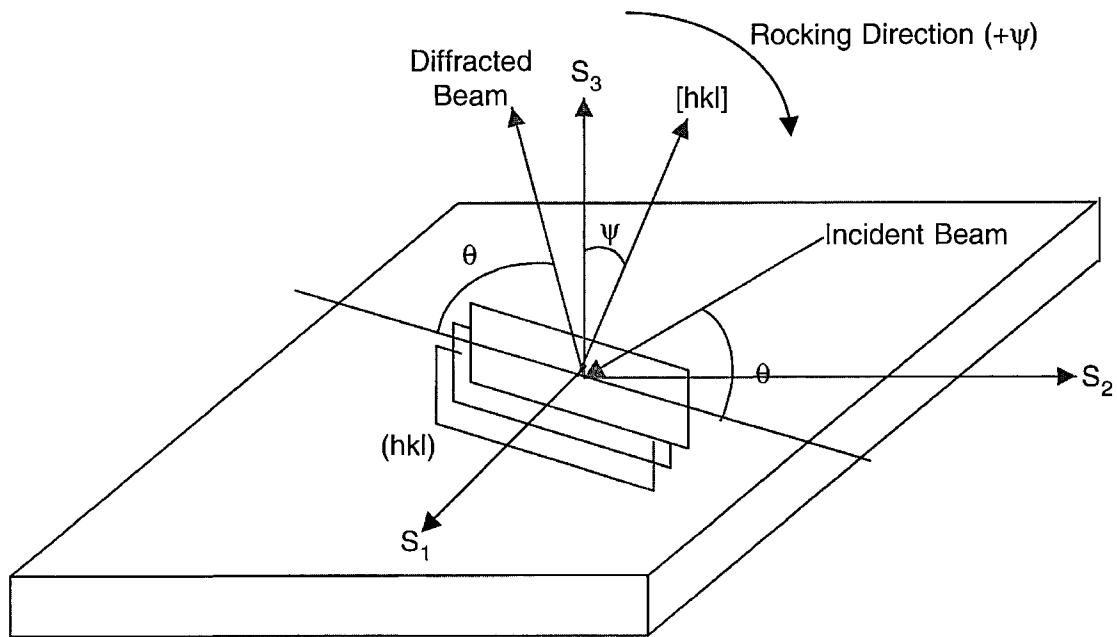


Fig. 2: Schematic of the rocking technique.

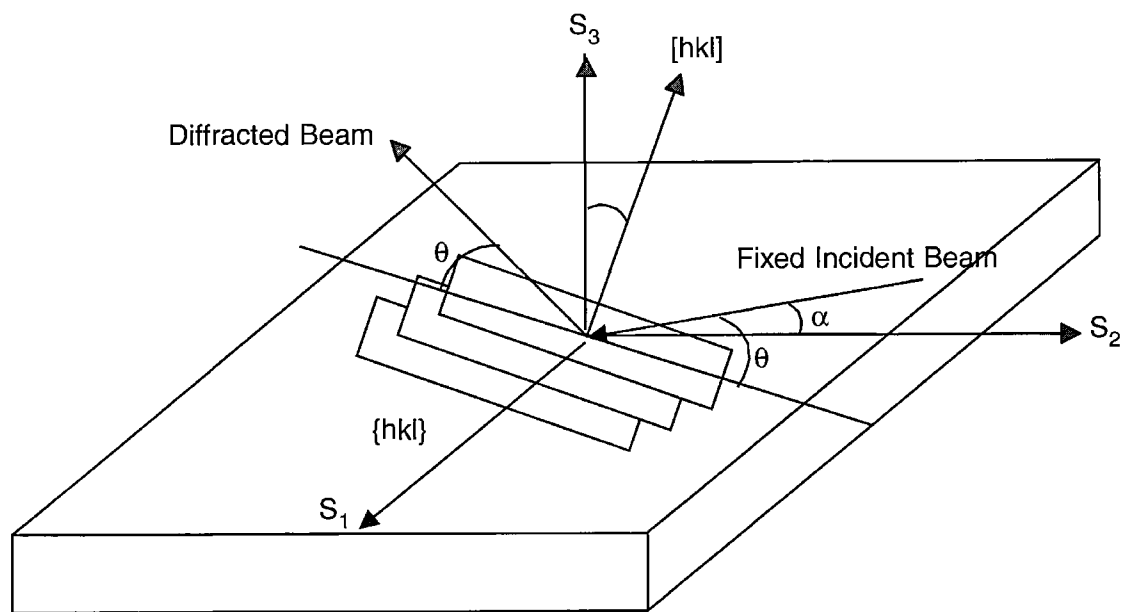


Fig. 3: Schematic of the Fixed Incidence Multiplane technique (FIM).

Table 2. Deposition Conditions of MoN and Mo₂N Films

P	Bias: -150 V (MoN)				Bias: -250 V (Mo ₂ N)			
	q	T _{first}	T _{last}	s	q	T _{first}	T _{last}	s
1.9	39	398	420	106 + 600				
0.8					27	410	510	90 + 600

P: N₂ Pressure (Pascal)

q: Gas flow amount (sscm)

T_{first}: Coating start temperature, **T_{last}:** Coating finish temperature (°C)

s: Mo interface forming time and gas pressure balancing time + Coating time (sn)

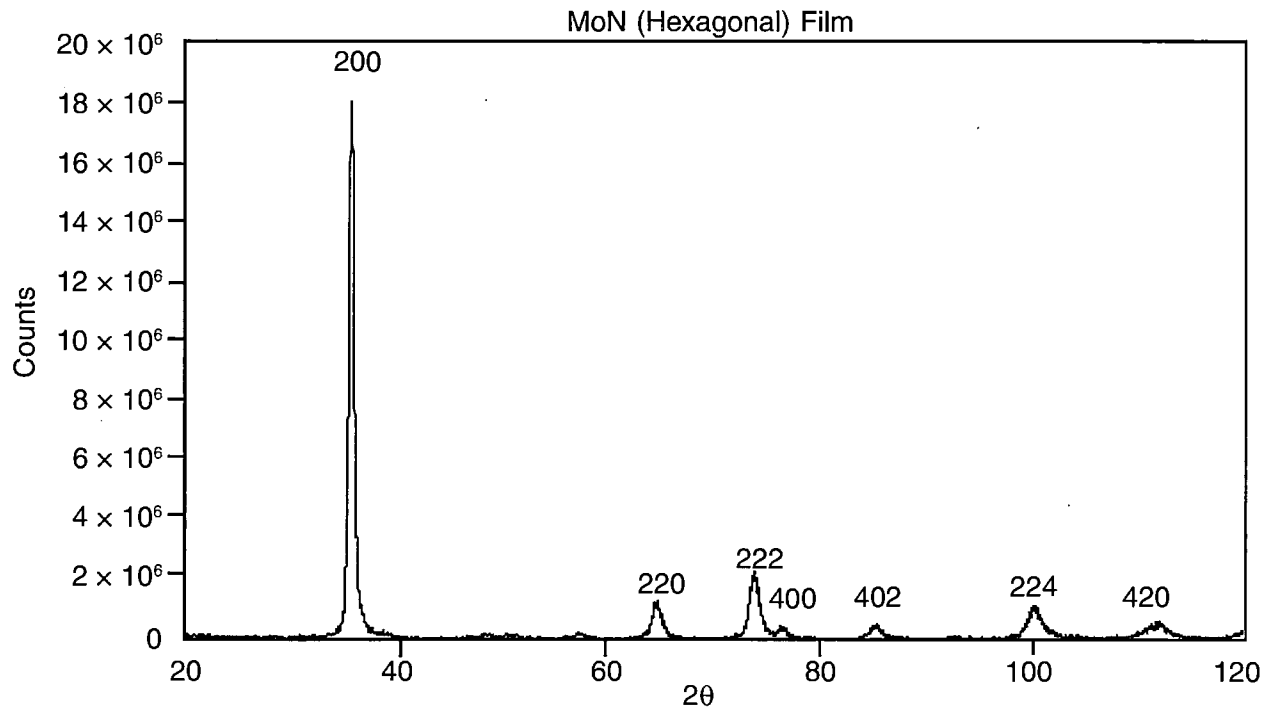


Fig. 4: The XRD patterns of MoN (hexagonal) film obtained by the thin film diffraction.

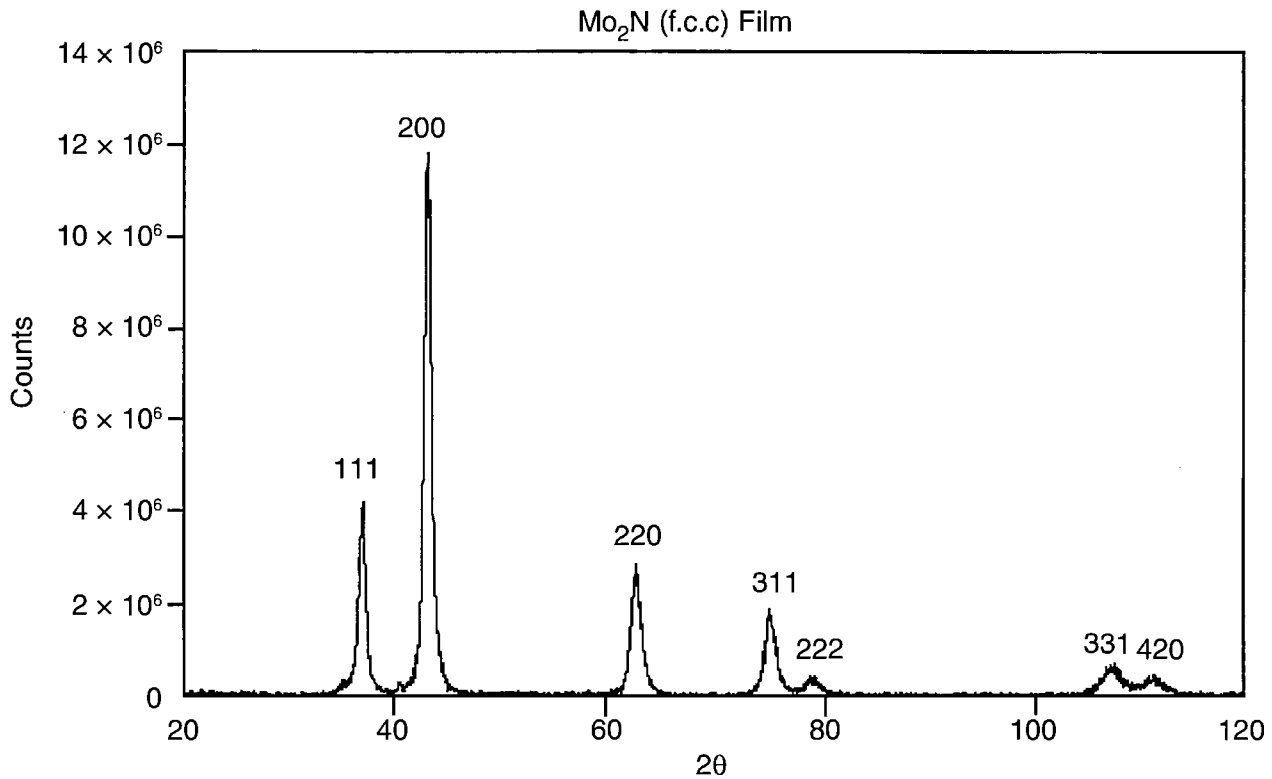


Fig. 5: The XRD patterns of Mo₂N (f.c.c) film obtained by the thin film diffraction.

of the d vs. $\sin^2\psi$ plot using the eqn. 1. The elastic constants used to calculate the residual stresses in MoN and Mo₂N films were 450 and 370 GPa respectively.³

FIM technique was also used to measure the residual stresses in MoN and Mo₂N films. In this technique, the sample position was fixed and more than one Bragg peaks were scanned as a “ ψ ” angle, Figure 3. The incident angle, α was selected as 1.5° for MoN and

3° for Mo₂N to eliminate the intensities and the effect of substrate. After applying the absorption and Lorenz Polarization Factor corrections to data, the position of the Bragg peak ($2\theta_b$) was found using curve fitting program and was converted to “ d ”-spacing. The residual stress was obtained from the slope of the line as described previously (eqn. 1) after plotting data as $(a_{\phi\psi})$ or $\epsilon_{\phi\psi}$ vs. $\sin^2\psi$ for the (hkl) planes. The “ $d_{\phi\psi}$ ”-spacing was

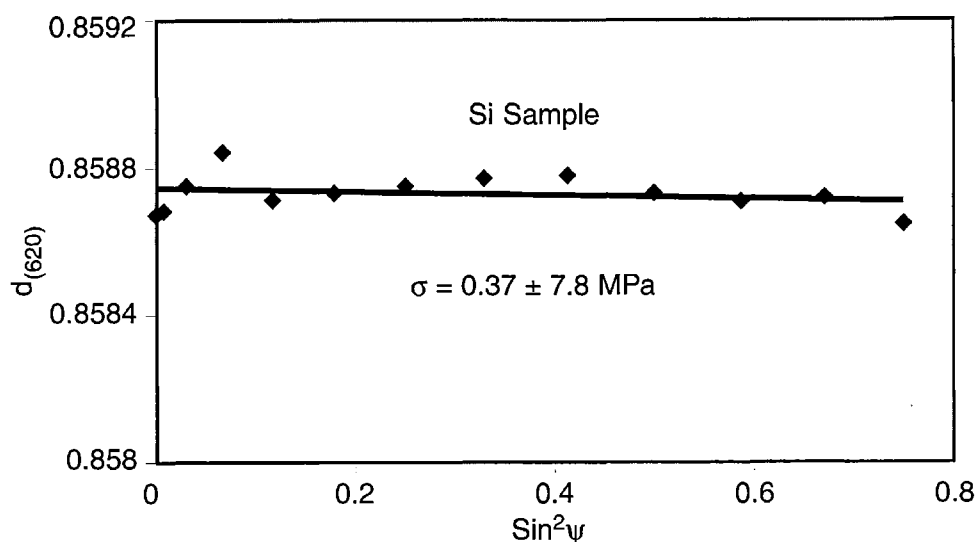


Fig. 6: The d vs. $\text{Sin}^2\psi$ for silicon sample determined by the rocking technique.

converted to " $a_{\phi\psi}$ " for cubic Mo_2N film and $\epsilon_{\phi\psi}$ was used for the hexagonal MoN . The statistical errors in measured residual stresses were calculated using "Excel" linear regression software. Error bars in measured residual stresses were calculated based on 80% confidence level and using "t" statistics. Due to small number of data point, the error bars might be high especially for the FIM technique.

3.0 Results and Discussion

Residual stresses in MoN and Mo_2N films were measured by XRD stress measurement techniques; Rocking and FIM techniques. Before the stress measurement, the diffractometer was aligned with silicon sample and stress-free silicon sample was used to check this alignment during stress measurement by the rocking technique.

Figure 6 shows the d vs. $\text{Sin}^2\psi$ for silicon sample measured by the Rocking technique. The measured stress was 0.37 ± 7.8 MPa close to zero if indeed existed. This result indicated that the alignment was stable during the stress measurement.

Residual stress in MoN and Mo_2N films were measured by the Rocking technique, the (422) plane, ($2\theta_b$ is 128°) for Mo_2N film and the (420) plane, ($2\theta_b$ is 110°) for MoN film were selected for two reasons: higher possible $2\theta_b$ value and not overlapping with substrate peaks. The results were shown in Figures 7 and 8. The residual stresses were calculated from the slope of the d vs. $\text{Sin}^2\psi$ plot for both films using eqn. 1. In eqn. 1, the elastic constant is assumed to be isotropic. The elastic

constants of films used were 450 GPa for MoN and 370 GPa for Mo_2N films. In the literature, usually the elastic constant of films was assumed to be isotropic and single elastic constant was generally used.^{5,6,8} Slope of the plots of d vs. $\text{Sin}^2\psi$, (e.g. Figure 7) was found to be same for different rotation angle ϕ (0 and 45°), indicating that the stress-state was equal-biaxial ($\sigma_{11} = \sigma_{22} = \sigma$). These results were expected for both films because of the way the deposition processes taken place.³ Residual stresses measured in MoN and Mo_2N films were 10.8 and 4.2 GPa compressive.

Residual stresses in MoN and Mo_2N films were also measured using the FIM technique. In the FIM technique, the substrate effect such as overlapping can be eliminated by using low incidence angle (α). The 1.5° and 3° of low incidence angles were selected for MoN and Mo_2N films respectively. This technique becomes the only available technique in the case of substrate and coating diffraction peak overlapping. In our case, even though, there was a peak that did not overlap with the substrate, FIM technique was used to compare the results obtained by the rocking technique for both films. Different (hkl) planes were used to obtain the plot of the $a_{\phi\psi}$ or $\epsilon_{\phi\psi}$ vs. $\text{Sin}^2\psi$, Figures 9 and 10. The plots were straight line, indicating that each plane had the same elastic constant. Another word, the planes were isotropic and the single elastic constant could be used for these planes. This result pointed out that the assumption of the isotropy in elastic constant for Mo_2N and MoN films in eqn. 1 was correct. The residual stresses were calculated from the slope of the lines in Figures 9 and 10. These stresses were 8.7 GPa for MoN and 3.5 GPa for Mo_2N films.

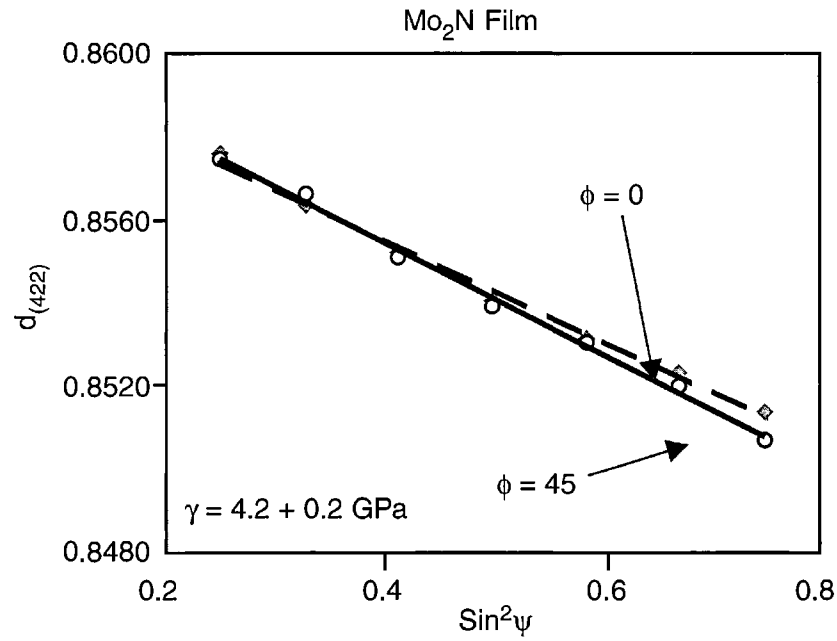


Fig. 7: The d vs. $\text{Sin}^2\psi$ plot for Mo₂N (f.c.c) film determined by the rocking technique with rotation angle (ϕ) of 0 and 45°.

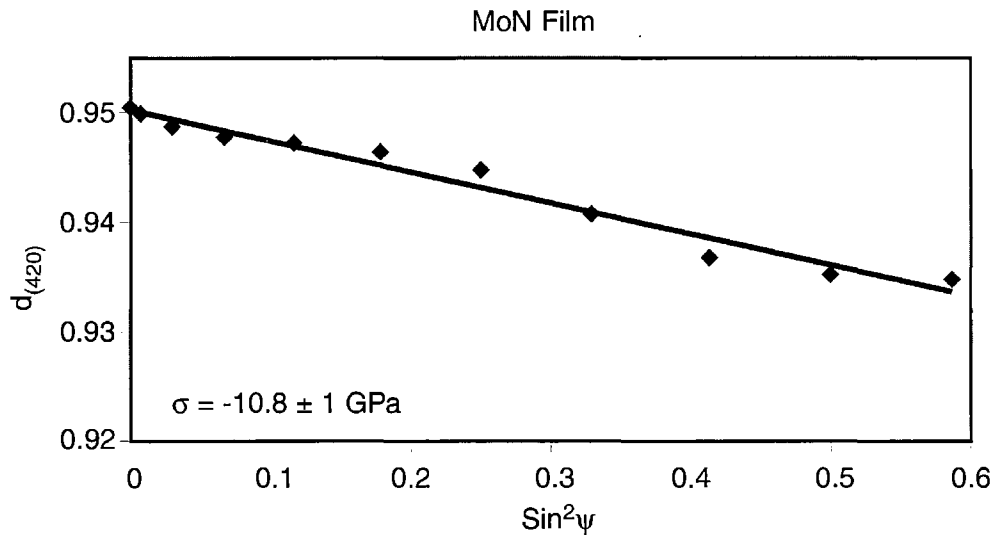


Fig. 8: The d vs. $\text{Sin}^2\psi$ plot for MoN (hexagonal) film determined by the rocking technique.

In Table 3, the residual stresses in MoN and Mo₂N films measured by both Rocking and FIM techniques were given. The residual stress in MoN (hexagonal) film was about two times greater than the residual stress in Mo₂N (f.c.c) film in both techniques. A number of reasons may be accounted for the differences. Residual

stresses in these films resulted from the growth and thermal stresses. Therefore, differences in one of these stresses vary the residual stresses. The process parameters such as bias voltage, temperature, gas pressure, deposition times determine the growth kinetic and morphologies developed during deposition. As a

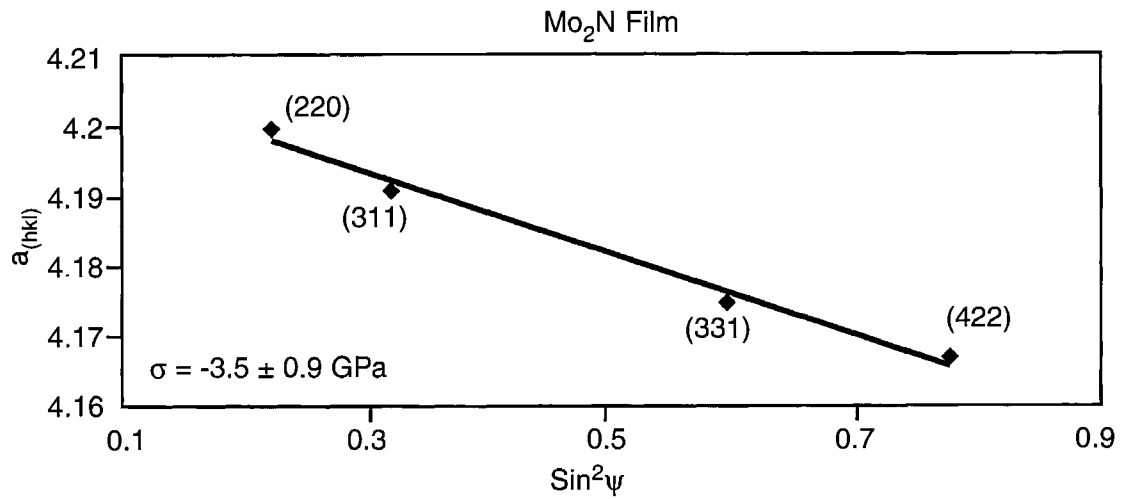


Fig. 9: The plot of the $a_{\phi\psi}$ vs. $\sin^2\psi$ determined by the FIM technique for Mo_2N film.

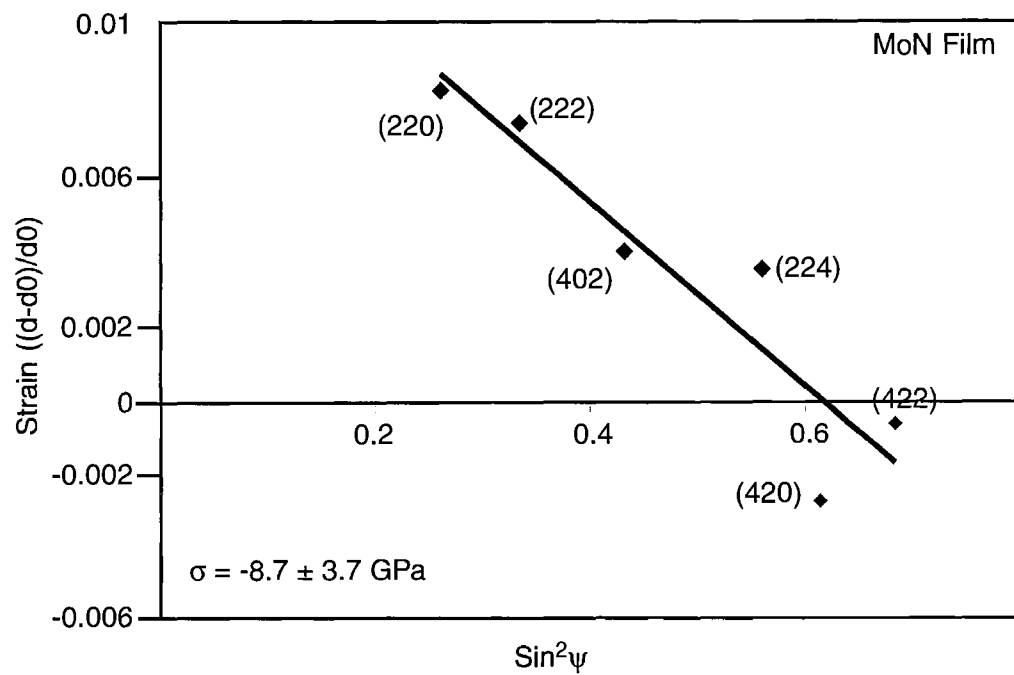


Fig. 10: The plot of the $\epsilon_{\phi\psi}$ vs. $\sin^2\psi$ determined by the FIM technique for MoN film.

Table 3. Residual Stresses in MoN and Mo_2N Films Measured by the Rocking and FIM Techniques

Coatings	Residual Stress Measured by the Rocking Techniques (GPa)	Residual Stress Measured by the FIM Tech. (GPa)
MoN (Hexagonal)	-10.8 ± 1	-8.7 ± 3.7
Mo_2N (f.c.c)	-4.2 ± 0.2	-3.5 ± 0.87

Poisson Ratio (ν) used was 0.3.

result, the growth and thermal stresses in these films depend on the process parameters.

Thermal stress can be calculated if the thermal expansion coefficients of both films are known. The thermal coefficient of the MoN was not found in the literature. Thus, thermal stress in MoN and Mo₂N films cannot be compared even though it is expected to be different due to crystal structure and elastic constant differences. The elastic constant of MoN (450 GPa) was 22% greater than the elastic constant of Mo₂N (370 GPa). In X-ray measurement, the strain-state of a film was measured and the stress was calculated using eqn. 1 with appropriate elastic constant. The part of the differences in the residual stress measured by the XRD resulted from the differences in elastic constant. Still, there are about 80% differences in the residual stresses in between MoN and Mo₂N films to be explained.

The bias voltage of MoN and Mo₂N film depositions was -150 and -250 V respectively, Table 2. This difference might be significant to affect the residual stress. Bendavid, Magnus Oden, and Karlsson observed that as the bias voltage increased the residual stresses changed significantly.^{5, 14, 15} The change in growth stress or intrinsic stress were explained by the model proposed by the Davis.¹⁶ They noted that the growth stress increased as the bias voltage increased at high bias voltage range (-200 to -800 V). Davis' model is based on the steady state of defect creation and annihilation rates. More research needs to be performed to investigate the effect of the bias voltage on the residual stress for MoN and Mo₂N films. After such a research, the differences in residual stress in these films can be clearly understood.

4.0 Conclusions

1. Residual stress (about -10 GPa) in MoN (hexagonal) film was two times greater than the residual stress (about -5 GPa) in Mo₂N (f.c.c) film. More research needs to be done to explain these differences found between MoN and Mo₂N films.
2. The FIM and Rocking techniques gave similar results, Table 3, indicating that both techniques could be used to measure the residual stresses in MoN and Mo₂N films. In case of overlapping and thin films, the FIM technique would be the only available technique to be used for residual stress measurement.
3. The residual stress measurement data by the FIM technique indicated that MoN and Mo₂N films had isotropy in elastic constant and the assumption made in the eqn. 1 was correct.
4. The stress-state of the both film determined by the Rocking technique was equal-biaxial.

5.0 Acknowledgments

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A Study of Grain Boundary Precipitation During Plasma Nitriding of Steel

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Table 1. Chemical Composition of HSS AISI M2 (in wt.%)

C	Cr	Mo	V	W	Si	Mn	Ni	Fe
0.83	4.31	5.11	1.77	6.60	0.32	0.31	0.20	Bal.

Abstract

The grain boundary precipitation observed after plasma nitriding of HSS AISI M2 was investigated. Samples were nitrided at temperatures between 450 to 550°C and characterized by Glow Discharge Optical Spectroscopy (GDOS) and Transmission Electron Microscopy. The Linear Muffin-Tin Orbital Method (LMTO) was employed to calculate total energies of nitrides and carbides as a function of the lattice parameters in order to obtain the total energy at equilibrium volume, which allows a discussion of their stability. It is suggested that during nitriding, nitrogen exchanges carbon in alloy carbides to produce nitrides. Thereby carbon would be released and work as a driving force to grain boundary precipitation.

1.0 Introduction

Plasma nitriding of steel components can produce numerous advantages as it improves tribological properties,^{1,2} fatigue strength,^{3,4} load bearing capacity⁵ and corrosion properties.⁶ Nevertheless all this advantages, a brittle layer sometimes is produced on the top of high alloy steels. It was showed in previous work¹ that plasma nitriding of HSS AISI M2 steel at 550°C results in very low toughness for nitrided layer. However, after nitriding at temperatures below 450°C a homogeneous layer is produced resulting in excellent mechanical properties.

Usually it is reported^{7,8} that compound layer is brittle but it was showed that the main factor to cause the brittleness is the grain boundary precipitation. After nitriding at high temperature, say 550°C, a intense grain boundary precipitation is observed. But no such grain precipitation is observed below 450°C. Results indicated that the grain boundary precipitation is cementite Fe₃C. This hard phase at the grain boundary significantly reduces the toughness of nitrided material.

Therefore the present paper intend to investigate what is happening in atomic level when nitrides precipitates, why cementite is produced in the grain boundary when nitriding is performed at 550°C and also discuss where the carbon comes from to produce cementite. For better understanding the problem, theoretic tools are used for allowing to treat the phenomena isolated. In this

way was possible to study the Cr₂₄C₆ and Cr₄N compounds. First is presented the experimental results and in the second moment is discussed the compounds stability. Finally is present the changes that occur by nitrogen pressure in HSS AISI M2 material.

2.0 Methods

2.1 Material and Sample Preparation

The substrate material used in the present investigation was the high speed steel AISI M2. Table 1 shows the chemical composition of the samples. The specimens in the form of discs (φ 16 × 12 mm) were submitted to the following heat treatment: austenizing temperature 1200°C, cooling media: oil, double tempering at 550°C for 2 hours each one. After heat treating, samples were grounded with SiC paper, polished up to 1 μm diamond and degreased in acetone just before nitriding.

2.2 Plasma Nitriding

Plasma nitriding was carried out using a 40 kW Klöckner ion nitriding unit. Samples were nitrided for short time (less than 10 hours) at temperatures from 450 to 550°C, steps of 50°C, using a gas composition of 10, 25 or 75% of N₂ balance H₂. The pressure in the chamber was 400 Pa (4 mbar).

2.3 Microstructure Characterization of the Sample

Glow discharge optical spectrometry (GDOS) has been used to provide elemental profiles through the layer into the substrate. This technique uses a DC glow discharge, and the elements are analyzed in an optical spectrometer. A circular area of 4 mm diameter was sputtered and analyzed with a depth resolution of 2 μm to analyze the nitrogen and carbon profile and study the decarburization phenomenon.

TEM analysis were performed at a Jeol 4000 FX 400 KV with a link detector and x-ray analyzer NA 10.000 plus an electron energy system loss (EELS).

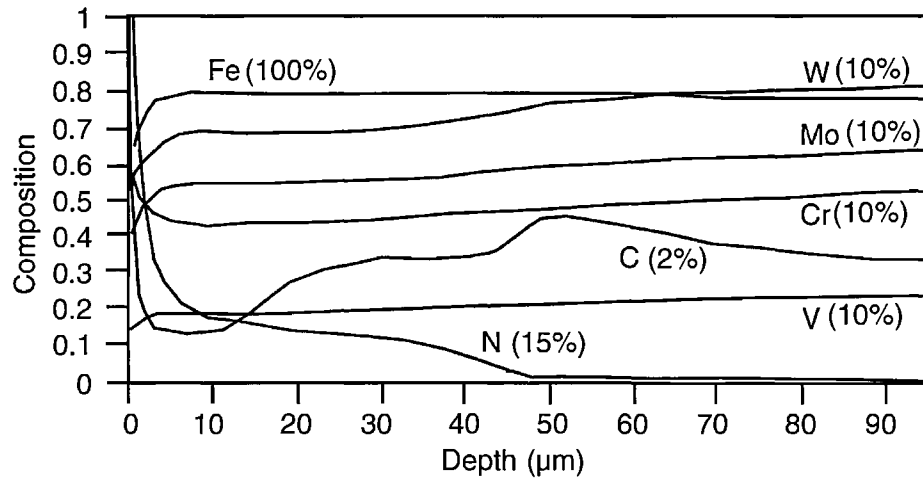


Fig. 1: GDOS analysis for sample nitrided at 550°C, 1 hour, 25% N₂.

2.4 Electronic Structure Calculations

First principle band-structure calculation is a very useful tool for studying nitride and carbide phases. Some theoretical works using first principle methods to solve the band structure of these systems^{9, 10} have given satisfactory answers to some questions such as bulk modulus, magnetic properties and total energy in the equilibrium volume.

For the calculations done in the present work it was used a FCC unit cell to simulate crystal structure for the compounds Cr₂₄C₆ and Cr₄N. It was assumed that the chromium atoms are in the position (0.0, 0.0, 0.0), (0.5, 0.0, 0.5), (0.5, 0.5, 0.0), and (0.0, 0.5, 0.5) while the N and C atoms are in the body center positions (0.5, 0.5, 0.5). The M2 steel has a Cr₂₃C₆ carbide that was approximated by Cr₂₄C₆ to facilitate the calculations.

The linear muffin-tin orbital method (LMTO)^{11, 12} was employed within the atomic spheres approximation (ASA) to perform total energy calculations for several lattice parameters in order to obtain their energy at the equilibrium volume. For the ferromagnetic calculations we used the spin density functional theory and the Von Barth-Hedin approximation¹³ for the exchange correlation energy of the electron gas. No spin-orbit is taken into account but we use combined corrections terms, and our solutions of the Schrödinger equation use s, p, and d LMTO basis functions. The self-consistently-converged potentials are obtained using 1,330 k-points reciprocal lattice and 1,500 points in the energy window. In the LMTO-ASA calculations the radius of the Wigner-Seitz spheres around each atom is obtained from the condition

$$\frac{4}{3}\pi \sum_i S_i^3 = a^3$$

where a is the lattice parameter. For both compounds we take the same Wigner-Seitz radius for chromium atoms. For nitrogen and carbon atoms the Wigner-Seitz radii were chosen as $S_N = S_C = 0.75S_{Cr}$ thus minimizing the interstitial volume among the planar spheres.

3.0 Results

3.1 Glow Discharge Optical Spectroscopy

Chemical composition profiles for nitrided layers are showed in Figures 1 to 3. It is clear that nitrogen has a high concentration near the surface, having a intense decreasing in direction to substrate. Also it is observed a region near surface that is impoverished in carbon. The level of decarburization is more intense for those samples nitrided in higher temperatures (550°C) and longer times indicating a diffusion-controlled process.

At the interface nitrided layer substrate occurs a region enriched in carbon, with a concentration higher than the matrix. This region was detected for all nitrided samples. With respect of iron and others alloy elements presents in the steel, no significant concentration changes was observed. With the nitrogen introduction in the surface there is a dilution but not apparent change in absolute values.

The steel AISI M2 showed a low level of decarburization when compared to steel En40B (C 0.23 Si 0.29 Cr 3.21 Mo 0.52) investigated by Hagman¹⁴

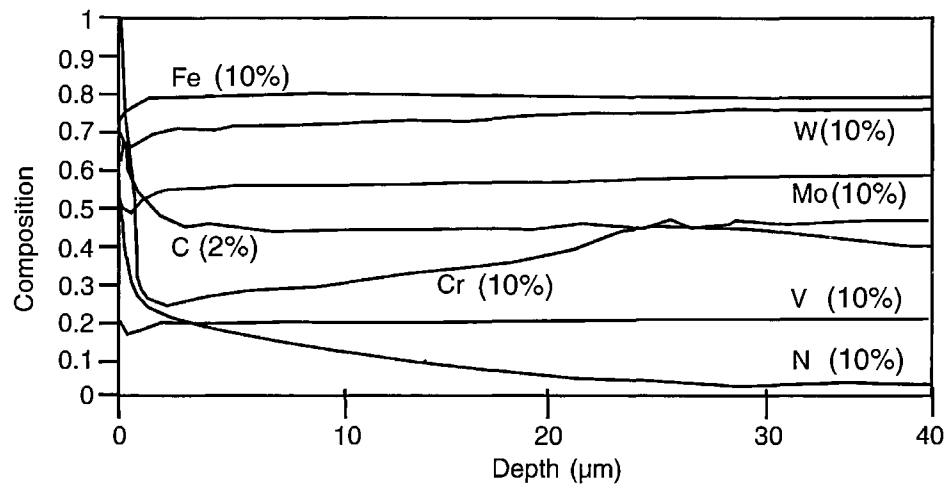


Fig. 2: GDOS analysis for sample nitrided at 450°C, 1 hour, 10% N₂.

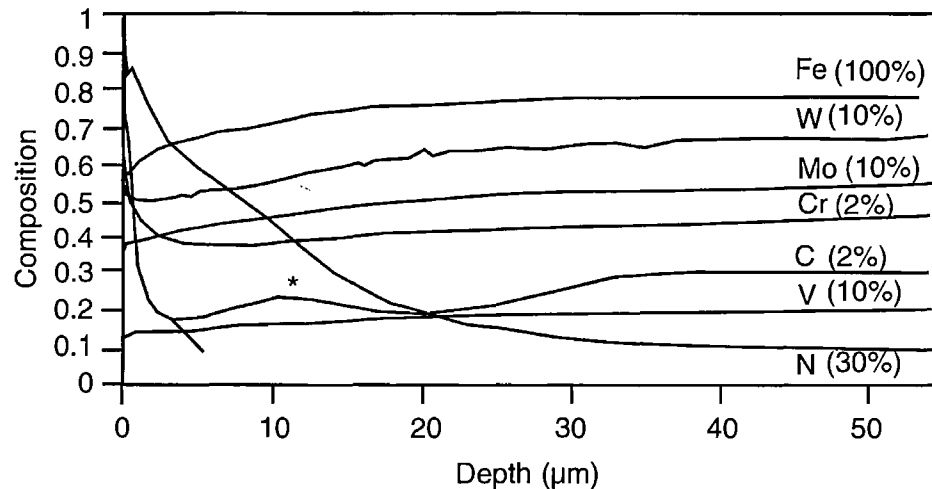


Fig. 3: GDOS analysis for sample nitrided at 550°C, 10 hour, 75% N₂.

where it was found a total decarburization in depth higher than 50 μm . In that work he reports that once carbon is removed during plasma nitriding, a concentration gradient is created between surface and deeper regions. Therefore carbon would diffuse only in direction to surface and high carbon region below nitrided layer would be suppressed. However it is observed that the region rich in carbon is present for all nitrided samples. In the Hagman experiments a long time nitriding process were used, higher than 10 hours. Therefore, the carbon rich zone was not detected probably because GDOS analysis cannot reach enough deeps.

Figure 3 shows the presence of a small peak of carbon (indicated by*) inside of a nitrided layer. That

small peak is located in about 8 μm from surface at the interface diffusion zone- γ' Fe₄N compound layer. The peak indicates that compound layer is working as a barrier, avoiding that carbon diffuse to surface.

3.2 Theoretical Results

3.2.1 Carbide and Nitrides Stability

The self consistent LMTO-ASA total energy calculations for Cr₂₄C₆ and for Cr₄N net parameters are shown in Figure 4. The binding curves were obtained through an analytical fitting of the calculated data points to a third degree polynomial. It was necessary to consider the atomic total energy for each element N and C since

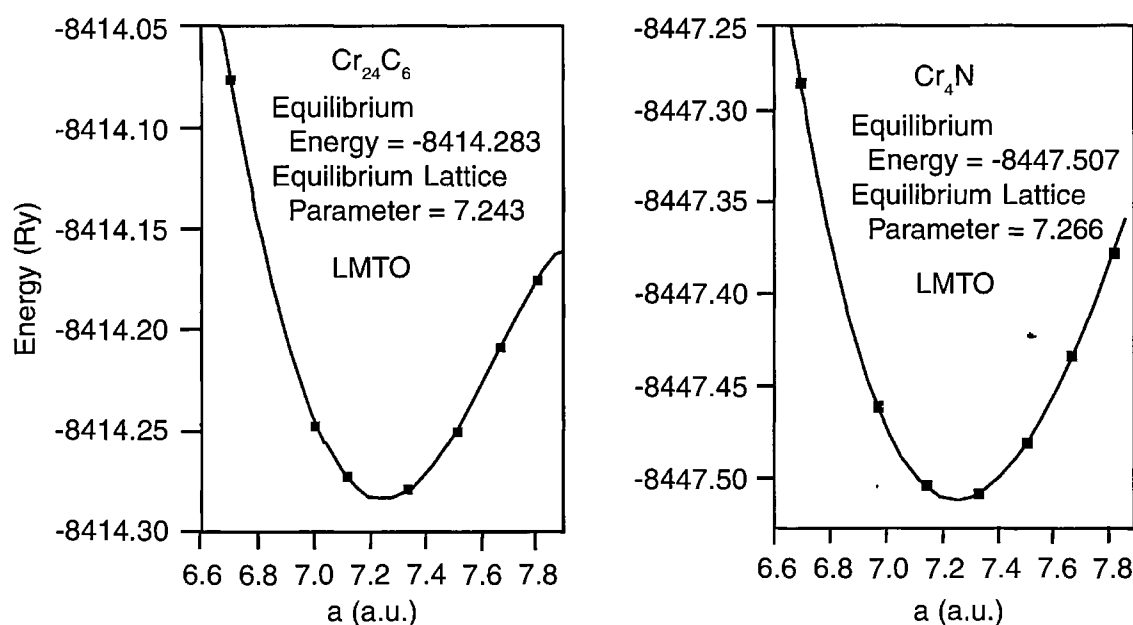


Fig. 4: The calculated total energies for the phases Cr_{24}C_6 and Cr_4N versus lattice parameter.

the number of Cr atoms is the same for the two compounds. Therefore it was necessary to subtract the atomic energies from the total energy of the compound for each element using the following equation:

$$\Delta E = E_T - \sum_i^N E_i - E_{\text{tot(metal)}}$$

E_T = Total Energy of the compound,

E_i = Atomic total energy for C or N atoms, and

$E_{\text{tot(metal)}}$ = Total energy of pure chromium in the FCC phase.

The calculated minima of the binding curves (Figure 4) correspond to the following lattice parameters: $a = 7.243$ a.u. for the Cr_{24}C_6 and $a = 7.266$ a.u. for the Cr_4N nitride. Obviously these lattice parameters are greater than pure chromium lattice parameter (bcc - Cr 5.4442 a.u.) but a theoretical calculation of pure chromium in the fcc phase gives a equilibrium lattice parameter around 6.90 a.u. which shows that there is a lattice expansion due the inclusion of carbon or nitrogen atoms at the octahedral interstitial sites.

From Figure 4 we see that our results shows that Cr_4N nitride is more stable than Cr_{24}C_6 (Cr_{23}C_6) carbide. However we must stress that this is a rough estimation of the cohesive energies since it is very difficult to obtain the exact cohesive energy for this kind of compounds. This may be related with the fact that it is necessary to expense some energy to manufacture these carbides and nitrides and also because these compounds may be characterized as metastable compounds. If we calculate

the internal excess energy subtracting from the total energy of Cr_{24}C_6 and Cr_4N at equilibrium volume the total calculated energy of pure chromium in the fcc phase (at theoretical equilibrium volume) and the atomic energies of carbon and nitrogen atoms we obtain $\Delta E_{(\text{Cr}_{24}\text{C}_6)} = -15.03$ Ryd/atom as the internal excess energy (or formation energy) for Cr_{24}C_6 and $\Delta E_{(\text{Cr}_4\text{N})} = -21.63$ Ryd/atom as the internal excess energy for Cr_4N . Therefore from our rough estimation it is very clear that the chromium nitride is more stable than chromium carbide.

3.3 TEM

Figures 5 and 6 shows needle produced on the surface of a molybdenum carbide. The diffraction pattern indicates that needles are molybdenum nitrides Mo_{16}N_7 .

4.0 Discussion

From GDOS analysis is possible to see that sputtering during plasma process produce a surface decarburization. According to present results the level of decarburization changes with nitriding parameters especially with temperature but it is always present in higher or lower level. Hagman in his work titled plasma decarburization and plasma nitriding of low alloy steel,¹⁴ report some GDOS results showing that after 10 hours of plasma nitriding of steel EN40B there is a complete decarburization in the nitrided layer. The steel studied

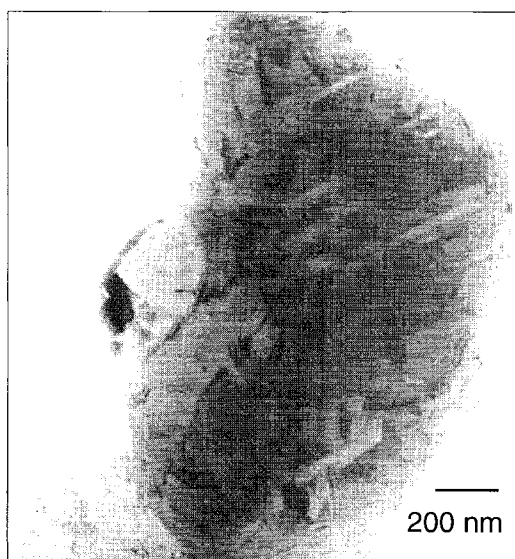


Fig. 5: Nitrides needles (Mo_{16}N_7) produced on a carbide surface.

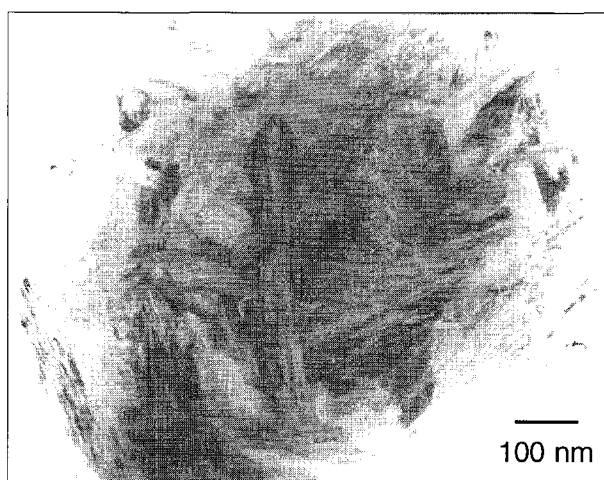


Fig. 6: Nitrides needles (Mo_{16}N_7) produced on a carbide surface.

has 2.8% of chromium and at hardened and tempered condition has some amount of chromium carbide. The level of carbon around zero indicates that during nitriding all amount of chromium carbides present in the layer, are dissociated at 550°C.

For the steel AISI M2 different alloy carbides are present in addition to the chromium carbides as tungsten, molybdenum and vanadium. The GDOS results indicate that after plasma nitriding for AISI M2 steel there is some amount of decarburization but the carbon never arrives to values near zero. The occurrence of only a partial decarburization for the AISI M2 steel suggest that there is a some kind of alloy carbides in the material

that are very stable. It seems that some carbides especially those from chromium transform more quickly during nitriding while tungsten and vanadium carbides for example would be difficult and transform slowly. The presence of nitrides needles detected on the surface of alloy carbide confirms that during nitriding the nitrogen induce carbide dissolution. This affirmation means that in the temperature range used for nitriding, the nitrides are more stable than carbides and therefore the nitrogen would exchange the carbon at the carbides to produce nitrides. LMTO results showed that Cr_4N chromium nitrides are more stable than Cr_{24}C_6 (Cr_{23}C_6) chromium carbides and suggest that carbide dissolution is possible during nitriding.

Another factor to influence the decarburization process is the presence of compound layer. The rate of carbon diffusion in the compound layer is small especially in $\gamma'\text{Fe}_4\text{N}^{15, 16}$ and may work as a barrier avoiding that carbon arrives to surface where it would be removed by sputtering and hydrogen reactions. The GDOS analyses confirm this affirmation. In samples that showed compound layer well defined the level of decarburization is lower than in those samples having only a diffusion layer. While for those samples having just a diffusion layer the carbon profile is decreasing in direction to surface, samples having the compound layer showed a more rectilinear profile. Also a concentration of carbon was found at the interface γ' compound layer diffusion zone (Figure 3) indicating that carbon cannot arrive to surface. Therefore carbon could precipitate at the grain boundary as cementite Fe_3C . This affirmation seems to be correct when it's compared with the metallographys from specimens nitrided at 550°C, 25% N_2 for 1 or 2 hours published by Tier et al.¹ For 2 hours treatment there is a presence of a continuous γ' compound layer and the level of precipitation in grain boundary is significantly higher than that found for sample nitrided for 1 hour. Some authors¹⁷ report that the compound layer γ' has low mechanical properties and should not be used for tool steel because would not support a high stress. However according to present results the problem is not with the kind of compound layer but the temperature in which they are produced. For the steel AISI M2 the $\epsilon\text{Fe}_{2-3}(\text{C}, \text{N})$ is produced at 450°C¹ and in this temperature the grain boundary precipitation is not present. However at 550°C the compound layer is predominantly $\gamma'\text{-Fe}_4\text{N}$ and at that temperature an intense grain boundary precipitation is observed after nitriding. Therefore it seem that the problem is not the kind of layer but the hard phase present on the grain boundary.

Summarizingly, we believe that during nitriding the nitrogen pressure inside of nitrided layer there exist an unstable alloy carbides especially those from chromium.

Therefore N atoms would replace carbon atoms in the carbide cell and produce nitrides. Thus carbon would be released and diffuse to both direction, surface and substrate base. The carbon diffused to core produce the enriched carbon region below nitrided layer. In other way, the carbon diffused to surface will be removed by sputtering and reaction with hydrogen and therefore is created a impoverish carbon zone near surface. However if there is a γ' Fe_4N compound layer on the top of nitrided material, carbon cannot arrive to surface and therefore is produced a carbon enriched zone at the interface compound layer/diffusion zone. Therefore the carbon released would work as driving force to the precipitation and at high temperatures is mobile enough to migrate to grain boundary and produce a cementite Fe_3C network. Reducing the temperature, the alloy carbides would be more stable and diffusion coefficient of carbon in the iron is reduced. At the same time the energy necessary to nucleate cementite increases.¹⁸ Than the phenomenon of nucleation and growth of cementite is strongly difficulty. This may explain why cementite network is observed after nitriding at 550°C and do not after nitriding at 450°C.

5.0 Conclusion

The main factor associated to intense toughness reduction is the intense grain boundary precipitation that occurs at 550°C. Therefore grain boundary precipitation plays an important influence on the nitrided layer toughness on high speed and high alloy steels.

The Fe_4N (γ') compound layer has showed an indirect effect to brittleness reducing the level of decarburization of the nitrided surface and therefore increasing the grain boundary precipitation.

There is a strong indication that carbide dissolution is occurring during plasma nitriding. Theoretical calculations indicates that Cr_4N nitride is more stable than Cr_{24}C_6 (Cr_{23}C_6) carbide.

6.0 Acknowledgments

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Replacement of Chromium and Cadmium

Overview of Alternative Technologies for Chromium and Cadmium

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Abstract

This overview discusses regulatory, technical, and business issues in chromium and cadmium replacement, especially for applications such as aircraft, where the requirements are particularly demanding. We discuss the driving forces (environmental, safety and health, cost/risk, technical, etc.) for Cr and Cd replacement, including existing and expected regulations, and relative costs and performance of replacement options.

The discussion concentrates on those technologies that are gaining the most currency, such as alloy and composite

electro- and electroless plates, HVOF and other thermal sprays, and IVD Aluminum, as well as new technologies that are showing promise for more specialized applications, such as internal diameters and small components. Information is presented on processes and materials, performance, qualified applications, advantages and shortcomings of the methods, and how to choose the best option for a particular application.

1.0 Introduction

Chromium and cadmium electroplating are coming under increasing pressure due to both environmental and

worker safety issues. Hard chrome plating is very widely used for producing wear resistant surfaces and rebuilding worn components, while cadmium plating is used for corrosion inhibition on diverse items such as aircraft components, locks, and fasteners.

For chrome plating, the problem is not the chromium itself, but the hexavalent chrome (Cr^{6+}) from the chromic acid used in its deposition. Hexavalent chrome is known to be carcinogenic and to cause a wide array of medical problems, especially in the nasal passages.¹ Since the plating process is very inefficient (typically about 15%) most of the energy goes to producing gas bubbles, which burst and disperse a fine chromic acid mist into the air. Chrome-contaminated rinse water must also be properly cleaned and disposed of. Recent changes to the EPA Clean Air Act have reduced the allowable hexavalent chrome levels in stack emissions from plating plants.² Under the EPA's Metals Products and Machinery (MP & M) guidelines proposed under the Clean Water Act³ chrome-contaminated waste discharges will be severely curtailed. Based on concerns over worker health and safety, OSHA has been considering more stringent regulations on the permissible exposure limit (pel) in the workplace.

The problems with cadmium are somewhat different. Cd is an inherently toxic heavy metal poison that is quite easily leached and therefore poses environmental and health problems throughout its life cycle. Not only does Cd pose ESH issues in the plating plant, but it can be leached (for example in aircraft engine wash-downs), and thus can contaminate ground water simply by being exposed to cleaning solutions during normal use. At end of life it can also be leached into ground water. The European Commission has proposed requiring substitution of almost all Cd, hexavalent chrome, and even lead in electrical and electronic equipment.⁴

2.0 Drivers and Barriers for Cr and Cd Replacement

While most people assume that the primary driver for replacing Cr and Cd is environmental, this is often not the case. Drivers and barriers fall into several areas.

2.1 Environmental and Health Regulation

This is generally the weakest driver, except where regulations are either very strict or the material is banned outright. Environmental regulations often provide an initial impetus for considering alternatives, but, absent stringent regulation, most business and engineering decisions are based on cost and performance. More

stringent regulation and clearly demonstrated health impacts increase direct processing costs (waste disposal, worker protection) and carry increased liability risks (e.g. there is concern in the chrome plating industry that at levels low enough to meet probable OSHA guidelines, the costs and complexity of compliance would be very high). Note that as more products are produced and sold globally the effect of regional regulation is now becoming global (e.g. European rules on end-of-use recyclability and disposal of consumer items⁵ are leading U.S. vehicle makers to eliminate chrome and cadmium plating).

2.2 Performance

Chrome plating is most frequently replaced when it fails to provide adequate performance in a particular application (e.g. replacement of Cr on aircraft landing gear with HVOF WC-CoCr). A strong argument for replacement is when the alternative provides a significant performance improvement, especially when it is possible to meet a more stringent customer performance requirement (e.g. replacement of Cr with plasma sprayed Cr_2O_3 on anilox rolls used in flexographic printing, a change that permits much higher resolution images). However, performance is a major barrier if the alternative fails to meet one or more critical requirements.

2.3 Cost

This is the strongest driver or barrier for replacement. For OEMs, process cost is the critical issue. For most users, life-cycle cost is more important. However, life-cycle cost reduction can be very difficult to predict, making it a weak basis for change unless it can be clearly and convincingly demonstrated. It is also important to remember that there can be a very high cost associated with replacement, including data generation, validation, drawing and contract changes.

3.0 Cost Issues

In most cases, of course, decisions on replacement are based on weighing all of the cost, performance, and environmental/regulatory factors. Cost is a particularly difficult issue to assess since the definition of cost depends very strongly on the what are the important cost factors in each situation. Evaluations that consider only processing costs fail to account for a wide range of additional costs or cost savings that may be of much greater significance. For most OEMs, cost is primarily determined by changes in processing, regulatory, and in-process time and money costs. However, for users, a

wide array of cost factors may need to be considered, including:

- Process cost - usually higher for most alternatives since Cr and Cd are basically inexpensive processes,
- Material cost - materials vary a great deal in cost, but rinse water is a much higher factor for plating than for dry processes,
- Waste disposal - including process residues, air emissions, rinse water,
- Regulatory cost - includes permitting, paperwork, testing, etc. Risk and cost of fines and penalties for non-compliance may be factored into this cost,
- Capital cost and depreciation - most new processes require capital expenditures, while most Cd and Cr plants are fully depreciated. However, a number of users have invested large sums in new plating plants to meet increasingly stringent regulations,
- In process time and cost of money - important for OEMs,
- Turnaround (out-of-service) time and costs - important for users such as airlines,
- Inventory cost - can be very significant for large fleets, and can be strongly affected by wear and corrosion performance,
- Failure or warranty cost - primarily important for cases in which the replacement is required by inadequate performance of the original coating, or in which serious collateral damage may be caused by failure commonly found in either the original or the alternative. An example is stress corrosion cracking failure of aircraft landing gear, which an alternative might alleviate, and
- Validation, approval, drawing changes - in the aircraft industry this can be one of the largest costs, and is an up-front expenditure.

In order to gain a true picture of the cost of adopting an alternative, all of the costs and savings relevant to the specific replacement need to be considered, and these will be different for different users and producers.

4.0 Cr Replacement Options

Because hard chrome has been in use for almost 75 years, and has been almost the sole available hard coating for most applications, its usage is so diverse that no single technology or material will be able to replace it.

There are two primary uses of chrome plating:

- Providing a wear resistant surface - Note that hard chrome is often used for wear resistance, but seldom used for corrosion resistance, because by itself it is a poor corrosion barrier. Where corrosion is an issue chrome is usually underlain with a Ni strike or

sealed with an epoxy sealant. As an OEM coating hard chrome plate is typically 25–75 μm (0.001" – 0.003") thick. The exceptions are thin dense chrome and flash chrome, which are typically about 8 μm (0.0003") thick and

- Rebuilding worn components - One of the largest volume uses of chrome plating is rebuilding worn mechanical equipment, such as bearings, hydraulic actuator rods, manufacturing rolls, engines, etc. Rebuild coatings are typically up to 250 μm (0.010") thick, and sometimes up to 375 μm (0.015") thick.

There is a tendency in the coatings industry to tout any hard coating as a "chrome replacement". In reality, however, while there are many hard coatings, there are few widely applicable chrome replacements, and most "chrome replacements" are niche products at best. To replace chrome, a coating must not only be wear resistant, but it must be cost-competitive, must be capable of replacing chrome from 50–250 μm thick, must have minimal fatigue debit for fatigue-critical applications, not cause hydrogen embrittlement for use on high strength steels, and it must meet a large number of rather ill-defined user requirements. These requirements are ill-defined because users seldom have detailed information on how chrome actually performs. All that many users (even very sophisticated ones) know is a set of general requirements and the fact that over many years of experience "chrome works".

The main options for replacing hard chrome plate are shown in Table 1.

4.1 Electro and Electroless Plates

Most plating methods are Ni-based. Examples are electroless Ni-P and Ni-B, and composite electroplates and electroless plates, which incorporate hard particles, such as SiC or diamond. The advantage of these plating methods is that they are familiar to most chrome users and have many of the same processing characteristics, including throwing power, ID coating, etc. The primary disadvantage is that Ni is also coming under environmental and health pressure and will probably become the next target for more stringent regulation. It has already been placed under the California Southern District Air Quality Board Rule 1401.⁶ Therefore it is likely to be an interim (perhaps 10 year) solution.

Electroless Ni is gaining in usage because it can be done on complex geometries. It can also be deposited in many composite forms, including hard particles or lubricious particles, such as PTFE (or even both, to combine wear resistance with lubricity).⁷ However, electroless Ni deposition is self-limited, usually to the

Table 1. Hard Chrome Replacement Technologies

Technology	Coating Materials	Comments
Electroplates	Primarily Ni, Some Co-Based	Various Alloys Available
Electroless Plates	Ni-P or Ni-B	Widely Available. Generally Limited Thickness. Good for IDs
Electro and Electroless Composites	Electro or Electroless with SiC, etc	Can also Contain PTFE or Other Materials for Lubricity
Plasma Spray	WC-Co, Cr ₃ C ₂ -NiCr, Hard Alloys, Cr ₂ O ₃	Thermal Spray. Used in Aerospace and Processing Rolls. Cr ₂ O ₃ for Anilox Print Rolls
HVOF	WC-CoCr, WC-Co, Tribaloy, NiAl	Thermal Spray. Most Heavily Used in Aerospace. NiAl for Build-Up
Micro-Arc Welding	Hard Alloys, Stellites, etc., Carbide Composites	Electrospark Alloying and Electrospark Deposition. Small Areas, Excellent Adhesion
Laser Cladding	Hard Alloys	Uses Powder or Slurry. Growing in Use
Explosive Bonding	Variety of Metals and Alloys	Niche Applications

range of 0.002" or 0.003", and it can seldom be plated thicker than about 0.007". This makes it of limited use for rebuild. Also, to achieve maximum hardness electroless nickel must be heat treated, typically at 300–400°C, which is above the tempering temperature of many high-strength alloys.

There are a few composite electroplates on the market, and the process is being developed further by Praxair and other companies in the U.S. and Canada. As with electroless nickel composites, the major advantage of composite plating is the ability to "dial-in" the properties by judicious choice of particulates. However, because it requires the suspension of particles in a bath it is more difficult to control than simple electroplates, and can result in uneven particle incorporation, and in processing problems such as particle contamination of the air-handling system for the bath.

A new hard electroplating method is being developed by Integran Technologies, Inc., of Toronto, Canada that uses pulse plating to achieve a nanograin structure. This approach makes it possible to achieve higher hardness than is typical of most simple electroplates, and the material appears to be microstructurally stable. As with most electroplates this method is based on Ni, but a new Co-based system is being developed.

4.2 Thermal Sprays

Thermal sprays have proved to be capable of replacing chrome in many applications.

- Aircraft landing gear, hydraulic actuators, flap, and slat tracks, etc.,

- Hydraulic rods in off-road and other equipment,
- Anilox print rolls,
- Mill rolls and other continuous processing rolls,
- Ball valves in the oil industry, and
- Undersea oilfield equipment.

The primary types of thermal sprays used for chrome replacement are plasma spray and High Velocity Oxy-Fuel (HVOF) spray. Both methods inject powder into a heat source (a plasma in the former case and a supersonic flame in the latter) and accelerate the softened powder into the surface on a high velocity gas stream. HVOF is the more expensive process because of its use of copious quantities of fuel gases (typically hydrogen and oxygen), but the quality of the coating is best, coating adhesion is better than 700 kg cm⁻² (10,000 psi), and the coatings can be ground without chipping. For these reasons HVOF is most commonly used for aerospace chrome replacement. HVOF can be used to spray a wide variety of coating materials, including alloys (such as Triballoys and Stellites) and composites (such as WC-Co and WC-CoCr).

Because the particles strike the surface at speeds in excess of 100 ms⁻¹, some coating materials (such as WC-Co) can "shotpeen" themselves during deposition so that the coating can be deposited in compressive stress. This allows the coatings to avoid the fatigue debit that always occurs with chrome plating and is an important issue for fatigue-critical aerospace components such as landing gear (see Figure 1). The velocity also allows the coatings to be deposited with porosity below 1%, making them suitable for applications such as gas-over-fluid shock absorbers, where the high pressure gas would escape through a porous coating.

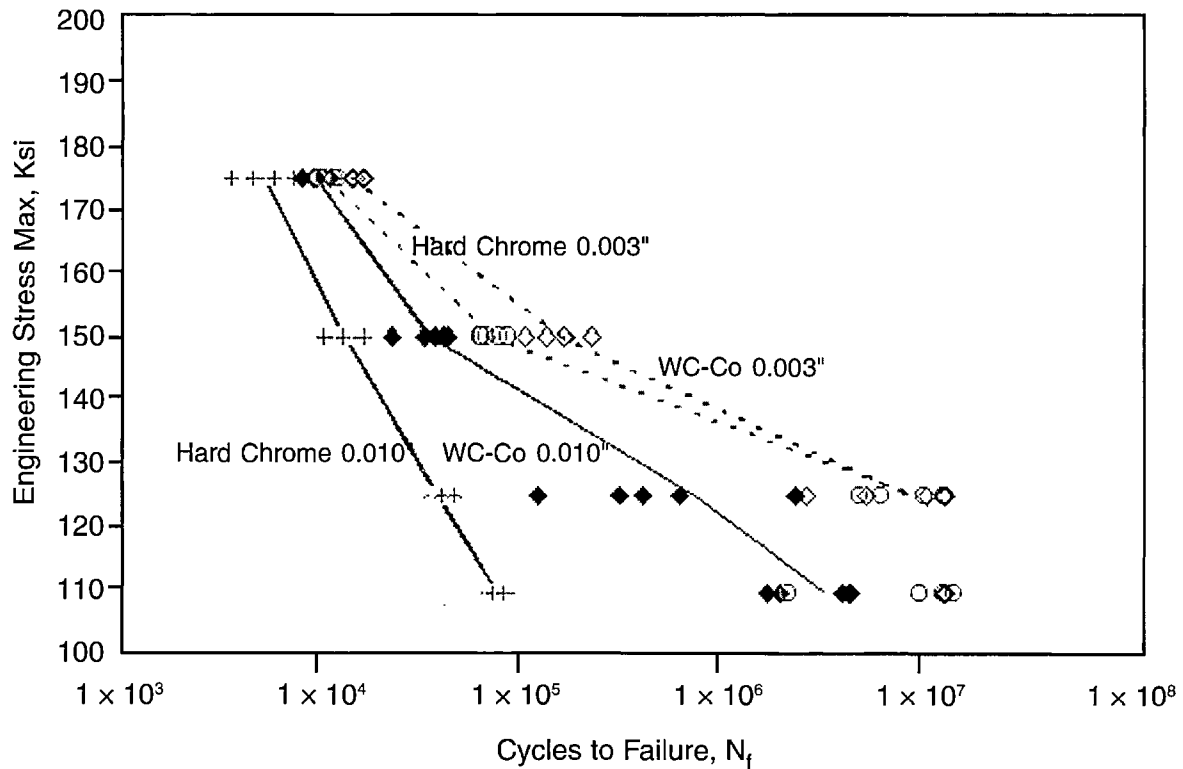


Fig. 1: Axial fatigue of 4340 high strength aircraft steel, $R = -1$ (full load reversal).

Thermal sprays are being used in place of chrome plating on hydraulic rods (including aircraft landing gear), hydraulic pistons, and in some cases IDs of hydraulic outer cylinders. In these applications it is important to superfinish the HVOF to a significantly better finish than chrome to avoid damaging the seals.⁸ When this is done, the coatings perform much better than chrome, both in reduced leakage and in rod wear.

The coatings can be made very thick, so that they can be used for rebuild. However, in general one would not make, for example, WC-Co coatings 0.060" thick both because of cost and because the material is relatively brittle. Instead one would use a coating method such as Ni-5%Al followed by WC-Co, which is the analog of the sulfamate Ni plus Cr plate approach commonly used for thick rebuild.

Plasma spray coatings do not adhere as well as HVOF coatings. However, the process is less expensive and a wider variety of coating materials is possible, including oxides that cannot be melted by the lower temperatures of HVOF.

Note that even though these coatings may incorporate Cr (as in WC-10Co-4Cr or Tribaloy 800, which has 18% chrome) the Cr is in metallic form. The only time that thermal spray creates a hexavalent chrome

problem is when Cr_2O_3 is used for anilox print rolls, since during spraying some material can oxidize to CrO_3 and pose a hexavalent chrome problem in the overspray waste.

The disadvantages of thermal spray methods are:

- They are line-of-sight and so cannot be used in small IDs or complex geometries. HVOF can only be used in IDs above about 30 cm. Plasma spray uses a smaller stand-off (spray gun to substrate distance) and can be used inside IDs down to about 7 cm.
- They cause local heating, which in some cases can be a problem with shot-peened high strength steels, which should be held below 177°C (350°F), and with some Al alloys, which must be kept below 93°C (200°F). However, careful consideration of cooling methods and substrate-gun motion can usually hold temperatures below these levels.
- Unlike Cr the bond is not metallurgical. It requires a physical lock on the surface, which is achieved by grit blasting prior to spraying. Under very high loads and bending the more brittle thermal sprays (such as the oxides and composites) can delaminate. The use of HVOF coatings for chrome replacement has been detailed in a recent report.⁹

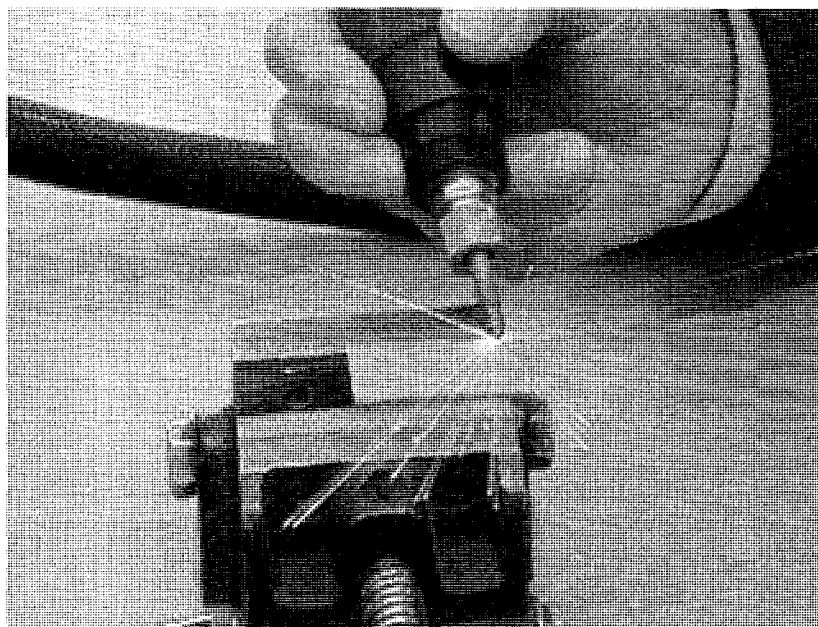


Fig. 2: Hand-held electrospark deposition in use (ASAP, Inc.).

4.3 Weld Methods

Weld facing is a common method of providing hard coatings for large equipment such as agricultural and mining machinery. A much finer method, known as electrospark alloying (ESA) or electrospark deposition (ESD) has been developed for applying a wide variety of coatings, generally over smaller areas.¹⁰ ESD is a micro-arc welding method in which a consumable electrode operates in contact with the surface. Although it is a welding method, the energy in each micro-arc is so small that the heat affected zone is only a few microns deep and there is very little heating of the component as a whole. The electrode is at most a few mm in diameter and is continuously moved across the surface to deposit the coating (see Figure 2). Because of the small electrode size and low deposition rate, the method is not generally suitable for large areas, but it is very good for small areas and even re-entrant geometries. ESA has been developed by Rolls Royce Aircraft Engines for repair of turbine engine components, and to date more than 40 repairs have been approved.

ESD may be regarded as the dry-coating analog of brush plating, which is widely used for localized repair of damaged components. It can be done in the open air using a hand-held electrode and produces a coating that is metallurgically bonded to the substrate.

A large number of coating materials is possible, the main proviso being that the coating material must

be conductive. Alloys are the most common (e.g. Stellites and Haynes alloys), but the method can also be used for composites such as WC-TaC-Co. Note, however, that the melt/solidification of the material prevents its incorporating the carbides in these cases as macroscopic particles - the material becomes either amorphous or nanograined.

As with other welding methods, the ESD coating material solidifies from the melt and is therefore almost always in tensile stress. As a result ESD coatings are often cracked and are not generally suitable for fatigue-critical components (e.g. they are not used for fatigue-critical turbine engine part repair).

As lasers have become more stable and user-friendly the use of laser cladding and other laser coating and surface treatment methods has begun to grow.¹¹ Laser cladding (welding of powder onto the surface by a laser beam) is proving a viable process and is used in production for some turbine blades. Material can also be added from wire form or from slurry. Because it is a melting process, the adhesion is excellent, but the same fatigue considerations are likely to apply as in the ESD process.

Another welding process that may have niche applications for chrome replacement is explosive welding. In this approach the surfacing material is laid on (or just above) the surface to be coated and driven into it by detonating a layer of explosive. The result is a full-area weld, which can be used to join dissimilar metals (such as Al and Cu). The chrome replacement applications for this technique are likely to be particularly

Table 2. Cadmium Replacement Technologies

Technology	Coating Materials	Comments
Aqueous Electroplates	Zn-Ni, Sn-Zn	Under Extensive Evaluation in the Aircraft Industry
Organic Bath Electroplates	Al	Only Commercial Process in the U.S. is Alumiplate™
Molten Salt Bath Electroplate	Al-Mn	Not Commercially Available. Under Development by Naval Air Warfare Center
IVD Aluminum	Al	Vacuum Deposition of Al Developed by McDonnell Douglas. Wide Use in Aerospace
Metal-Filled Composites	Al or Zn in Ceramic or Polymer	Metal/ceramic SermeTels™ Used in Aircraft. Polymer/Al and Zn Used in Vehicle Bolts
Stainless Alloys	Stainless Steels	Used in Aircraft Engine Fasteners and Aircraft Hydraulics. Under Development for Aircraft Landing Gear

difficult coating problems such as tube IDs for oilfield equipment, gun barrels, etc.

5.0 Cadmium Replacement Options

The main options for replacing cadmium are shown in Table 2.

There are three primary uses for Cadmium (Cd) plating.

1. Providing corrosion resistance for components,
2. Providing proper torque-tension (i.e. proper lubricity) for threaded fasteners, and
3. Providing oxidation-corrosion resistance and reliable conductivity for electrical connectors.

As with Cr plating, it is unlikely that a single alternative will supplant all applications of Cd. The most widely applied corrosion coating is of course Zn, which is used on galvanized steel. For many of the applications for which we use Cd, however, Zn is not a viable option because many applications involve high strength steels, where the hydrogen evolved by Zn during corrosion would cause embrittlement failure. For this reason all aircraft applications use more complex alloys, which, although they often include Zn, do not appear to pose serious embrittlement problems. It should be noted that, in common with Cd itself, all Cd alternatives at present require chromate (hexavalent chrome) conversion coating to reach the highest levels of corrosion inhibition required for aircraft applications.

Cd is a sacrificial material that continues to provide galvanic protection even when breached to expose the underlying surface. It cannot in general be replaced by simple barrier coatings since, once a barrier coating is scratched, the underlying material corrodes. Cd is thin (<25 µm) and soft so that it remains adhered under bending, and its corrosion products are low volume and do not build up electrically insulating layers on electrical connectors.

5.1 Electroplates

There are two primary aqueous electroplates that are proving to be useful Cd replacements.

- Zn-Ni - This alloy can be deposited by acid or alkaline baths. It was developed by Boeing¹² and is gaining wide currency for Cd replacement.
- Sn-Zn - It is uncertain whether Sn-Zn is a true alloy or an intimate mixture. It is not as widely applicable as Zn-Ni, but appears to be somewhat better in some applications, such as electrical connectors.

Even though these are majority-Zn materials they do not appear to cause environmental embrittlement (re-embrittlement) from hydrogen evolution during corrosion. Both of these alternatives appear to work well and are being evaluated by Boeing and by the Navy at present. Note that, since these are alloys, the deposition process will be more complex than deposition of Cd, since the alloy chemistry (and hence performance) will depend on solution chemistry, current density, and other process parameters. Because they are aqueous electroplates hydrogen embrittlement of high strength steels during plating will be an issue.

5.2 Electroplated and IVD Aluminum

The closest single material to a drop-in Cd replacement is Al. Testing has shown that in general Al can be used in place of Cd for almost every Cd application. Unfortunately Al cannot be electroplated from simple aqueous baths. There are two methods for obtaining Al coatings.

- Oxygen-free organic plating - The only commercially available Al electroplate in the US is Alumiplate™, which is deposited from a toluene-based solution. The deposition must be done in an

enclosed, oxygen and water free atmosphere, and components introduced through a load lock system. Extensive testing has been done on electroplated Al under DoD funding, and it has met most corrosion requirements.¹³

- IVD Aluminum - The IVD process is a vacuum deposition method that was developed by McDonnell Douglas Aircraft Co as a corrosion coating.¹⁴ Al is deposited in a large vacuum chamber by evaporation under weak plasma bombardment of the substrate. The resulting coating is very porous and must be densified (or burnished) by light peening and then chromate converted to provide sufficient corrosion resistance. IVD coatings are widely used on aircraft components such as landing gear, and their use is growing. They are available from a number of commercial vendors, while a growing number of aircraft overhaul shops and military depots have in-house units.

Another Al alloy electroplate currently under development and evaluation is Al-Mn.¹⁵ This alloy must be deposited from a molten salt bath (i.e. Al and Mn chlorides), which operates at a temperature of 170°C. This is too high a temperature for aluminum alloys used in some electrical connectors, but is low enough for most aircraft steels. The molten salts are highly reactive in contact with water, producing HCl fumes. Consequently, in common with the Alumiplate process, the Al-Mn process must be done in an enclosed bath and may require load lock materials handling. It is not yet clear how sensitive the process might be to water contamination either from the air or brought in on aqueous-cleaned components. Removal of all remaining salts after plating is very important since they will react with atmospheric water vapor to produce corrosive HCl, which could lead to hydrogen embrittlement.

The corrosion protection provided by Al-Mn appears to be comparable to Cd. The process appears to be suitable for most aircraft components and fasteners. However, it is still under development and is not commercially available.

5.3 Metal-Filled Ceramic and Polymer Composites

There are a number of commercial products on the market that consist of a polymer filled with metal flakes (typically Zn or Al). The most common use for this type of coating is automotive fasteners. These coatings are normally deposited by the dip-spin method, in which the fasteners are loaded into a basket which is dipped into the polymer resin composite, then raised out of it

and spun at high speed to throw off the excess. They are then baked to set the resin. This type of coating has been tested by the Army Tank Automotive Command (TACOM) and found to be as good as Cd plating in this type of application.¹⁶ With this coating method it is important to maintain the proper resin viscosity to avoid excess coating that clogs fastener threads.

Another composite material that is often used in aircraft components such as engine parts and landing gear, is SermeTel™, which is the general name of several coating materials produced by Sermatech, Inc. It comprises Al particles dispersed in a solution of phosphates and dichromates that is sprayed onto the surface. When heat treated at 190-370°C the coating forms a glassy matrix filled with Al particles. It is then etched to expose the metal filler.

5.4 Stainless Alloys

Coatings can be completely avoided by the use of stainless steels in place of Cd plated steels. For example:

- Pratt and Whitney has designed the F-119 engine used in the F-22 and planned for the Joint Strike Fighter as a “green engine” by eliminating the need for Cd and Cr. To eliminate Cd, Cd-plated fasteners were replaced by stainless steel fasteners. Note, however, that while this approach works well for engines, it can seldom be used for airframes because of galvanic corrosion between the stainless steel and the aluminum skin of the aircraft.
- Most aircraft actuator manufacturers have replaced Cd-plated high strength steels, such as 4340, with 15-5 PH precipitation hardened stainless steel. This type of stainless steel does not have as high a tensile strength as the original high strength steel, but avoids the need for Cd plating.
- A new stainless landing gear steel, designated S-53, has been designed and is currently under test.¹⁷ Unlike most steels, this material was created through a “materials by design” approach that permits an alloy to be designed from scratch to specification (in this case the specification was mechanical equivalence to standard 300M landing gear steel). Unlike other stainless steels, therefore, its use would not require downgrading mechanical specifications. If this approach proves to be successful it will demonstrate a new ability to create new alloys to meet very specific technical requirements. Apart from eliminating Cd, it is expected that this approach will also reduce stress corrosion cracking, which is the primary failure mode for military landing gear.

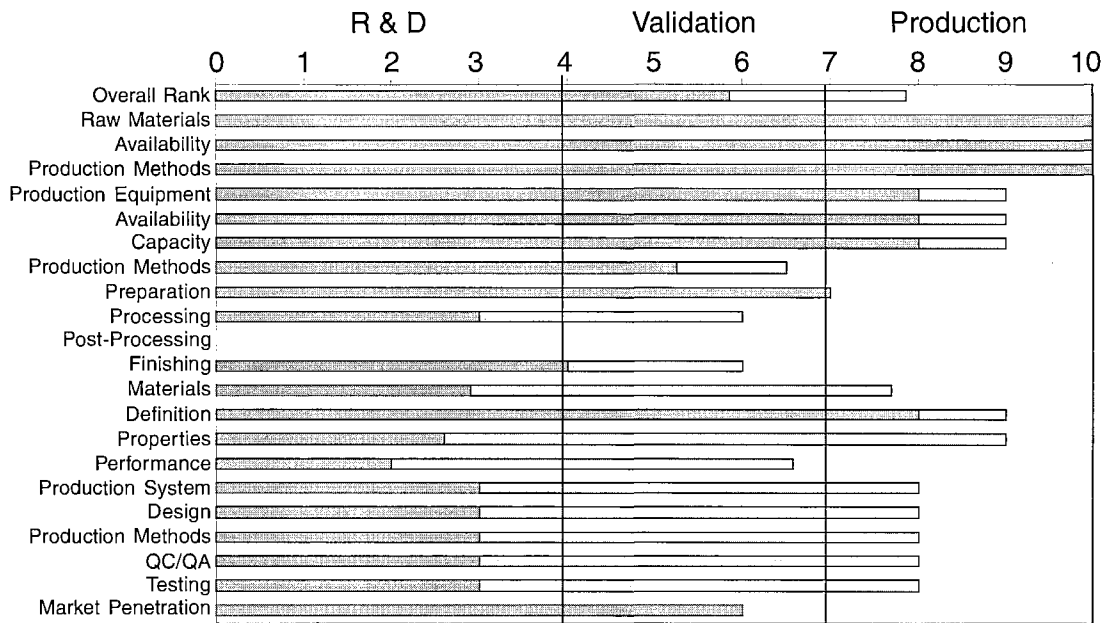


Fig. 3: Technology assessment matrix graphical output for plasma sprayed ID coating. Light colors - helicopter blade damper and dark colors - general aerospace use.

6.0 Choosing the Best Option

Both Cr and Cd are very widely used and require a great deal more than simply hardness and corrosion resistance. A chrome replacement is not simply a hard coating, nor is a cadmium replacement simply a corrosion resistant one. In choosing a replacement option it is necessary to take into account a wide variety of issues, including

- Substrate materials and allowable heat treating temperatures,
- Size and geometry - whether an OD or an ID, for example,
- All of the engineering requirements, not just for the coating (hardness, friction, electrochemical potential, etc.), but also for the entire coated system and its working environment. These may include wear and corrosion resistance, fatigue, embrittlement, galvanic corrosion from other components, and impact resistance, and
- The total production and use environment. An alternative must fully fit with the way the item has to be used. Aircraft parts, for example, must be stripped and recoated periodically, so the material must be strippable. Hard chrome is used to rebuild components, so its alternative must be able to be ground or finished to the required final dimensions

and finish. When original coated items may be used in the field together with items coated with the alternative, some means must be provided for tracking or identifying the two types.

Given all of this complication, how can one decide which of the many alternatives is a good match for a particular application? The first part of any evaluation involves detailed discussion of requirements with both OEMs and users to establish, not just the engineering requirements, but the way in which the coated item is used over its entire life-cycle. This establishes how the coating is to be produced and what critical properties it must have. We have developed a Technology Assessment Matrix method¹⁸ that we use to establish whether an alternative is a viable option, whether it meets the technical requirements for properties and performance, and how advanced it is in development from the laboratory to full production. The method considers all of the steps required to produce and use the coating, including raw materials, production equipment and methods, finishing, and coating performance, and assesses how advanced each is and whether it is qualified for the application. The results are plotted graphically, (see Figure 3) and show immediately how well developed the process is. The bars show the degree of development for each aspect of the coating production process - the longer the bar, the closer it is to full scale commercial

production. Just as importantly, this type of analysis shows immediately where the information and development gaps are so that we can quickly see what will be needed to bring the method to full production. In this example, it is clear that, while the equipment and process are well defined, extensive work is still needed to validate coating properties and performance for the general case.

7.0 Summary

Replacing a process as widely used as chrome or cadmium plating is not a simple matter of finding an alternative that is hard or corrosion resistant. There are a great many properties and performance requirements that must be met, not only to meet the engineering specifications, but also to fit the alternative into the environment in which it will be produced and used.

Because hard Cr and Cd are so widely used, in so many disparate applications, no single replacement will work. There are a number of viable alternatives for both chrome and cadmium. Thermal spray methods are gaining wide acceptance as chrome alternatives in many industries, but do not work everywhere and are especially difficult to do in small internal areas. Zn-Ni electroplate and IVD Aluminum are both gaining wide acceptance for Cd replacement in the aircraft industry, while materials replacements are gaining ground as a means of avoiding the problem all together.

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Role of Electroplated Chromium on the Corrosion Resistance of Decorative Thin Film Coatings

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Abstract

The commercial decorative coating of zirconium nitride on a brass substrate derives its corrosion resistance from a thin electroplated inter-layer of chromium. However, in certain atmospheric environments the corrosion protection is not adequate after the zirconium nitride layer is deposited on electroplated chromium using the cathodic arc evaporation PVD process. In addition, the use of hexavalent chromium ion baths for electroplating has environmental pollution problems.

Corrosion behavior has been correlated with the thin film deposition process parameters. Two critical process conditions

were substrate bias and total system pressure. Anodic polarization current (e.g. anodic current) was lower for coatings deposited at lower substrate bias and higher system pressures. A study of the microstructure and density of the coatings revealed that the more corrosion resistant coatings were oriented in the (200) direction and contained a greater number of macroscopic (macro-particle) defects. It is suggested that the former attribute decreases the driving force (half-cell potential) and the latter distributes the corrosion current over a wider area, thus avoiding severe localized attack.

Experiments were also conducted with a removed or replaced layer of chromium. In the case of replacement, a

PVD layer of intermetallic or ceramic material has been used. Data is included to show the improved corrosion resistance when a PVD layer replaces the electroplated chromium layer. However, removal of chromium without a corrosion barrier layer is found to be inadequate. The removal of electroplated chromium helps resolve environmental issues as well as eliminates a process step in the fabrication of decoratively coated parts.

1.0 Introduction

Decorative and corrosion resistant thin films have been offered for several years and are now commonly found on everyday household items. Coatings such as ZrN, ZrCN, and TiZrN are commonplace in many industrial and household applications such as plumbing fixtures and lock set components. Several papers have been published describing the optical properties of nitrides and carbides from group IV transition metals (Ti, Zr, and Hf).¹⁻³ In addition to the ideal optical properties that provide brass and gold-like colors are the excellent wear and corrosion properties of these nitrides and carbides. Both ZrN and TiZrN are commonly used as decorative coatings to replace gold plating and organic coated brass.

Several manufacturers of PVD decorative coatings offer lifetime guarantees on the appearance and functionality of the finish. Thus it is necessary to provide a PVD coating that is both hard and durable but also corrosion resistant in various aqueous environments, including strong oxidizers, bases and marine environments. This investigation focused on characterizing thin ZrN coatings in an acidic salt-water aqueous solution in an attempt to overcome corrosion in marine and chloride rich environments.

2.0 Experimental Procedures

The substrate used for ZrN deposition experiments and characterization was Ni/Cr plated brass with coupon dimensions $40 \times 40 \times 3$ mm. The nickel and chromium layers were deposited by galvanic electroplating techniques at a thickness of 10 and 0.25 μm , respectively. The base substrate was a 60/40 naval brass commonly used in plumbing and door component hardware.

Zirconium nitride coatings were deposited by cathodic arc evaporation with a cylindrical arc source located in the center of the chamber. Nitrogen and argon gases were introduced into the chamber through mass flow controllers and distributed via gas manifolds inside the chamber. The arc was generated using a high current DC power supply with the zirconium target being the cathode and the chamber wall the anode. Substrate bias

was supplied by an Advanced Energy 30 KW DC power supply. A schematic illustration of the vacuum chamber and cathode/substrate arrangement is shown in Figure 1. A base pressure of 2.0×10^{-2} mtorr was achieved prior to the start of the process. Once base pressure was reached a vacuum plasma cleaning and substrate heating was performed prior to deposition. Coupons were cleaned by glow discharge at 25 mtorr Ar pressure and 500 V DC bias and soaked for 10 minutes at 100°C. An arc discharge was then initiated on a water-cooled zirconium target to first deposit a metal adhesion layer then a hard reacted nitride. The entire coated stack consisted of a 750 Å layer of Zr followed by 2750 Å of ZrN.

In these experiments, two process conditions were varied during deposition. Substrate bias and deposition pressure were varied between 25-150 V and 3.0-9.0 mtorr respectively. Arc current and Ar:N₂ flow ratio were both held constant at 200 amps and 0.1, respectively. The coupons were held stationary at a source to substrate distance of 380 mm.

Corrosion experiments were carried out using a model 263 EG & G potentiostat. Coupons were placed in a flat cell with the electrolyte in direct contact with 1 cm² of the working electrode (i.e. coating/substrate). Ag/AgCl saturated KCl was used as a reference electrode and the IR drop from the working to reference electrode, was minimized by using a lugin capillary. A Pt counter electrode was located opposite the working electrode. The experimental setup is shown schematically in Figure 2.

The electrolyte for these experiments was a CASS solution (ASTM B368). The mixture contained 5% NaCl with 0.25 g/l cupric chloride and 1.5 ml/l glacial acetic acid added to the solution. This particular solution was used in an attempt to correlate salt spray chamber results with electrochemical characterization of zirconium nitride coated plated brass.

Tests were performed by first holding the exposed material at open circuit potential (OCP) for up to 24 hours or until equilibrium was established. Equilibrium was defined as the point at which the open circuit potential changed by less than 1 mV over a 10 minute period. Once equilibrium was achieved it was observed that any subsequent soak time resulted in little or no change of the OCP. Samples were monitored for a minimum of two hours prior to polarization regardless of steady state conditions. The coating stack was then anodically polarized to +300 mV relative to OCP for 5 minutes, and the anodic current was recorded. The coupons were then taken out of the cell for macroscopic and microscopic characterization.

A modified Philips low angle x-ray diffraction unit was used to determine crystalline orientations and phase formation. A constant incident angle of two degrees was

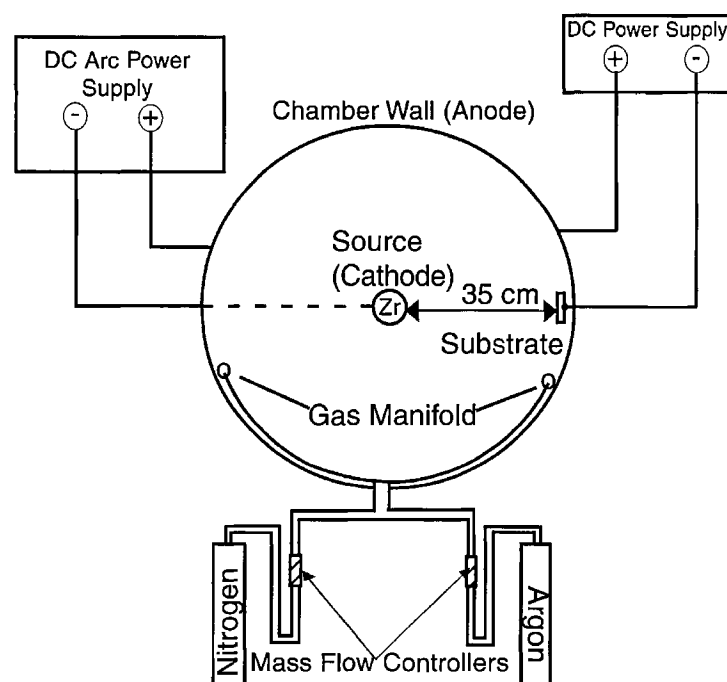


Fig. 1: Schematic of vacuum chamber.

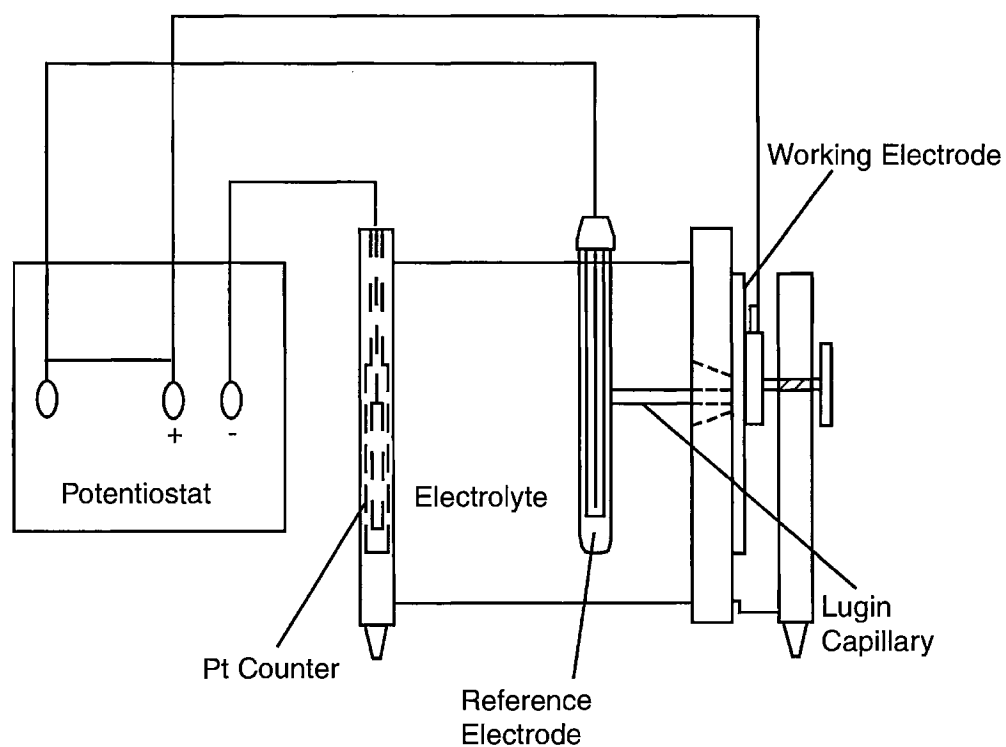


Fig. 2: DC electrochemistry cell.

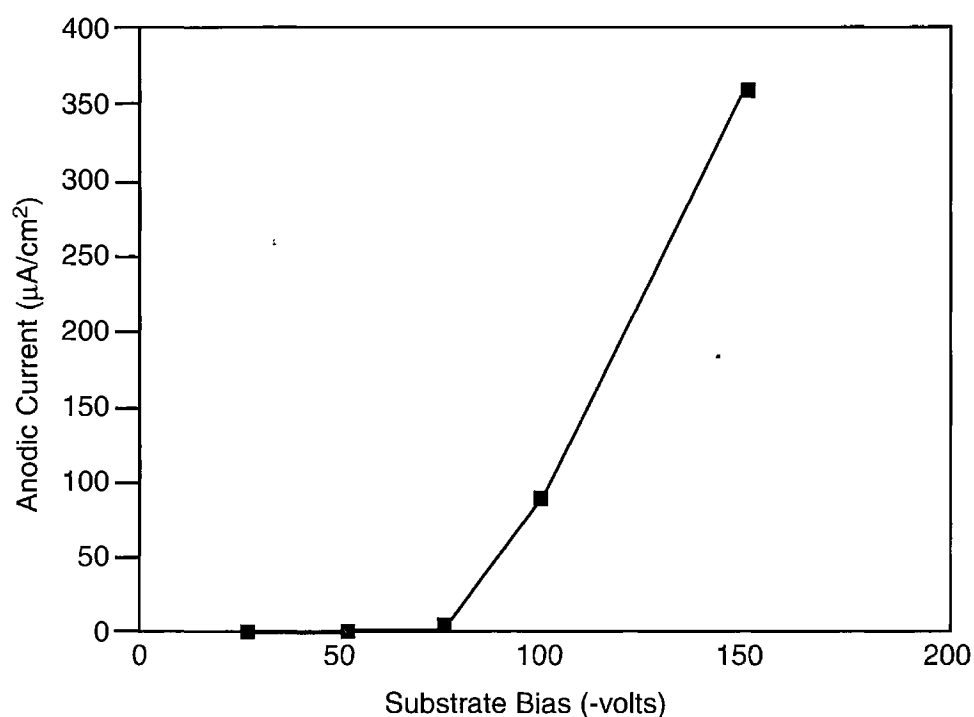


Fig. 3: Anodic polarization current at various substrate bias conditions.

used in order to avoid substrate contribution to the diffraction signal. A silicon reference powder was lightly spread on the surface of the coating to ensure correct alignment of the detector. Standard JCPDF (X-Diffraction Data File) were used to identify coating phases and orientations.

A JEOL 5900 with EDAX attachment was used to qualitatively and quantitatively examine corrosion defects as well as overall microstructural characteristics of the coating. Corrosion products were identified by energy dispersive spectroscopy. A Nikon inverted metallurgical light microscope was used to count the number of pinhole defects formed by macroparticle generation and deposition during the arc process. Particle counting software was used to quantify the size and density of defects by analyzing a dark field image of the coating at 500x.

3.0 Results

The anodic current density for the substrate bias experiments is shown in Figure 3. There was a sharp increase in the anodic current after 5 minutes of polarization with coatings deposited at a substrate bias greater than 75 V. Current density on the order of $0.1 \mu\text{A}/\text{cm}^2$ was measured on coatings deposited with substrate bias less than 75 V while the anodic current for coatings deposited

with substrate bias at values greater than 75 V reached $350 \mu\text{A}/\text{cm}^2$.

Likewise, there was a similar rise in the anodic corrosion current as the deposition pressure was decreased as shown in Figure 4. For pressures from 5.0 to 9.0 mtorr there was very little corrosion current measuring less than $45 \mu\text{A}/\text{cm}^2$. However, very large anodic corrosion currents were measured for pressures less than 5.0 mtorr. Severe pitting into the brass base metal was observed at high anodic current density values for both substrate bias and pressure experiments.

Grazing angle x-ray diffraction indicated that there was a direct effect of substrate bias and deposition pressure on the orientation of the ZrN coatings. As the substrate bias increased and the deposition pressure decreased there was a rise in the (111) orientation as shown in Figures 5a and b for bias and pressure, respectively. This effect is similar to that shown in the research of Kadlec, et al.⁴

Scanning electron microscopy of the surface after exposure to electrochemical testing revealed either no corrosion products or defects in the case of low anodic current density, or evidence of base metal pitting like that shown in Figure 6. This micrograph demonstrates how pitting to the base metal causes the electroplated layer to collapse in the pit once the base metal is corroded and can no longer support the plated layers.

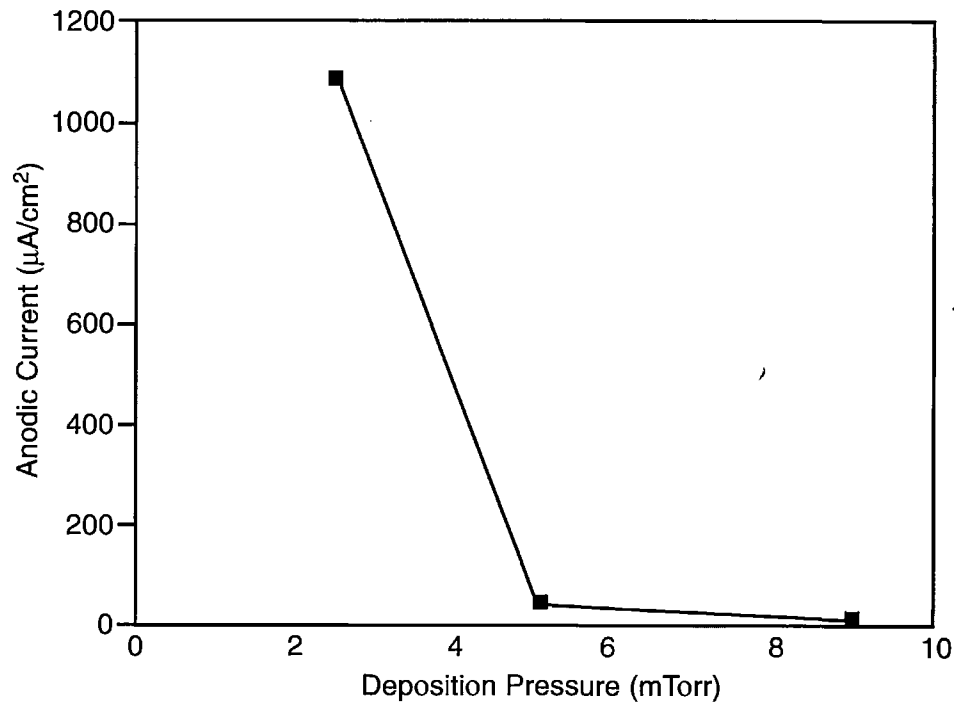


Fig. 4: Anodic polarization current at various deposition pressure conditions.

4.0 Discussion

Both substrate bias and deposition pressure are observed to affect corrosion properties of the multi-layer ZrN/Cr/Ni/Brass coating stacks. One consideration in explaining the effect of deposition pressure and substrate bias is the possible contribution of growth structure and residual stress. Though it was difficult to determine the residual stress due to the high orientation of the low indexed planes, the peak shift due to lattice distortion was calculated. The calculated lattice strain for the (111) and (200) planes of ZrN are shown in Table 1. Also shown in the table are the anodic corrosion currents measured from the DC electrochemical experiments. The results indicate that as the (111) and (200) lattice strain increases the anodic corrosion current decreases. This is equivalent to saying that as the stress or strain in the coating decreases the corrosion current increases. We hypothesize that the stress/strain is providing a more active cathodic area (i.e. ZrN), which is large relative to the anode area as shown in Figure 7. In this schematic, we realize the opportunity for galvanic corrosion of the nickel plated layer and eventually the brass substrate. The ZrN layer is more noble than both the chromium and nickel plated layers. Therefore, the potential for pitting corrosion is very high due to the large cathode to

anode surface area ratio. In actuality, the galvanic couple is initially established between the ZrN and the electroplated nickel through cracks and pinholes in the electroplated Cr layer. Our research of this multi-layer system indicates that the galvanic corrosion is minimized at high pressures and low substrate bias levels as schematically illustrated in Figure 7b. Because the strength of the galvanic couple is dependant on the state of the ZrN (cathode), the larger strain states and change in orientation will minimize the galvanic couple strength.

As the orientation of ZrN changes from (111) to (200) there is a change in the Fermi energy or electrochemical potential.⁵ Thus, the potential (driving force) for galvanic and uniform corrosion will change as various crystalline orientations are exposed at the surface. Pourbaix diagrams indicate that zirconium will form a hydrated oxide on the surface when exposed to aqueous chloride environments.⁶ In addition, the higher strain/stress states associated with the coatings deposited at higher pressures and lower substrate bias levels increase the electrochemical potential and thus the propensity to form the hydrated oxide of zirconium. It has been shown that a passive hydrated zirconium oxide is capable of alleviating pitting corrosion due to the reduction of galvanic potential between the PVD coating and substrate.⁷

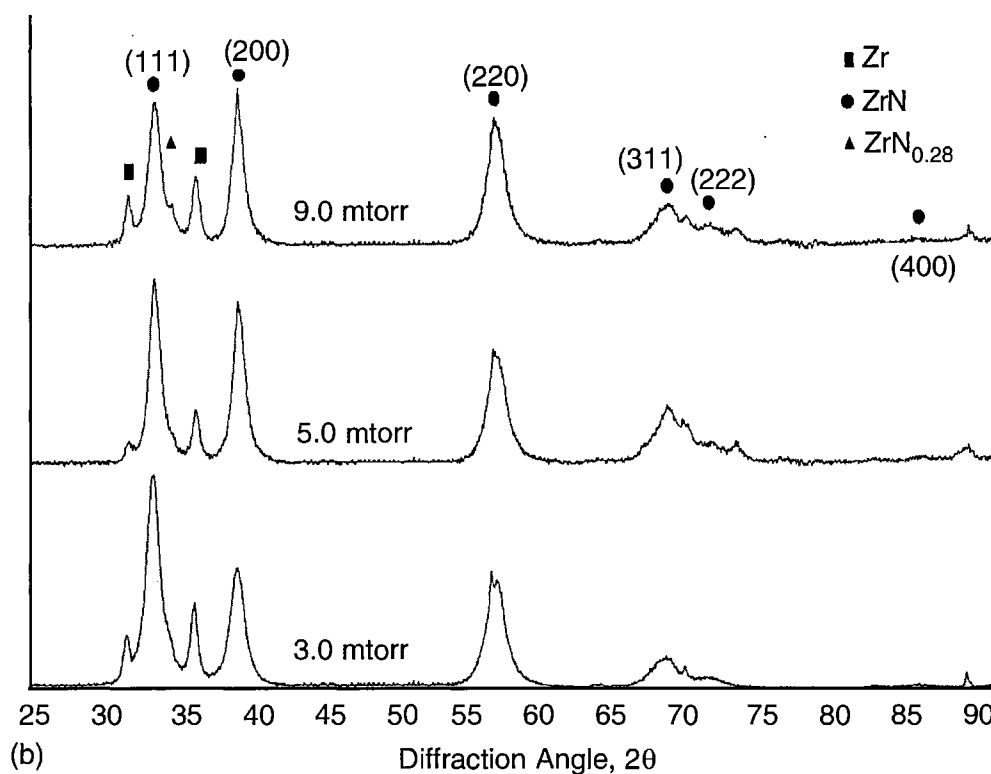
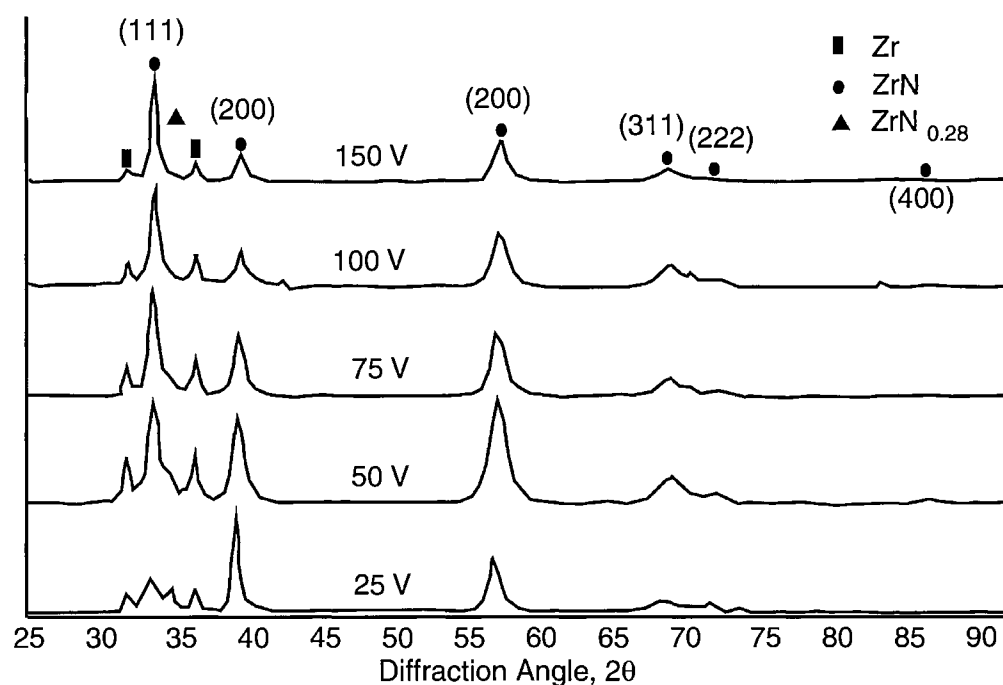


Fig. 5: XRD patterns for coatings deposited at various substrate bias and deposition pressures. (a) bias and (b) pressures are labeled next to the diffraction pattern.

5.0 Conclusions

DC electrochemical characterization has provided useful information in developing ZrN PVD coatings that are less susceptible to corrosion. Specifically, substrate

bias and deposition pressure affect the electrochemical properties of the multi-layer stack. Both lower substrate bias and higher deposition pressures appear to yield a coating that is less susceptible to pitting corrosion. A relationship between the microscopic and macroscopic

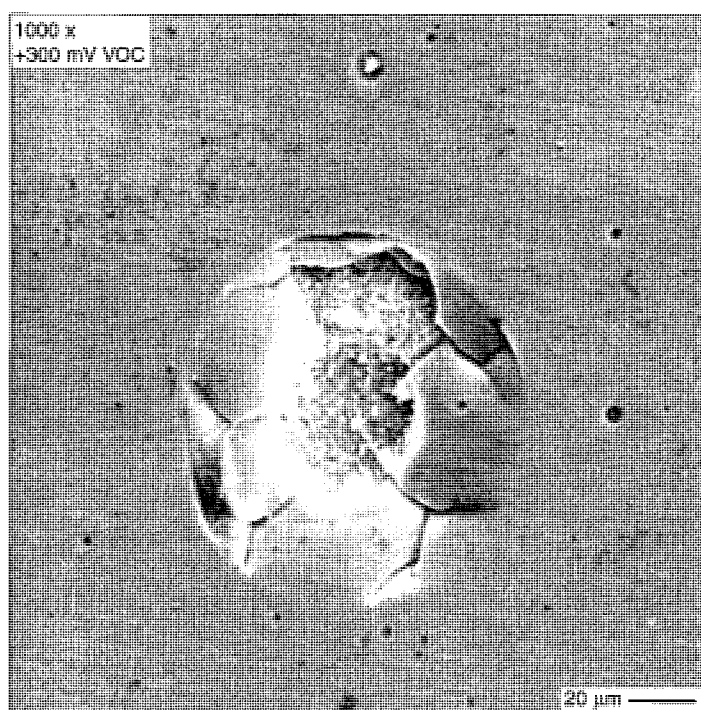


Fig. 6: A micrograph of typical pitting corrosion generated during anodic polarization

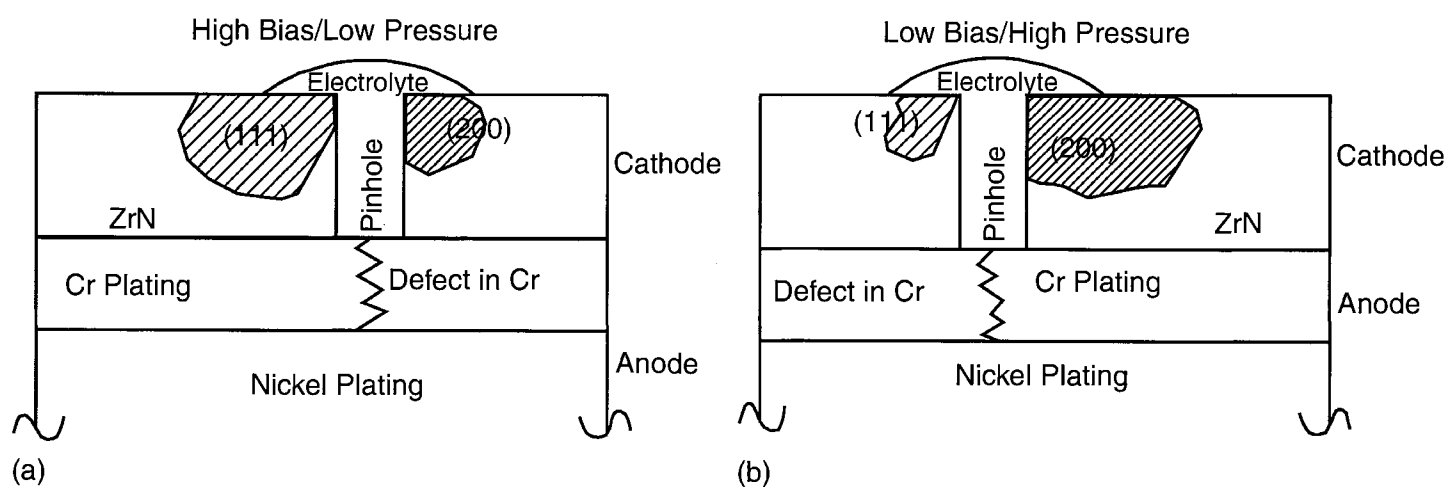


Fig. 7: Galvanic corrosion is minimized at high pressures and low substrate bias levels since stress/strain provides a more active cathodic area (i.e. ZrN), which is large relative to the anode area.

Table 1. Stress, Strain and Anodic Current as a Function of Substrate Bias and Gas Pressure

Condition (Bias, Pressure)	Strain (111) $(d-d_0)/d_0$	Strain (200) $(d-d_0)/d_0$	Anodic Current ($\mu\text{A}/\text{cm}^2$)
25 V	0.0215	0.260	0.32
50 V	0.0076	0.0166	0.402
75 V	0.0039	0.155	2.46
100 V	0.0015	0.0140	89
150 V	0.0015	0.0140	360
3.0 mtorr	0.0039	0.0155	1100
5.0 mtorr	0.0076	0.0170	0.402
9.0 mtorr	0.015	0.0215	0.114

structure of the PVD coatings revealed that a (200) orientation and higher lattice strain helped to avoid the formation of localized pitting into the brass base metal. Future work will explore the effects of other process conditions on the electrochemical properties.

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Eco-Friendly Chromium and Cadmium Dry Plating

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Abstract

Eco-friendly chromium and cadmium Dry Plating methods that eliminate wet chemicals have been developed. The significance of these vacuum based methods is their competitive process economics. The Dry Plating provides plating rates over 1 $\mu\text{m}/\text{min}$ on large surface areas ($> 5000 \text{ cm}^2$). At the same time, the load-to-unload process cycle for typical commercial coatings is under 15 minutes. The cadmium Dry Plating process has been commercialized since 1997. These coatings are in use in commercial airplanes, missiles, and helicopters. In the case of chromium, decorative chrome has

been developed for commercialization and other applications are being explored. The Dry Plating is applicable to most substrate materials such as metals, plastics, ceramics and glass. Many other metals and alloys are being Dry Plated in production for the commercial sector.

1.0 Introduction

Chromium and cadmium electroplating is widely used for wear and corrosion protection of industrial components. This is a relatively large industry with

hundreds of job-shop and captive operations in the U.S.¹ These operations use toxic chemicals such as chromic acid and cyanide in their plating. As a result, the industry is known for generating large quantities of hazardous solid and liquid waste. For the past two decades, considerable effort has been made to minimize this waste, yet effective economical solutions have not been found. In addition, to comply with the Environmental Protection Agency (EPA) and Occupational Safety and Health Administration (OSHA) regulations, costly waste treatment and disposal methods are required. On the other hand, the conventional, alternative physical vapor deposition (PVD) techniques, also known as vacuum coating or vacuum metallizing, have not been able to compete with electroplating in large-scale production economics. The cost of PVD is typically an order of magnitude higher than that of the electroplating. Most PVD processes in general have long process cycles and low throughput. Besides, a substantial amount of coating material is wasted on chamber walls and fixtures causing higher operating costs. However, only vacuum based techniques can deposit most metals and alloys, a large number of compounds and polymers as well as ceramic or glassy materials on most types of solid surfaces.² Consequently, vacuum coatings have established a niche in the semiconductor, optical, electronics and several other high technology fields.²

The technology developments described here are for the purpose of relatively thick ($> 5 \mu\text{m}$) industrial quality metal and alloy coatings. The developments at Ion Edge have been targeted toward improving process economics of PVD methods using innovative and novel approaches. These projects have received funding from the EPA, National Science Foundation (NSF) and other federal agencies under their pollution prevention programs.³ In the techniques described here, a sufficient quantity of a desired metal or alloy is vaporized in a short period to generate a large quantity of vapor that condenses rapidly on relatively cooler commercial parts. The advantage of the vacuum based methods is that there are no liquids involved in the coating process. Therefore, there are no spent chemicals to dispose of or fumes to worry about. This presentation describes the commercialized cadmium Dry Plating as well as chromium Dry Plating currently in progress. Relative simplicity of hardware and process in the pursuit for environmentally safe coating methods has been emphasized. The technique used to vaporize each metal in large quantities followed by condensation on parts is not the same, however.

2.0 The Dry Plating Methods

In order to plate a large number of commercial parts within a reasonable period of time ($< 20 \text{ min.}$), the PVD

process should be capable of vaporizing several grams of material quickly followed by uniform deposition on all intended surfaces. The most economical conventional PVD process that can vaporize large quantities of material rapidly is evaporation.² In the classical vacuum evaporation, the desired metal to be coated is typically evaporated from a crucible by applying thermal heat or using an electron beam. The most significant drawback of this method is the non-uniform distribution of vapors across the chamber analogous to an expanding gas from a point source, resulting in non-uniform coating on the parts. In addition, more material is wasted on walls and fixtures than that deposited. Remedies such as mechanical manipulation of parts using complex fixtures in vacuum add to the cost and make the process cycle long and uneconomical.

2.1 Cadmium Dry Plating

Cadmium is a unique metal that sublimates rapidly at temperatures well below its melting point (321°C) at a vacuum level of a few milli-Torr (mT). It can be vaporized in vacuum at temperatures above 150°C from the solid state, and its vapors can be prevented from depositing on walls that are maintained at elevated temperatures. The sublimation concept allows for evaporation of cadmium in large quantities ($> 10 \text{ gm}$) from a relatively large surface area such as a cadmium sheet as shown in the schematic of Figure 1. In this case, the walls of the vacuum chamber are lined with cadmium sheets, and parts are loaded on a rack in the center. When the walls are heated using an argon glow discharge or thermal means, the emitted cadmium vapors fill the chamber rapidly creating a vapor-bath-like effect. Any substrates submerged in this vapor-bath get a rapid and uniform coating thickness ($> 10 \mu\text{m}$) within two to three minutes.

2.2 Chromium Dry Plating

The proprietary features of this system and process are not available for disclosure at this time. However, a summary description can be made as follows. As shown in the schematic of Figure 2, the basic process and apparatus consists of a relatively large ($> 750 \text{ cm}^2$) surface area vapor source emitting vapors rapidly toward substrates loaded on a rack. These vapors are generated using an intense argon glow discharge (plasma) at a vacuum level of a few mT. A substantial portion ($> 20\%$) of the vaporized species is ionized allowing denser coatings. The vapor flux is highly directional and nearly perpendicular to the vapor-source surface resulting in higher deposition rates and reduced waste deposits on

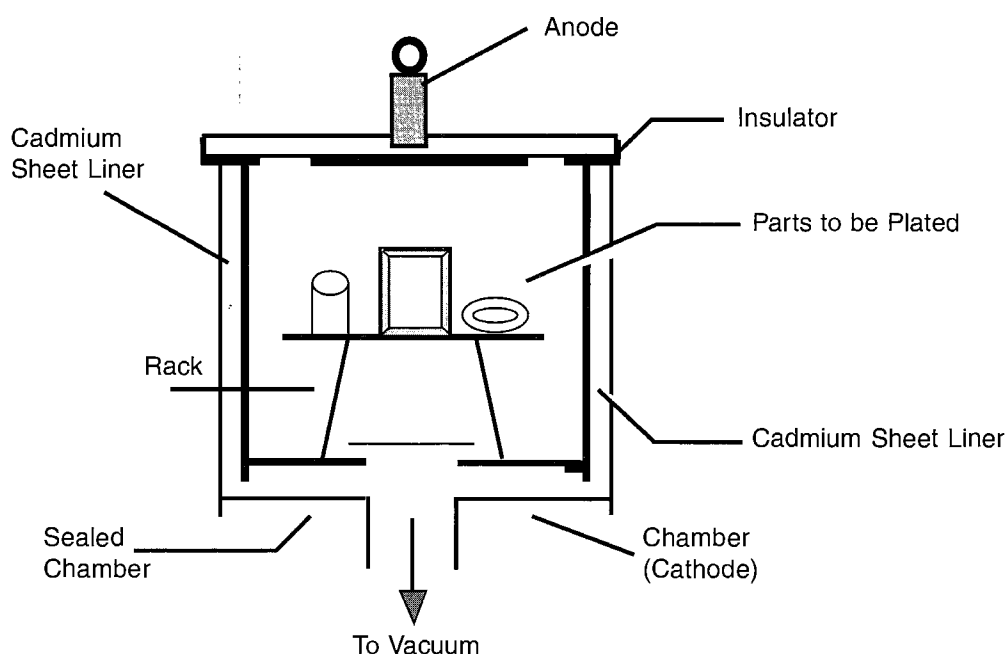


Fig. 1: A schematic of the cadmium Dry Plating system.

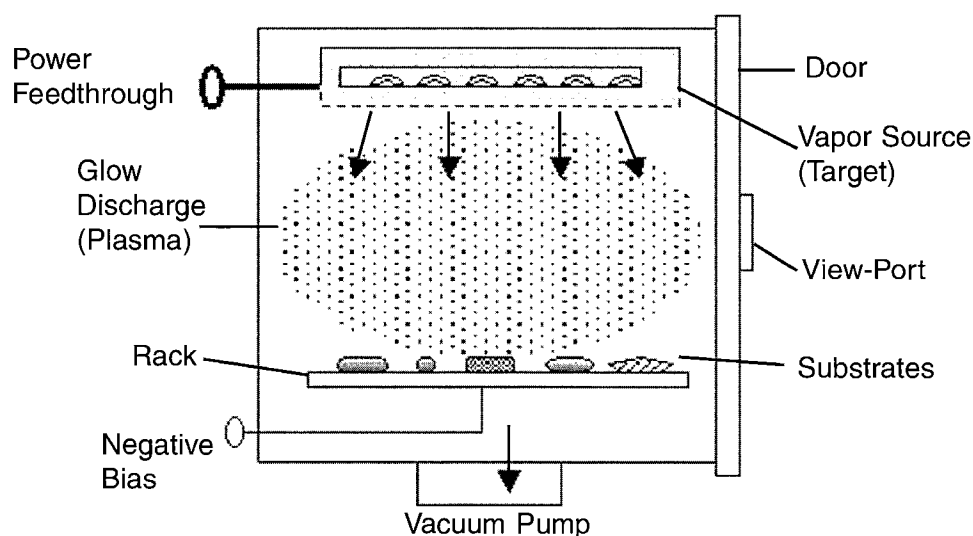


Fig. 2: A schematic of the chromium Dry Plating apparatus.

the walls. At the same time, intense plasma also allows deposition on surfaces parallel to the vapor stream to a depth of a few centimeters. Consequently, it is not a line-of-site deposition. The vapors can be directed in a desired direction by changing the angle of the vapor source as well as applying a bias to the substrates. For example, the substrates can be suspended from a vertical rack in front of a vertical vapor source. In that case, all sides of the parts can be simultaneously coated when two vapor sources are located across from each other.

3.0 Results

The deposition rate as a function of process parameters has been studied for both the cadmium and chromium Dry Plating processes as shown in Figures 3 and 4, respectively. The rate of cadmium deposition varies directly with the bias voltage to the cadmium foil (cathode) because at higher voltage, higher energies of impinging argon ions result in higher cadmium-foil surface temperature and proportional rise in vaporization

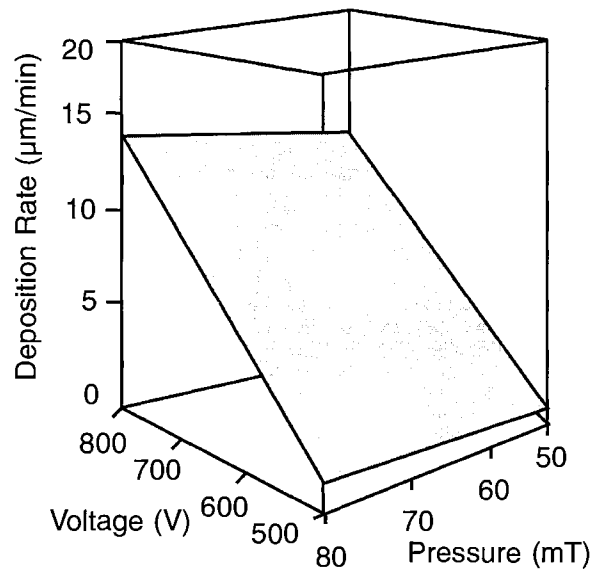


Fig. 3: Effect of process variables on cadmium Dry Plating rate.

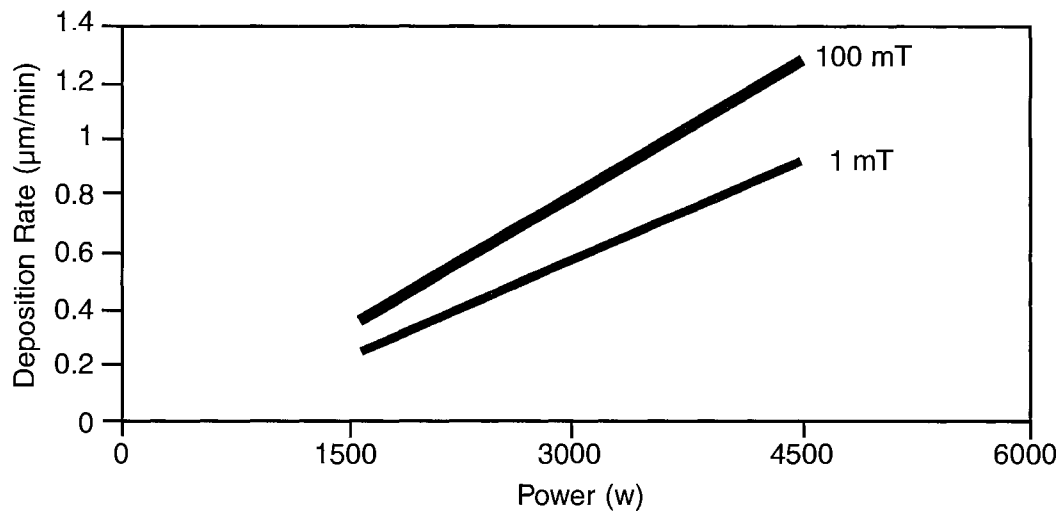


Fig. 4: Effect of process variables on chromium Dry Plating rate.

rate. Note the relatively high deposition rates, up to $20 \mu\text{m min}^{-1}$, for cadmium in this process. On the other hand, the effect of argon pressure is minimal within the experimental space because increased pressure did not change the process thermodynamics noticeably. It is likely that the generation of large quantities of neutral cadmium atoms by the foils resulted in quenching the argon plasma to an extent that there was no net change in the energy equation.

In contrast, according to Figure 4, there is a noticeable increase in the chromium deposition rate as a result of the large increase in argon pressure. It is believed that this increase in deposition rate with higher pressure is due to more argon ions causing a proportional increase in impingement rate on the vapor source (target). The plasma quenching or neutralizing effect is not observed here because neutral chromium atom density is relatively small compared to that of the cadmium in

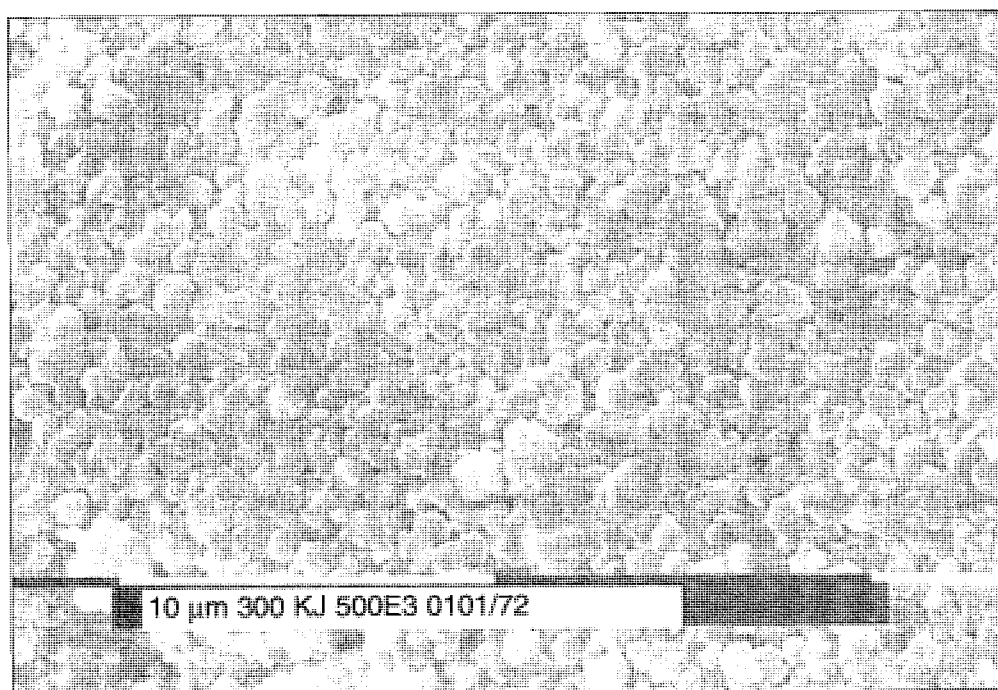


Fig. 5: SEM micrograph of dry plated cadmium surface after chromating (5000X).

its Dry Plating. The rate of vaporization is proportional to the power input to the vapor source as expected for such evaporative processes. Consequently, control of vaporization as well as deposition rate is excellent for both cadmium and chromium Dry Plating. The typical load-to-unload process cycle is about 10 to 20 minutes depending on the thickness required and the type of metal desired.

3.1 Coating Quality

Dry Plated cadmium indicates randomly oriented and non-columnar crystal structure as observed under the SEM at magnification up to 1500X. The grain size was determined after chromating treatment using surface micrograph (5000X) of Figure 5, and it appeared to be under 1 μm. The grains were exposed by the acidic nature of the chromating solution. The cavity coverage in Dry Plating is acceptable to a minimum depth of 4X the diameter for blind cavities and 2X the diameter for through cavities. The quality of Dry Plated cadmium meets federal standard QQ-P-416, military specification MIL-C-8837 as well as aerospace material specification AMS 2426. The Class 2 (7.5 μm thick) with Type II (iridescent yellow chromate) cadmium coating passed well over 7,000 hours in salt-spray corrosion testing as per ASTM B 117 at the Army Research Laboratory in

Rock Island Arsenal, IL.⁴ The uniformity of the coatings is excellent and is within 1 μm from lot to lot. The adhesion of the coatings to steels is equal to that of electroplated cadmium as determined by a pull-test according to ASTM D 4541 and a bend test per ASTM B 571. Epoxy enamel paint adhesion is also acceptable according to ASTM D 3359. There is no hydrogen embrittlement of high strength steels due to the absence of hydrogen in this process.

Preliminary studies on chromium coating density and hardness on steel substrates have been conducted. The data indicates that the density is above 99% as determined by the gravimetric method. Again, there is no evidence of columnar crystal structure as determined from SEM cross-sectional studies. A cross-sectional micrograph of a relatively thick (16 μm) chromium coating at the magnification of 2500X is shown in Figure 6. The uniformity of metal coatings across a 5,000 cm² surface area on a flat table is within ± 10% and improvement to ± 5% appears feasible. This uniformity is considered competitive with electroplating, and acceptable for most intended industrial applications. Under certain process conditions, the chromium coating hardness was measured to be above 1150 VHN on mild steel substrates. The feasibility of depositing chromium coatings up to 120 μm thickness at the rate of 1 μm per minute has been demonstrated. A cross-sectional photograph of a

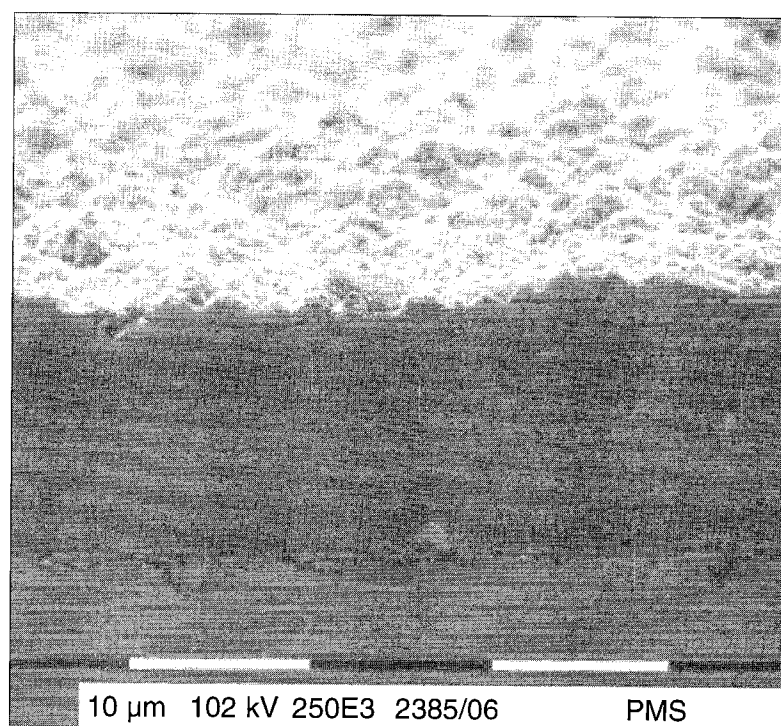


Fig. 6: Cross sectional micrograph of a relatively thick (16 μm) chromium coating (2500X).

120 μm chromium coating as seen under an optical microscope at the magnification of 250X is shown in Figure 7.

4.0 Dry Plating Operation

The cadmium production rack plating system has been arranged horizontally for loading convenience, and the inner hot-wall chamber is separated from the larger outer vacuum chamber as shown in Figure 8. The production chamber size is about 70 cm dia. $\times$ 75 cm long, and the process cycle consists of pump-down, argon glow discharge, cadmium evaporation and deposition, and nitrogen backfill. This chamber has the capacity to coat three dimensional objects with a surface area over 5,000 cm^2 every 10 minutes. A loaded cadmium dry plated rack after a coating run is shown in Figure 9. Note that the rack has no cadmium deposits, nor do the other parts of the chamber, because these are prevented from cadmium accumulation. Consequently, this method is called “zero-waste Dry Plating”. The typical load-to-unload Dry Plating process cycle for cadmium is about 10 minutes for a 7 to 8 μm thick coating required for most military applications. Overall heat dissipation per hour being relatively low, this system does not require a water-cooled chamber.

For chromium, nickel, copper and other metals, a production system has been developed as shown in Figure 10, for large area ($> 6500 \text{ cm}^2$) coating and process studies. The chamber is cubical in shape with each side about 91 cm long and the chamber walls are water cooled due to relatively high heat dissipation ($> 15 \text{ kw}$) during deposition. The system has enough ports to be able to mount multiple targets vertically or horizontally allowing for increased coating rate and three dimensional coverage.

The Dry Plating operation consists of only two or three process steps as opposed to a dozen or so hazardous, fuming liquid baths in electroplating as shown in Figure 11. Furthermore, the Dry Plating does not require a waste treatment facility or related sludge disposal and effluent discharge. The operation consists of a wet bench for degreasing parts using an alkaline degreaser, Dry Plating system and a chromating bath for cadmium. In the case of chromium, chromating is not used. The Dry Plating operation reduces the use of water to less than 10% of that in the electroplating. On the plating line, the thickness variation is minimized and uniformity is maintained using statistical process control (SPC) an example of which is shown in Figure 12. This chart demonstrates how the thickness variations were methodically reduced in the early phases of cadmium



Fig. 7: Optical micrograph of a relatively thick (120 μm) chromium coating (250X).

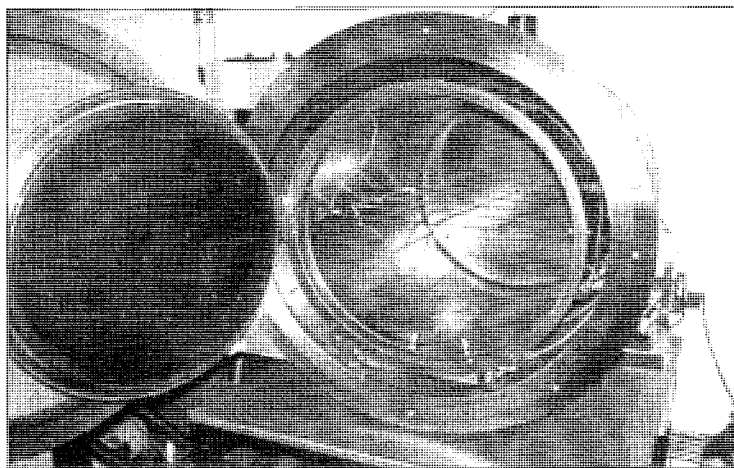


Fig. 8: A photograph of the cadmium Dry Plating apparatus.

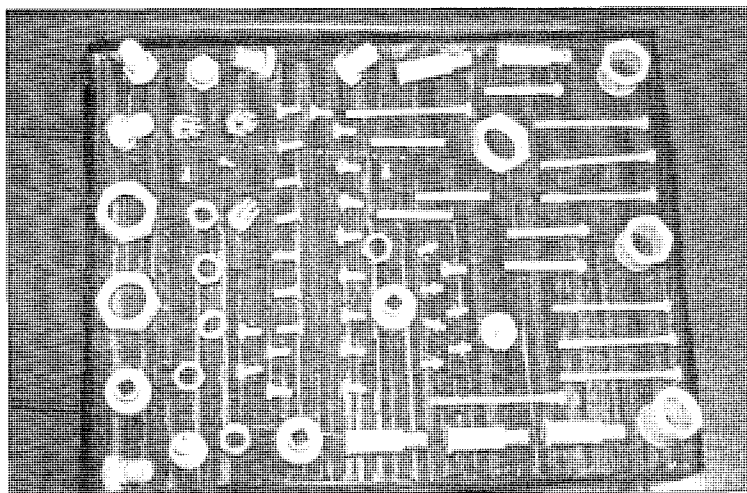


Fig. 9: A photograph of Dry Plated steel parts after a cadmium coating run.

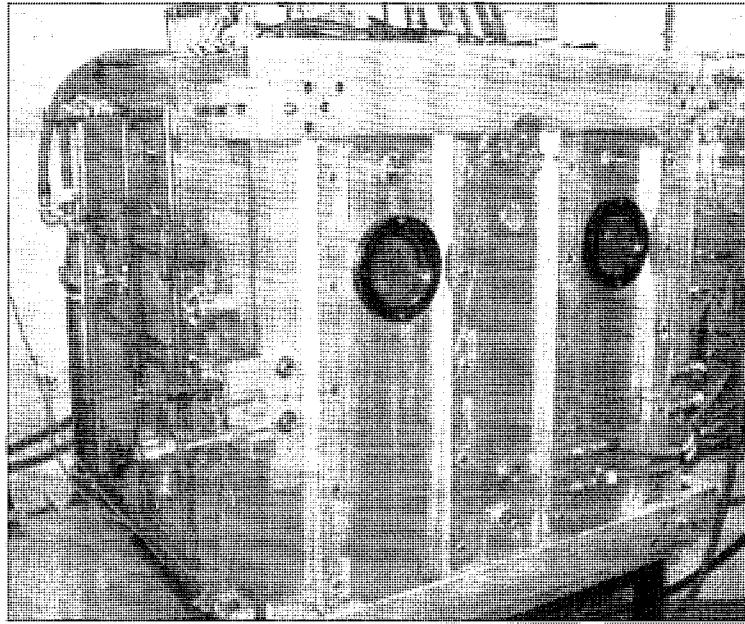


Fig. 10: Prototype production system for chromium and other metals Dry Plating.

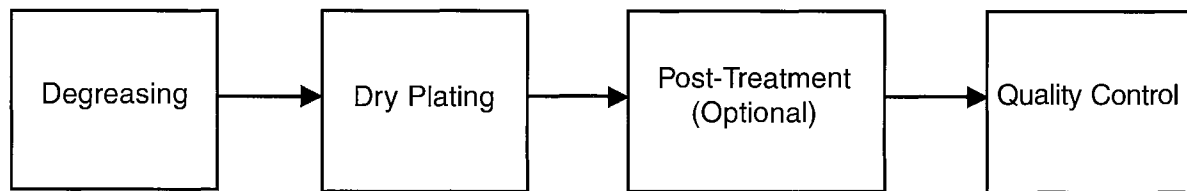


Fig. 11: A process flow chart of the Dry Plating operation.

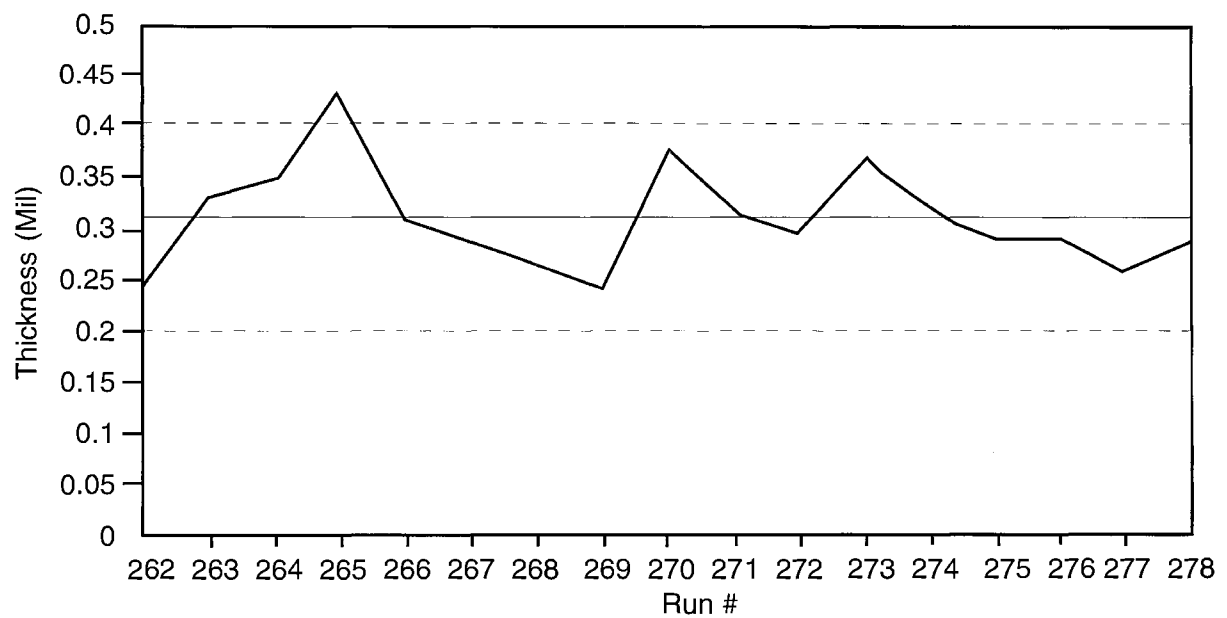


Fig. 12: Dry plating thickness variation reduction using SPC control.

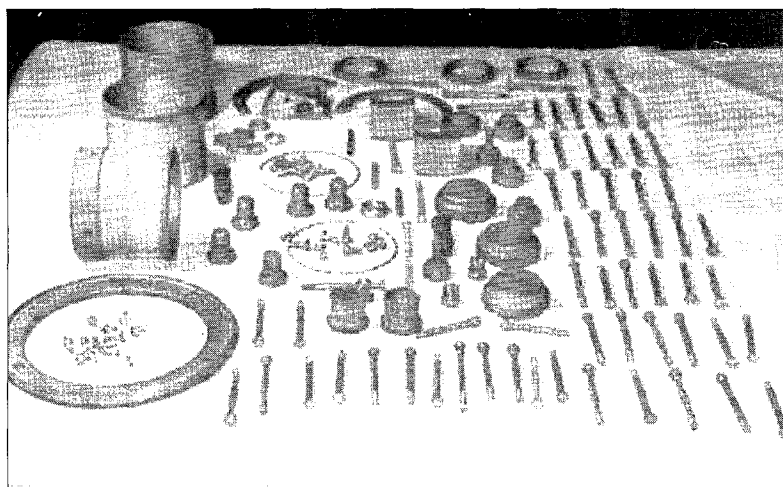


Fig. 13: Various cadmium Dry Plated and post-treated aerospace parts.

Dry Plating development. Similar work is in progress for the chromium Dry Plating.

5.0 Cost Savings in Dry Plating

There are two significant factors that contribute to cost savings in Dry Plating compared to electroplating: waste treatment and management cost savings, and energy cost savings. It is known that approximately 10,000 gallons of waste water are generated in each shift in a typical medium size electroplating shop.⁵ In addition, hundreds of thousands of dollars are spent in each shop on waste treatment hardware, hazardous emission control equipment and scrubbers.⁶ The current cost of waste treatment and management in the U.S. is over 10 cents per gallon of water used. At this rate, the cost of waste management exceeds \$1,000 per day.⁵ Similarly, it is estimated that 95 kW of power is consumed in electroplating every hour mostly for plating bath heating or cooling, bake ovens, exhaust and ventilation and facilities heating or cooling.⁶ Most of these operations are eliminated by the Dry Plating process. It is estimated that Dry Plating will consume less than 20 kW every hour saving over 75% in energy costs. There are additional savings in material and chemical costs in Dry Plating. It is estimated that the cost of labor and equipment maintenance in Dry Plating is likely to remain about the same as in electroplating in the early phases of its market introduction.

6.0 Dry Plating Applications

Cadmium being a known toxic metal, its applications in the industry are being limited only to

high strength steel components and fasteners where no other coating is acceptable. Cadmium is still considered the most reliable corrosion protection for steels especially in a marine environment. Consequently, it is used extensively in the military and in aerospace applications. The Dry Plating production line has coated hundreds of thousands of high strength steel fasteners for aerospace and military applications to date, and some of these are shown in Figure 13 after the chromating post-treatment. These are in use in airplanes, missiles and helicopters. The first successful application of chromium Dry Plating has been developed for decorative applications as shown in Figure 14. Commercialized applications of Dry Plating include copper, nickel and aluminum coatings for electromagnetic interference (EMI) shielding, ceramic circuit boards and capacitors, printed wiring boards (PWBs) and other plastic or composite materials. A job-shop coating service is now in operation for these applications. A photograph in Figure 15 shows various commercial plastic and ceramic components dry plated with nickel, copper aluminum and chromium.

7.0 Conclusions

The Dry Plating operation has demonstrated that it is a robust, economical and environmentally safer method as compared to conventional electroplating. Several disadvantages of conventional PVD have been overcome by reducing the cycle time and increasing the throughput for Dry Plating resulting in competitive process economics. The coating apparatus has provided repeatable performance and process control for every batch. The noteworthy advantages of Dry Plating include

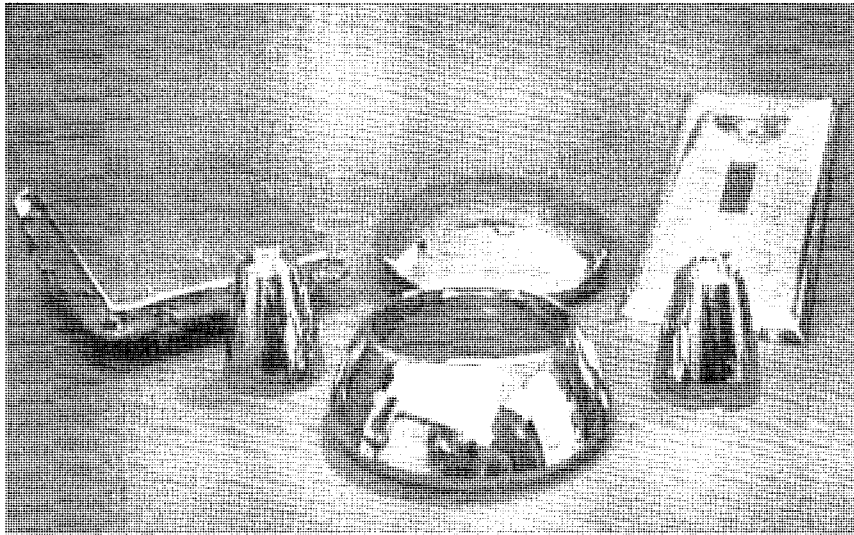


Fig. 14: Dry Plated decorative chromium finish on various types of plastics.

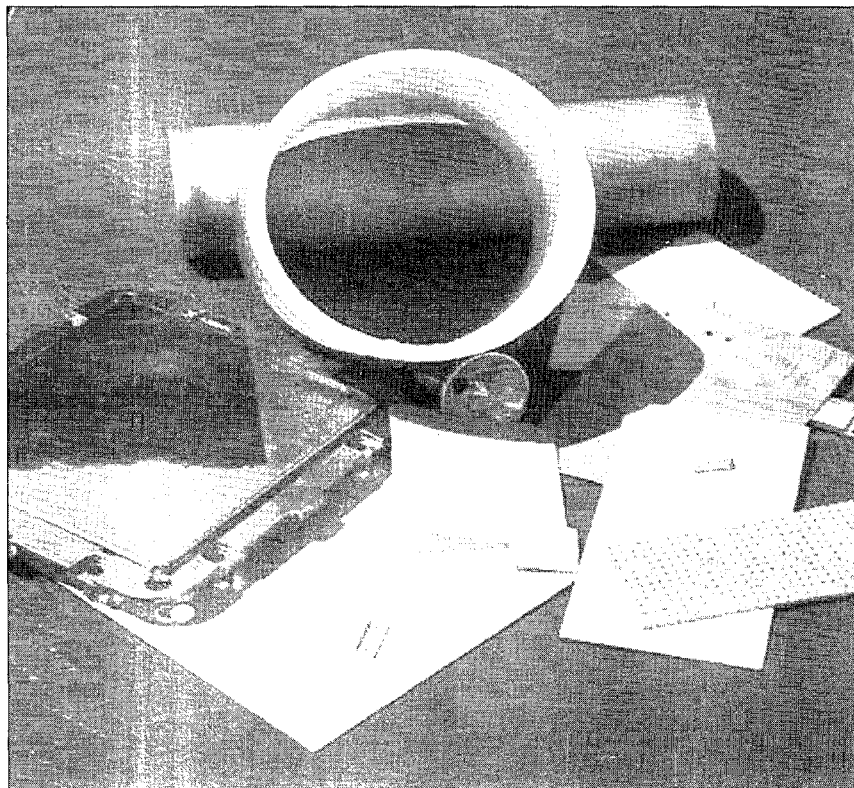


Fig. 15: Various commercial parts Dry Plated with aluminum, copper, and nickel.

75% cost savings in energy consumption, over \$1,000 per day cost savings in waste management, and elimination of several toxic chemicals and their disposal. Both described versions of the Dry Plating technology have been commercialized and a job-shop coating service is in operation for the commercial sector.

8.0 Acknowledgments

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Evaluation of Aluminum-Manganese as a Cadmium Replacement

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Abstract

The Department of Defense (DoD) is reducing, and will eventually eliminate its current reliance on cadmium-based coatings for defense systems due to the environmental and health hazards posed by cadmium, a toxic metal and a human carcinogen. Compliance with environmental, safety and health regulations is becoming prohibitively expensive due to cadmium's toxicity. In addition, the potential for limited operations overseas exists due to foreign restrictions regarding cadmium containing parts. As a result, non-toxic substances

must be found to replace cadmium coatings. Aluminum-manganese may provide the functional performance of cadmium without its detrimental toxic properties. This effort will demonstrate the efficacy of electroplated aluminum-manganese coatings in replacing cadmium coatings.

Using a molten salt bath, aluminum-manganese can be easily and inexpensively plated onto components, including internal diameters, complex geometries, and threaded applications. The salt bath is operated at 190°C and is composed of aluminum chloride, sodium chloride, potassium chloride, and a small amount of manganese chloride. The goal

of this effort is the implementation of a production scale molten salt electroplating system at Naval Aviation Depot (NADEP) North Island in San Diego, California. Aluminum-manganese coatings are targeted for use in applications in which other coating technologies have been unsuccessful in replacing cadmium. The replacement of toxic cadmium coatings with non-toxic aluminum-manganese coatings will save DoD environmental compliance costs, and will provide protection to human health and the environment.

1.0 Introduction

Cadmium is commonly used to protect metallic components from corrosion. However, cadmium is toxic and carcinogenic to humans in relatively low doses. Maintenance of cadmium coated parts routinely exposes workers to cadmium-containing dust and fumes. Alternative coating systems which successfully inhibit corrosion of metallic components, but do not contain cadmium, are being investigated.

The Navy Environmental Health Center (NEHC) evaluated the general toxicity and carcinogenicity of cadmium, as well as the chemical constituents of potential alternative coatings.^{1, 2} Potential alternative coatings may contain nickel, manganese, aluminum, zinc and/or tin. NEHC evaluated the metal, oxide and hydroxide forms of each of these metals. NEHC referenced Material Safety Data Sheets and chemical and toxicological reference sources and databases for health effects data.

NEHC's evaluation of cadmium determined that cadmium poses a significant health hazard to exposed workers. Cadmium inhalation exposure is proven to cause serious acute and chronic respiratory effects, as well as reproductive effects. Inhaled cadmium is easily absorbed into human organ tissue, and then very slowly eliminated. For example, it takes 30 years for half of an absorbed dose of cadmium to be eliminated from the body. Relatively low doses of cadmium (9 mg/m³) inhaled over several hours have caused fatalities. Cadmium is recognized as a known human carcinogen by the International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP), and is regulated as a carcinogen by the Occupational Safety and Health Administration (OSHA). OSHA has regulated the maximum air concentration, or Permissible Exposure Limit (PEL), at which workers may be exposed to cadmium at 0.005 mg/m³ averaged over an eight-hour period.

NEHC also evaluated nickel, manganese, aluminum, zinc and tin, ingredients of potential alternative coatings. Nickel was found to be the most hazardous of the alternative ingredients. Inhalation of nickel is proven to cause acute and chronic respiratory

effects, and skin and eye irritation. In addition, nickel can be passed from mother to fetus. Nickel metal is recognized as a possible carcinogen by IARC, and nickel oxide is recognized as an anticipated carcinogen by NTP.

The NEHC also reported that exposure to manganese dust or fumes can cause central nervous system and respiratory effects, as well as eye irritation. Once exposed, it takes 37 days for half of an absorbed dose of manganese to be eliminated from the body. Inhalation of aluminum can cause respiratory effects, dementia and convulsions. Aluminum ingested by drinking water may cause birth defects, but evidence is inconclusive. Exposure to zinc dust or fumes can cause metal fume fever and skin, eye and gastrointestinal irritation. Inhalation of tin dust can cause respiratory effects. Manganese, aluminum, zinc and tin are not known or suspected carcinogens.

OSHA has regulated the maximum air concentration at which workers may be exposed to nickel metal and insoluble nickel compounds at 1 mg/m³, manganese compounds or fumes at 5 mg/m³, aluminum metal at 15 mg/m³ total dust and 5 mg/m³ respirable dust, zinc oxide at 15 mg/m³ total dust and 5 mg/m³ respirable dust and fumes, and inorganic tin compounds (except oxides) at 2 mg/m³. All limits apply to exposure averaged over an eight-hour period, except for manganese, which applies to exposure in any given instant in time.

Cadmium compounds clearly pose a more significant health hazard than the potential alternative coating ingredients. The maximum air concentration at which exposure to cadmium is regulated is 3 orders of magnitude lower than any of the alternatives. Investigation of alternative coatings is justified by the possibility of eliminating or reducing the use of cadmium-containing coatings on metallic components, and thereby reducing the health hazard to workers.

2.0 Life Cycle Perspective

Compliance with current environmental, safety and health regulations regarding the use of cadmium must be considered over the whole life cycle. Coating deposition costs of cadmium are only a small portion of the total ownership costs of cadmium coatings. Coating deposition is conducted in a controlled environment with trained personnel, personal protective equipment, and engineering controls. The raw material and equipment costs for cadmium plating in a cyanide bath are minimal. The cost of compliance with environmental, safety, and health regulations concerning the deposition of cadmium are easily and affordably addressed, although costs are increasing.

Cadmium coatings, regardless of the coating deposition process, are toxic and lead to significant in-service costs. In-service costs of cadmium coatings are attributed to a wide variety of factors. Generation of cadmium containing wastes is unavoidable when cadmium coated parts are used in-service. Performance of required maintenance procedures on cadmium coated parts yield cadmium containing wastes or cadmium contamination. Cadmium contamination has been observed in rinse waters for equipment containing cadmium coated parts. Cutting or grinding of cadmium coated nuts and bolts that have seized will generate cadmium fume or dust. Stripping of cadmium coatings by mechanical means generates cadmium dusts. Chemical stripping of cadmium coatings generates large amounts of hazardous wastes. Collection, treatment and disposal of cadmium containing wastes are expensive. Exposure to small amounts of cadmium dust or fumes can easily exceed the OSHA PEL, and may result in significant medical and legal costs. Compliance with environmental, safety and health regulations and the potential legal liabilities for the continued in-service use, removal and disposal of cadmium coatings are making the continued use of cadmium coatings extremely expensive and unacceptable. These types of costs are difficult, if not impossible, to quantify, and therefore are not taken into account in cost studies. Considering deposition costs alone cadmium alternatives will likely be more expensive than cadmium plating. However, tremendous cost savings will be realized over the total life cycle by replacement of cadmium with a less hazardous alternative.

3.0 Aluminum-Manganese & Other Cadmium Alternatives

There are several alternative coating compositions applied by various deposition techniques that are being evaluated as cadmium alternatives: zinc, tin-zinc, zinc-nickel, aluminum, and aluminum-manganese. Zinc, tin-zinc, and zinc-nickel can be deposited by aqueous plating. Aqueous plating processes are the most affordable coating deposition methods. Due to thermodynamic limitations, aluminum coatings can not be deposited using aqueous plating techniques. Aluminum can be deposited using non-aqueous plating techniques or ion vapor deposition processes.

One non-aqueous aluminum plating process, called Alumiplate, is conducted in a toluene-based electrolyte containing pyrophoric organometallic aluminides and must be kept dry and free of air.³ Although the quality of the plated aluminum is high, toluene-based plating of aluminum poses serious environmental, safety and health risks.

Ion vapor deposition of aluminum is a clean, environmentally friendly process.⁴ Typically, ion vapor deposition of aluminum costs significantly more than plating processes due to expensive capital equipment, vacuum system maintenance and large energy requirements. Also, ion vapor deposition is limited for deposition on internal diameters and for bulk quantity processing.

Aluminum-manganese coatings are deposited by a standard electroplating process using a molten salt electrolyte. Typical of aqueous plating processes, aluminum-manganese can be deposited on internal diameters, threads and other complex shapes. Thus, the molten salt technique yields process capability and flexibility similar to aqueous plating without the technical or health ramifications of other aluminum deposition techniques.

Regardless of deposition process, any of the alternative coatings systems that do not contain cadmium are expected to provide significant environmental, safety and health benefits over the continued use of cadmium, resulting in life cycle cost savings.

4.0 Toxicity of Aluminum-Manganese

Toxicity testing was conducted on aluminum-manganese powder.⁵⁻⁸ The powder composition was 30 wt.% manganese, roughly twice that of the nominal composition of the electroplated aluminum manganese coating. The toxicity testing results for Al/Mn 70:30, -100 Mesh Batch #98-9082S were as follows: LD₅₀ is greater than 2000 mg/kg of body weight, is not a dermal irritant, is an ocular irritant but is not corrosive.

For comparison, manganese-based 3000 series aluminum alloys are used in the manufacturing of soft drink cans. Aluminum Alloy 3003 has 0.5-1.5 wt.% manganese and is used in the manufacturing of cookware. Although an aluminum-manganese deposit containing 15 wt.% manganese has a higher concentration of manganese than most 3000 series alloys, the deposit is likely to have low toxicity characteristics similar to 3000 series aluminum alloys, which have allowed their use in human food applications.

Manganese has detrimental health effects if ingested or inhaled in large enough quantities. Manganese will be present in the deposit, salt bath and rinse waters. Manganese in the aluminum-manganese deposit is in the form of an Al₆Mn intermetallic compound and is not likely to be ingested or inhaled. Manganese or manganese chloride additions to the salt bath will be made with pellets to minimize dust generation and inhalation exposure. Manganese hydroxide will be present in rinse waters in small amounts.

Manganese in all of these forms should not provide for significant environmental, safety and health concerns. It is unlikely that manganese will be inhaled or ingested in any of these forms with conventional handling procedures and personnel protective equipment. Even if an individual is exposed to small amounts of manganese, no adverse effects are expected. The Estimated Safe and Adequate Dietary Intakes for manganese are 2.0-5.0 mg per day as listed by the American Society for Nutritional Science at <http://www.faseb.org/asns/NIMANG.html>. However, grinding any material without proper engineering controls or personnel protective equipment may expose individuals to dust at concentrations above the OSHA PEL of 15 ppm for inert dust. The ceiling PEL for manganese is 5 ppm.

5.0 Process Parameters and Issues

Electroplating of aluminum-manganese is conducted in a molten salt bath with a nominal wt.% composition of: 79% aluminum chloride, 10% sodium chloride, 10% potassium chloride, and 1% manganese chloride. The bath is operated at 190°C (374°F). The bath temperature will not adversely affect high strength steels and stainless steels since they are typically post-baked for hydrogen embrittlement relief at the same temperature. Molten salt plating of some non-ferrous alloys, most notably aluminum, is not recommended with this system due to alloy temperature limitations. Aluminum alloy annealing temperatures for various alloys range down to as low as 120°C. Depending on time required for deposition, exposure to the 190°C molten salt bath may change the material properties of the aluminum alloy. This is unacceptable for a deposition process.

In preparation for plating, clean dry parts are first media blasted. Teflon tape, or other appropriate material, is used as a maskant. Then parts are submerged into the agitated salt bath and plated, using a modulated reverse current. Micrographs show a good quality deposit with a nodular surface at 95 and 500× (see Figure 1). The nodular surface is amenable to post treatment, and provides a good adhesive base for paint. EDAX shows that aluminum and manganese are the only materials deposited, with a nominal manganese concentration of 15 wt.% (see Figure 2). The manganese content in the salt bath primarily controls the manganese content in the deposit. Approximate plating rates are on the order of 1 mil per hour. Residual salt deposits are best removed by rinsing in hot water, with a triple rinse recommended. High strength steels may be embrittled by the formation of hydrogen chloride during rinsing. As a result, post baking for hydrogen embrittlement relief is required for

aluminum-manganese plated steels. Aluminum-manganese coatings are removed using a caustic solution. Residual manganese products may remain and can be removed by light scrubbing with an abrasive pad. A cost-performance tradeoff study is currently being conducted to optimize materials of construction for the molten salt plating tank.

Sublimation of the molten salt bath is the key operational issue concerning the environment, safety and health. At operational temperatures, the high vapor pressure of aluminum chloride generates vapors that react with moisture in the air to produce hydrogen chloride fumes. Proper equipment design and engineering controls address these fuming issues. To test this, a 10-gallon rectangular tank was constructed and operated in a fume hood. The surface area of the molten salt in the 10-gallon tank was 1.5 square feet. At operational temperatures, fuming of the molten salt bath was minimal when covered. When uncovered the tank generated a large volume of white fumes that did not exceed the capacity of the fume hood. Dregar tubes were used to analyze for hydrogen chloride around the tank. The hydrogen chloride concentration was below detection level outside the hood. The hydrogen chloride concentration was 1.5 ppm or less inside the hood on all sides of the tank below the top of the tank. The hydrogen chloride concentration exceeded 10 ppm above the tank and along the top inside portion of the fume hood. The OSHA PEL for hydrogen chloride is 5 ppm. Fuming of an open molten salt bath was easily addressed using a properly sized conventional fume hood.

Simple engineering controls, such as ventilation directed to a scrubber, should be capable of handling fuming from production scale equipment that is not directly exposed to the atmosphere. Figure 3 exhibits a molten salt plating equipment design that is not directly exposed to the atmosphere. The work pieces and anodes will be fixed to a cover for the tank and will be referred to as the "fixture". The fixture will be lowered into the upper chamber while the inner lid remains in place. The inner lid will be removed and the fixture will be lowered into the molten salt bath. After the coating has been deposited the fixture will be raised and allowed to drain and cool for several minutes. The inner lid will then be replaced and the fixture will be removed and immediately rinsed. Fumes will be generated as the fixture is immersed in the rinse tank, and therefore the rinse tank will have adequate ventilation. Care will be taken in the design of a molten salt plating line so that water will not come into contact with molten salt during normal operations or in the event of a spill.

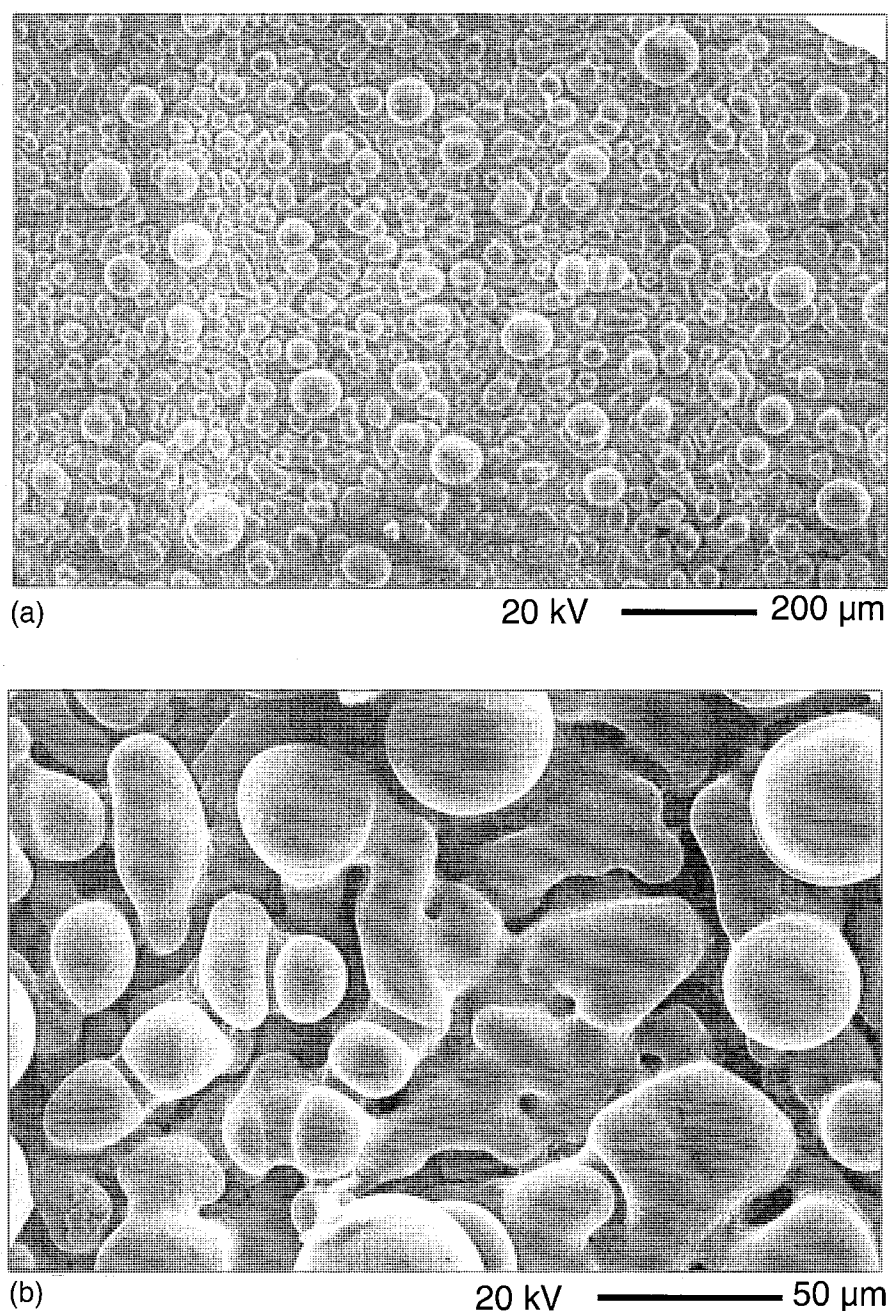


Fig. 1: Micrographs of aluminum-manganese deposit with 15 wt.% manganese.

6.0 Salt Bath Costs

The salt bath is composed of standard industrial chemicals that are readily available and affordable. A cost estimate for makeup of a 1,000 gallon salt bath follows. The approximate mass of a 1,000 gallon salt bath is 4,960 kg, based on the specific gravity of aluminum chloride at 200°C. Table 1 lists the chemical, wt.%, mass, price per mass, total cost of each chemical and total cost of the 1,000 gallon bath. Chemical costs were obtained from industrial suppliers in September 2001 and are subject to change. Instead of manganese

chloride, manganese pellets may be added directly to the salt bath or a manganese anode may be used to electrochemically charge the salt bath. The chemical make-up cost for a 1,000 gallon salt bath is less than \$15,000.

Molten salt plating of aluminum-manganese will cost more than typical aqueous plating processes. Capital equipment costs have yet to be established but should not be exorbitant due to the simple nature of the equipment. Using aluminum-manganese coatings will alleviate the concerns of environmentally assisted cracking of high strength steels associated with zinc

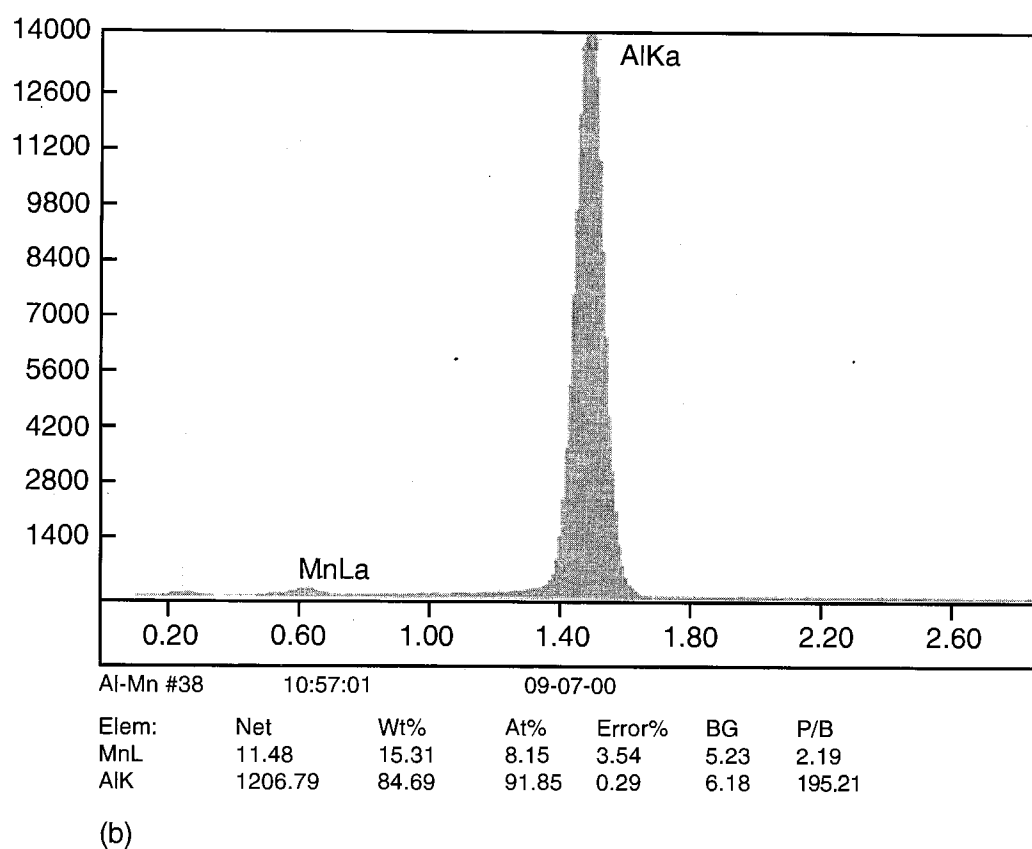
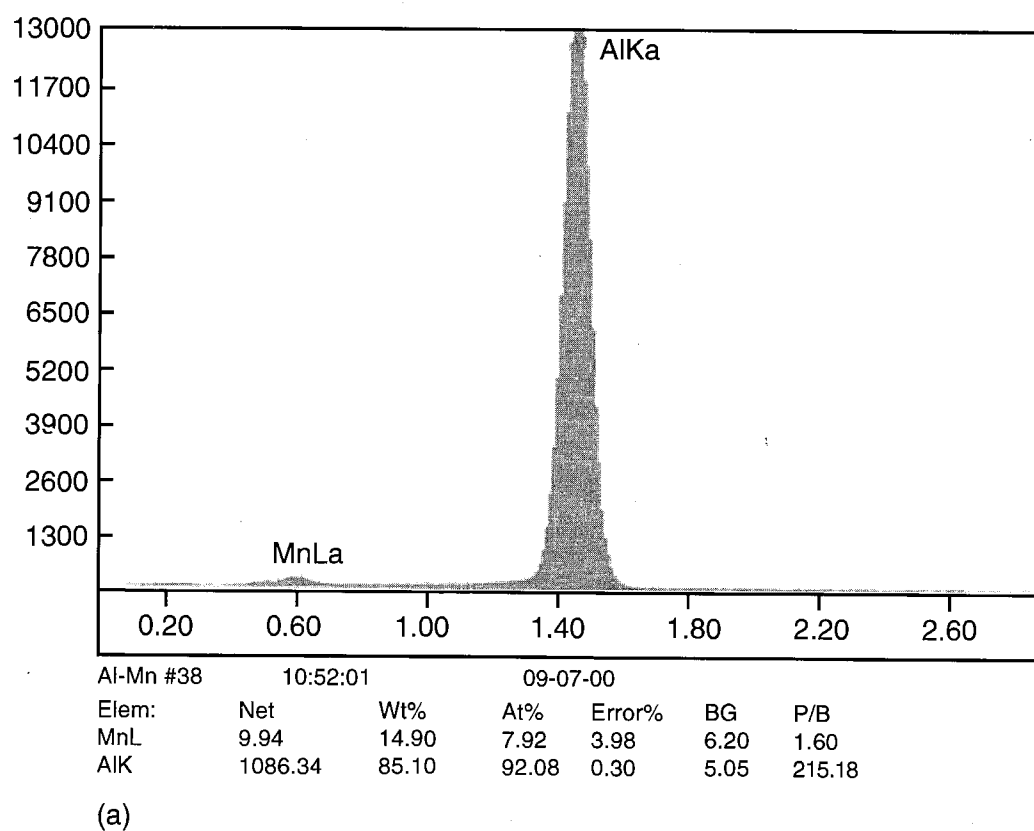


Fig. 2: EDAX of Aluminum-manganese deposit with 15 wt.% manganese.

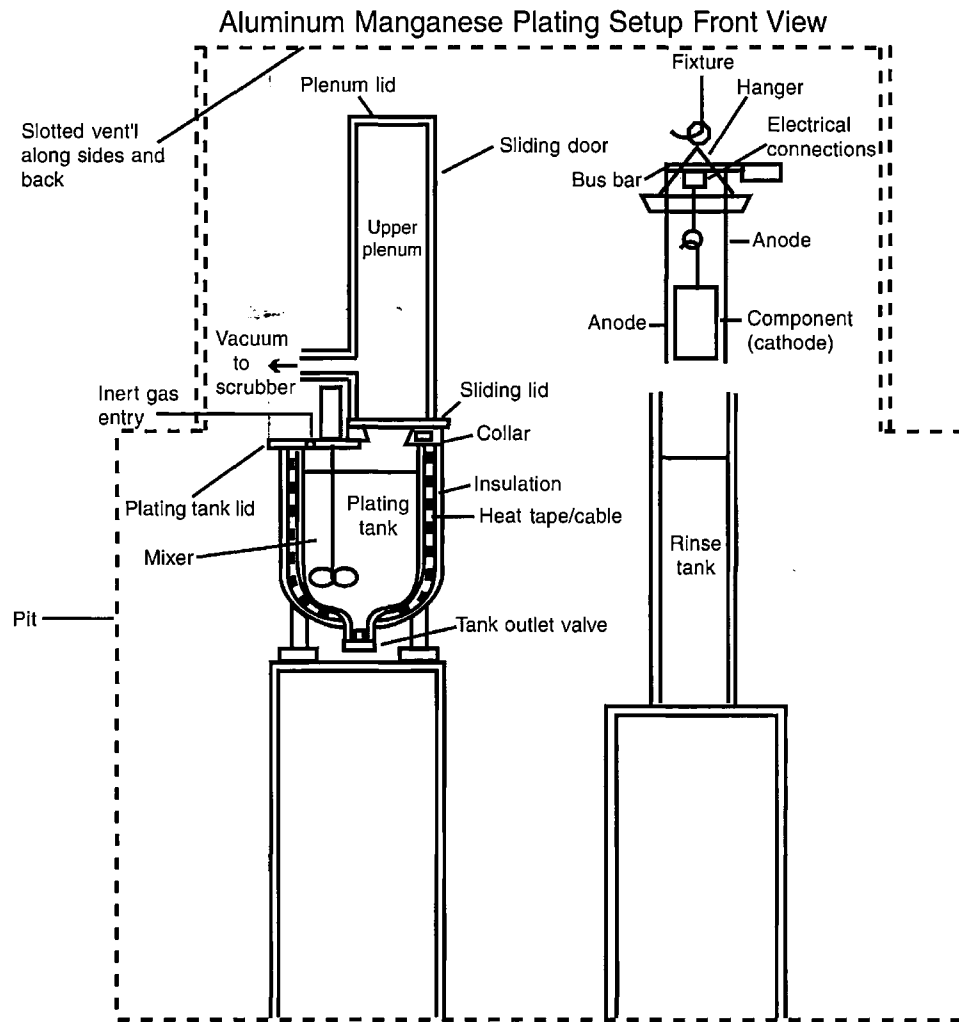


Fig. 3: Molten salt plating equipment set-up.

Table 1. Chemical Make-up Costs of a 1,000 Gallon (4,960 Kg) Salt Bath

Chemical	Wt.%	Mass (Kg)	Price (\$/Kg)	Cost (\$)
Aluminum Chloride	79	3,918	2.50	9,795
Sodium Chloride	10	496	1.54	764
Potassium Chloride	10	496	2.06	1,022
Manganese Chloride	1	49.6	16.80	834
Total Cost				12,415

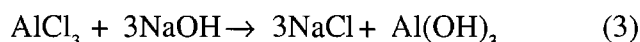
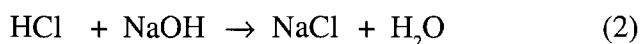
containing alloys. In addition, aluminum-manganese plating will provide functionality that is not possible with ion vapor deposition of aluminum.

7.0 Salt Bath Neutralization

Neutralization and disposal of the molten salt bath is simple and affordable. The following example will outline the neutralization of the molten salt bath. For

simplicity in this example the molten salt bath is assumed to be 100% aluminum chloride rather than the nominal bath composition of 79 wt.%. Equation 1 shows the reaction of aluminum chloride with water. For every mole of aluminum chloride three moles of hydrogen chloride are produced. Equation 2 shows the neutralization of hydrogen chloride with sodium hydroxide. One mole of sodium hydroxide is required to neutralize one mole of hydrogen chloride. Combining

Equations 1 and 2 and dropping out intermediary steps yields Equation 3, the neutralization of aluminum chloride with sodium hydroxide. The reaction shown in Equation 3 can be conducted safely in an aqueous solution by limiting the exothermic reaction rate with a controlled addition of molten salt to aqueous solution. Depending upon the rate of addition of molten salt bath to aqueous solution, cooling, or an excess of water, may need to be applied.



A one liter quantity of aluminum chloride liquid at 200°C with a specific gravity of 1.31 and a gram molecular weight of 133.34 converts to 9.82 moles (1.31 Kg). For every 9.82 moles of aluminum chloride 29.5 moles of hydrogen chloride would be produced requiring 29.5 (1.18 Kg) moles of sodium hydroxide to neutralize. This quantity of aluminum chloride can be neutralized with 4.92 liters of 6 M sodium hydroxide solution. The neutralization process, using an approximate volume ratio of 5:1 of 6 M sodium hydroxide solution to aluminum chloride, will result in 4.9 M sodium chloride solution with insoluble aluminum hydroxides/oxides. The solubility of sodium chloride in salt water is 6.1 moles per liter, and in this example all of the sodium chloride will be in solution. The volume and concentration of sodium hydroxide solution can be adjusted to suit specific process needs.

The sodium hydroxide concentration could be reduced to account for the 21% reduction in aluminum chloride from the previous example. The neutralized salt bath will contain sodium chloride, aluminum hydroxides, potassium chloride and manganese hydroxides. Disposal of a 4.9 M salt solution that is pH neutral should be practical and affordable. The insoluble aluminum hydroxides and manganese hydroxides can be filtered or separated from the salt solution before disposal if required by regulation.

8.0 Corrosion Performance

Aluminum-manganese coatings were deposited on 4130 Steel. Processing parameters and bath chemistries were varied to provide deposits of varying thickness, morphology and manganese content. Aluminum-manganese deposits approximately 0.5 mil thick with a nodular structure at roughly 15 wt.% manganese performed the best with respect to corrosion resistance. Aluminum-manganese plated panels with chromate post treatment performed well in an ASTM B117 neutral salt

fog. Scribed panels lasted greater than 2,100 hours in the salt fog chamber with no visible signs of red rust. Panels with no scribe exceeded 3,000 hours in the salt fog chamber with no visible signs of red rust. This performance is equivalent to or better than that of 0.5 mil-thick cadmium coated control specimens. Thicker 1.0 mil aluminum-manganese coatings may provide even better corrosion performance. A Trivalent Chromium Post-treatment (TCP) is being developed as an alternative to chromate post-treatment for aluminum-manganese. Aluminum-manganese with trivalent chromium post-treatment may provide an environmentally acceptable replacement for the standard coating of cadmium with a chromate post treatment.

9.0 Ongoing Work

Demonstration efforts for the transition of aluminum-manganese salt bath plating to DoD facilities are ongoing. Technical and practical issues regarding scale-up and implementation of aluminum-manganese molten salt bath plating are being addressed. To date, only limited data regarding coating corrosion performance, coating composition and surface structure have been developed. However, process parameters for optimized coating composition, deposition rates, coating thickness, coating adhesion and appearance continue to be refined. Quality control procedures for salt bath maintenance and coating deposition are also being developed. Functional performance of the aluminum-manganese deposit will continue to be evaluated for sacrificial corrosion performance, torque-tension relationships, fatigue performance, paint adhesion, hydrogen embrittlement and environmentally-assisted cracking.

Design, construction and installation of a production scale system is being pursued at NADEP North Island. The production scale plating system will be capable of plating a component of nominal size of 25.4 × 25.4 × 61 cm. The molten salt plating system will provide production representative aluminum-manganese deposits. Successful operation of the 200 gallon system, and corresponding aluminum-manganese coating performance, will validate the aluminum-manganese plating process as a viable replacement for cadmium plating.

10.0 Acknowledgment

This work was funded by the Environmental Security Technology Certification Program and the Aviation Pollution Prevention Technology Program (CNO 45).

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Zinc-Tin: A Versatile Alternative to Cadmium for Brush Plating Applications

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Abstract

On going research to find a replacement for cadmium continues. Some of the materials that have been investigated are electrodeposits of zinc alloys and other types of coatings such as IVD aluminum. Brush plating concerns, like their counterparts in other metal finishing processes, have been working to find a material that will provide the benefits of cadmium without the toxicity. The following paper describes a brush plating deposit of a newly developed zinc alloy: Zinc-Tin. This material is currently being tested and has been

found to be easy to use, has superior corrosion resistance and is compatible with existing metal coatings. In addition, this versatile material is being tested to determine if it is a viable repair coating for damaged coatings of IVD aluminum that, up to the present time, did not have a practical, on site repair process. Zinc-Tin was tested and found to be suitable for use on high strength steels with no post-plate baking requirement.

Although this new material has yet to find its way into process specifications, it is being studied by several companies for use on a wide variety of aircraft components whose coating are susceptible to damage or wear during use. Because it can save both time and money if damaged/worn coatings can be

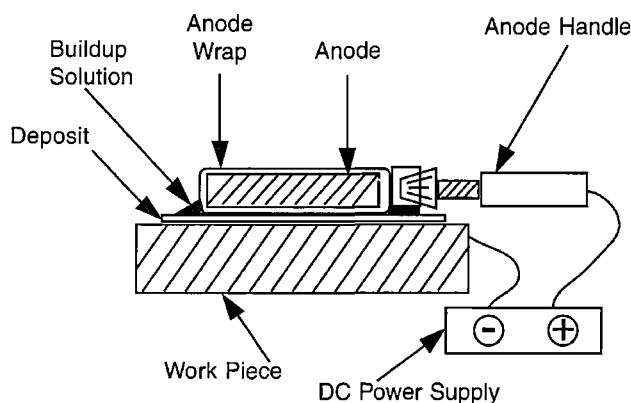


Fig. 1: Manual operation of selective plating process.

repaired in the field without having to disassemble, remove, re-coat and replace the damaged components.

1.0 Introduction

The search continues to find environmentally acceptable replacements for cadmium electrodeposits. Cadmium, like chromium, has been included on the US EPA list of environmentally hazardous chemicals that are designated for reduction or removal from the workplace. Government and private industrial concerns have been working on several fronts to find alternatives to cadmium coatings. These replacements include electrodeposits, primarily of zinc alloys and vapor deposited coatings such as IVD aluminum.¹

Brush plating concerns have also been looking into developing and testing electrodeposits to replace cadmium. Brush electroplating is a specialized form of electroplating that uses hand held electrodes and does away with the conventional plating tank. Brush plating (Figure 1) is primarily involved in selective plating applications where smaller areas of larger parts require plating. Brush plating is applied directly to the area that requires the coating. This not only reduces the need for masking but also reduces the amount of solution required, thereby generating significantly less waste products than conventional tank plating processes.

However, even with this reduced amount of chemical generation, the ever-restricted use of cadmium has made the search for alternatives important for brush plating concerns as well.

The main emphasis of research for the electrodeposit replacement of cadmium has centered on alloys of zinc.² These include zinc-nickel, zinc-cobalt, zinc-iron and tin-zinc. After reviewing the existing data, we centered on an alloy of zinc and tin. Previous studies

on tin-zinc alloys have shown this alloy to have excellent corrosion protection, low contact resistivity, good ductility, the ability to plate into corners and threads, and the deposit is free of bimetallic corrosion due to the presence of dissimilar metals.²

During this review process we also looked at the performance of zinc-nickel deposits. These deposits performed well and are used as another alternative to cadmium. However, nickel, like cadmium and chromium, is listed on the same US EPA grouping of seventeen chemicals that are being studied for reduction or elimination from the workplace.³ While we believe nickel is not on the same timeline as cadmium or chromium, there is some apprehension in replacing one toxic metal with another, suspect one.³

The alloy, which we chose to study, has a nominal composition of 30-40% tin and 60-70% zinc. This alloy has a higher concentration of zinc than the tin-zinc alloys mentioned in previous studies.⁴ We felt that an alloy with a higher zinc concentration will add hardness to the deposit thus increasing the durability of the deposit in the field. In fact, the zinc-tin that was tested had a hardness of 50 Knoop, this is significantly harder than alloys which have previously been studied.²

It was also decided to use an alloy with higher zinc content in order to make the deposit more receptive to a post chromate conversion coating for type II applications. This chromate conversion coating dramatically increases the corrosion resistant properties of the zinc-tin deposit.⁶ Finally, an alloy with a higher zinc concentration will make the deposits more sacrificial to the steel base metal instead of acting more like a barrier coating. The sacrificial properties of this coating will help protect the base metal from small scratches and nicks that may occur during use.⁴

2.0 Testing Requirements

This zinc-tin alloy has been designed to replace cadmium. Therefore, it was decided to use the performance criteria described in AMS-QQ-P-416 for electrodeposition of cadmium as a guideline. However, brush plating deposits must have capabilities above and beyond what is listed in this specification. One of the most common applications of brush plating is the repair of parts with damaged or worn coatings. Conventional tank plating processes call for completely stripping the old coating and re-plating the entire part. Conversely, brush plating processes repair the damaged or worn areas while leaving the existing coating in place. Therefore brush plating deposits must adhere equally well to the base metal and the existing coating. In addition, the deposit has to be compatible with the existing coatings

Table 1. Electro-Chemical Activation

- | | |
|-----|---|
| 1. | Clean surface of any oils or grease. |
| 2. | Etch the surface with an acid-etching solution set polarity on reverse. |
| 3. | Rinse. |
| 4. | If surface is dark gray to black a smut has been left on the surface. Desmut the surface with a desmutting solution, set polarity on reverse. |
| 5. | Rinse. |
| 6. | Some alloy metals with high nickel contents become passive after etching. These metals must be activated using an activation solution, set polarity on forward. |
| 7. | Rinse. |
| 8. | Plate with Zinc-Tin to the appropriate thickness. |
| 9. | Rinse. |
| 10. | Lightly burnish the surface with an abrasive pad and apply chromate coating for Type II applications. |

Table 2. Mechanical Preparation

- | | |
|----|---|
| 1. | Clean area of oils and grease. Remove any loose or damaged plating from the repair area. |
| 2. | Abrasive-blast the work area and immediate surrounding area. Use aluminum oxide 120-220 grit at 70-120 PSI. |
| 3. | Plate immediately with Zinc-Tin to the appropriate thickness. |
| 4. | Lightly burnish the surface with an abrasive pad and apply chromate coating for Type II applications. |

and base metals. Finally, the coatings we use can not cause any galvanic interactions that will have a detrimental effect on either the base metal or the existing coating.

A series of tests were then designed to test the performance criteria in order to determine the ability of zinc-tin to replace cadmium electrodeposits. These tests include:

- Salt spray testing for corrosion resistance,
- Hydrogen embrittlement testing of non-post plate baked notched bars,
- Deposit adhesion of the zinc-tin onto base metal and existing coatings, and
- Deposit compatibility with dissimilar metals in a corrosive environment.

3.0 Metal Preparation

Typical brush plating procedures include steps to prepare the base metal for bonding of the electrodeposited coating. These steps usually include the use of acid etching and activating solutions that will remove any passive or oxide films that will impede the bonding of the deposit. This procedure for plating zinc-tin onto base metals such as steel can be found in Table 1 below.⁵

This process is highly reliable and will always yield good results. However, this procedure is designed to prepare base metals that are new or free of any existing coatings.

Because brush plating has important repair applications, the solutions must have the ability to be plated over the exposed base metal and the existing coatings. Likewise, the metal preparation procedures have to be modified to fit the application. For example, corrosion resistant coatings such as cadmium, zinc and its alloys are acid sensitive. A problem occurs when an acid solution is used over the surface during the normal preparation steps as noted in Table 1. In fact, if the steps in Table 1 are followed, the existing acid sensitive coatings can be removed almost as quickly as the newly exposed metal can be prepared. This will result in the expansion of the area of repair. In addition, any run off of the acid preparation solutions may remove the chromate coating from surrounding areas leaving the surrounding area with stains and streaks.

Alternative preparation procedures were developed for these types of applications. These procedures involve mechanical preparation Table 2⁵ and a combination of mechanical and chemical preparation. Table 3⁵

This preparation procedure provides a well prepared surface that works equally well with all metals.

Table 3. Mechanical-Chemical Preparation

1. Clean area of oils and grease. Remove any loose or damaged plating from the repair area.
2. Wet a piece of abrasive pad with the Zinc-Tin solution and scour the repair and the area immediately surrounding the plating area.
3. Plate immediately with Zinc-Tin to the appropriate thickness.
4. Lightly burnish the surface with an abrasive pad and apply chromate coating for Type II applications.

It also has the benefit of removing any additional loose metal from the existing coating. This preparation procedure can also be used on clean metal surfaces that normally use the electrochemical procedure listed in Table 1. However, abrasive blast activation is very dusty and may not be suitable for environments where precision machinery is located. Therefore, electrochemical activation while taking a little longer, may be preferred when working in areas where the abrasive dust is a concern.

This is the least effective of the preparation procedures. It has limitations in that it is not effective on certain metals, such as IVD aluminum. Technicians should consult a process manual from the brush plating manufacturer to determine if a preparation procedure will work for a given base metal.

In any case, all of the above preparation procedures will enable the zinc-tin deposit to pass the adhesion testing over metals such as steel and cadmium as described in AMS 2451 Brush Plating; General Requirements, and MIL-STD-865 which has been the benchmark for brush plating quality.

4.0 Testing Procedures

4.1 Corrosion

Corrosion tests were performed on clean metal coupons to determine the degree of corrosion protection of the zinc-tin deposit. The test specimens were made of 4340 normalized steel. The dimensions of these specimens are 15.2 (6.0) × 10.2 (4.0) × 0.1 cm (0.04 in.). The coupons were prepared using the abrasive blast procedure outlined in Table 2.

The coupons were plated at room temperature (18-25°C). The current density used to plate the zinc-tin was approximately 0.6 amps per cm² (4 amps per sq. in.). The panels were plated to a thickness of 0.001-0.0015 cm (0.0004-0.0006 in.). The panels were then checked using an electronic thickness gauge that measures non-magnetic coatings over magnetic

substrates. It was determined that the thickness of the deposit was in conformance to the specified thickness. The parts were then lightly burnished and chromated to conform to AMS-QQ-P-416 Class 2 Type II coatings. The parts were then placed in a salt spray chamber and tested for corrosion resistance. The test was run in accordance with ASTM-B-117. Parts were to be left in the chamber and checked periodically for red rust corrosion. This test was to run for 2,000 hours or until red rust occurred. The results of the corrosion test can be found in Table 4.

Another type of corrosion test was also run to determine if the more sacrificial zinc-tin alloy would protect steel base metal from small nicks and scratches that occur on components during use. For this test we used the same 15.2 × 10.1 × 0.064 cm 4340 steel panels. The panels were plated to the same AMS QQ-P-416 Class 2 Type II specification. The panels were scored down to the base material leaving the steel base metal exposed. The parts were then subjected to salt spray testing in accordance with ASTM-B-117. This test was run for 2,000 hours or until red rust becomes evident in the scored areas. The results of this test can be found on Table 5.

4.2 Hydrogen Embrittlement

The purpose of this test is to determine if the zinc-tin solution causes hydrogen embrittlement of high strength steels during the plating process. Typical plating processes call for a post plate bake for electroplated parts that have been hardened above 40 Rc. In the case of conventional tank plated parts it is simply a matter of baking the parts after they have been removed from the various plating activities.

However, brush plating employs a different procedure. Many of the parts that require brush plating have damaged or worn areas that are part of much larger assemblies. It is impractical and sometimes impossible for post plate heat treating on these larger components, especially if they are brush plated in the field. To

Table 4. Corrosion Resistance Test Zinc-Tin Over Steel Substrates: Hours to Red Rust

Coating	Testing Specification	Hours in Chamber
Zinc-Tin	ASTM B 117	
Coupon 1		+ 2,000 hrs.
Coupon 2		+ 2,000 hrs.
Coupon 3		+ 1,500 hrs.
Coupon 4		+ 2,000 hrs.

Table 5. Corrosion Resistance Test Scored Panels: Hours to Red Rust

Coating	Testing Specification	Hours in Chamber
Zinc-Tin	ASTM B 117	
Coupon 1		+ 1,000 hrs.
Coupon 2		+ 1,000 hrs.

eliminate the necessity for post plate baking, it was essential that brush electroplating concerns develop solutions that can be plated onto high strength steels without inducing hydrogen into the base metal. Cadmium brush plating solutions have been developed to meet this requirement. It is therefore, important that any replacement solution also have this “no post plate bake” feature.

The hydrogen embrittlement test was performed using the small notched bar test specimens. These bars were made of 4340 steel conforming to MIL-S-5000, condition E4 and were prepared according to ASTM-F-579, Type 1A. The specimens had a notched root diameter of 0.44 cm (0.175 in. $\pm$ 0.012 cm (0.005 in.) and a notched radius of 0.025 cm (0.010 in.) $\pm$ 0.001 cm (0.0005 in.) and had an average notch tensile strength of 340 K psi.

The notched bars were prepared using a standard brush plating preparation for high strength steels.⁵ This procedure uses the same acid preparation procedures that are found in Table 1 with one important difference. When working with high strength steels it is important that all of the preparation steps involving the acid solutions be performed on negative or reverse polarity. In this mode any hydrogen present will be moving away from the work piece. This means that process step 6 in Table 1 must be omitted. This exception is for electrochemical preparation of high strength steels. It should also be noted that the other preparation procedures; mechanical and

mechanical/chemical do not produce hydrogen at the plating area and can be performed with no modifications.

The notched bars were plated to a nominal thickness of 0.0011 cm (0.0005 in.) and were lightly burnished and chromated. The parts were then rinsed and dried and sent to a lab for embrittlement testing. The specimens were loaded and subjected to a sustained load test at applied stresses equivalent to 75% of the average notched bar strength of unplated control samples. The test was run for 200 hours and results noted in Table 6.

4.3 Adhesion

The adhesion of the zinc-tin alloy to the base metal, as well as to existing metal coating is vital for its use as a repair coating. Adhesion testing for brush plating deposits, particularly for coatings of 0.0025 cm (0.001 in.) or less is performed using the tape test method that is described in brush plating specifications; MIL-STD-865 C and the more recent AMS 2451.

The test is described as using a 2.5 cm (1 in.) wide strip of Tape; 3 M Code 250 (or equivalent) in the case of MIL-STD-865 C and tape having adhesive strength of 0.66/N/mm (60 oz./in.) in the case of AMS 2451. The tape is firmly pressed onto a cleaned and dried plating surface and is quickly removed in a single 90° pull. Any metal adhering to the tape is cause for rejection.

Table 6. Notched Bar Test for Evidence of Hydrogen Embrittlement

Sample No.	Sample Type	Hours Run
Test 1 Bar 1	Notched Bar	200 hrs.
Test 1 Bar 2	Notched Bar	200 hrs.
Test 1 Bar 3	Notched Bar	200 hrs.
Test 1 Bar 4	Notched Bar	200 hrs.
Test 2 Bar 1	Notched Bar	200 hrs.
Test 2 Bar 2	Notched Bar	200 hrs.
Test 2 Bar 3	Notched Bar	200 hrs.
Test 2 Bar 4	Notched Bar	200 hrs.

In a more severe test, test panels of 2.5 (1) × 10.2 (4) × 0.1 cm (0.04 in.) were plated with zinc-tin to a thickness of 0.0003-0.0005 in. Some coupons were bare steel. Other coupons had both cadmium and steel areas plated with zinc-tin and the last set of panels had areas of IVD aluminum and steel plated with zinc-tin. The panels were then bent to a 90° angle in a single motion. The area of the deformity was then subjected to a tape test. The metal deposit in the bend area may exhibit "orange peel" appearance. This is acceptable as long as these small cracks do not result in flaking or peeling of the deposit. The panels for adhesion testing were prepared using the 3 preparation procedures described in Tables 1-3. The results can be found in Table 7.

4.4 Deposit Compatibility

Any type of brush plated repair coating has to be compatible with other types of metals found in the repair area. Therefore, no detrimental galvanic interaction can occur between the various metals present in this area. The potential galvanic interaction was tested by means of a salt spray test to produce galvanic corrosion. The tests were performed on deposited coatings of the zinc-tin on coupons that had existing coatings of either cadmium or IVD aluminum.

All test pieces were made of 4130 steel. The dimensions of these panels were 10.2 (4) × 15.2 (6) × 0.1 cm (0.04 in.). The panels were then coated according to the following specifications. Panels for cadmium plating were masked down the center with a 2.5 cm (1 in.) wide piece of polyvinyl tape. The panel was then plated with cadmium to an approximately thickness of 0.001-0.0015 cm (0.0004-0.0006 in.). After plating, the panels were dried and the tape was removed exposing the bare steel centerline. The panels were then masked on either side

of the steel centerline leaving the bare steel and approx. 1 cm (0.4 in.) of the newly plated cadmium surface exposed. The area was prepped, using the abrasive blast procedure. The area was then plated with zinc-tin to the same approx. thickness 0.001-0.0015 cm. The zinc-tin coating was deposited at a current density of approximately 0.6 amps per square cm (4 amps per sq. in.). When the plating was completed the masking was removed and the entire part was lightly burnished and chromated to provide a type II coating.

An IVD aluminum processing facility provided test coupons which were coated in accordance with MIL-C-83488C Class 1 and 2 Type II. Two panels of class 2 thickness 0.0012-0.002 cm (0.0005-0.0008 in.) and two panels of class 1 thickness 0.0033-0.0038 cm (0.0013-0.0018 in.) were used. On each of these panels a 0.64 cm (0.25 in.) area of the base metal, 4130 steel was left exposed. The panels were then plated with zinc-tin using the abrasive blast metal preparation procedure described in Table 1. It is evident that the abrasive blast was the only viable option for preparing the different metal samples for plating. The zinc-tin coatings were plated to a thickness equaling the IVD coatings. After plating, the panels were lightly burnished and chromated to provide a Type II coating.

5.0 Testing Results

5.1 Corrosion

The coupons submitted for corrosion testing were checked periodically for red rust. The results in Table 6 show that red rust corrosion did not become evident on any panel until the +1,500 hour mark. It was determined that the corrosion products came from the corner or edge, of sample 3 and the coating itself did not fail.

Table 7. Adhesion Test Results

Preparation Procedure: Mechanical (Table 2)		
Substrate	Test Performed	Results
4130 steel	Tape Test	Passed
4130 steel	90° Bend	Passed
4130/Cadmium	Tape Test	Passed
4130/Cadmium	90° Bend	Passed
4130/IVD Al	Tape Test	Passed
4130/IVD Al	90° Bend	Passed
Preparation Procedure: Electrochemical (Table 1)		
4130 steel	Tape Test	Passed
4130 steel	90° Bend	Passed
4130/Cadmium	Degraded Existing Deposit	
4130/IVD Al	Degraded Existing Deposit	
Preparation Procedure: Mechanical/Chemical (Table 3)		
4130 steel	Tape Test	Passed
4130 steel	90° Bend	Passed
4130/Cadmium	Tape Test	Passed
4130/Cadmium	90° Bend	Passed
4130/IVD Al	Tape Test	Failed
4130/IVD Al	90 deg. Bend	Failed

5.2 Score Test Results

The Score or scribe test was also submitted for salt spray corrosion testing. The panels were tested in a similar fashion to the panels prepared and plated for the corrosion test. The results can be seen in Table 5.

5.3 Hydrogen Embrittlement

The notched short bar test was used for this test. Two tests using the same solution were performed 6 months apart to prove repeatability of the test and to determine the stability of the solution. The results of these tests can be found in Table 6.

This notched bar test is run for 200 hours or evidence of failure. All bars were run to the 200 hours time requirement. There were no failures.

5.4 Deposit Adhesion

Deposit adhesion tests were run on samples that consisted of bare steel, bare steel and cadmium and bare

steel and IVD aluminum. All three preparation procedures were tested on these samples. It is evident by the results of Table 7, the abrasive blast activation procedure is the only universal procedure for preparing all three types of samples.

The electrochemical procedure removed existent cadmium and heavily damaged the IVD coating on the test coupons. The chemical/physical preparation method was not sufficient to adequately prepare the IVD coating for the repair coating.

All of the above tests were performed on 4 test coupons each. There was no variation of the adhesion results for each of the four coupons using the three preparation procedures.

5.5 Deposit Compatibility

The test coupons were placed into a salt spray chamber and run to 2,000 hours or until red rust appeared. Special attention was paid to the interface areas between the various substrates and the zinc-tin deposits. The results can be reviewed in Table 8.

Table 8. Composite Compatibility as Tested by Galvanic Interaction in Salt Spray Testing

Coupon #	Deposit	Hours in Chamber
1	Cadmium/Zinc-Tin	+ 2,000 hours
2	Cadmium/Zinc-Tin	+ 2,000 hours
3	Cadmium/Zinc-Tin	+ 2,000 hours
4	Cadmium/Zinc-Tin	+ 2,000 hours
1	IVD Al/Zinc-Tin	+ 2,000 hours
2	IVD Al/Zinc-Tin	+ 2,000 hours
3	IVD Al/Zinc-Tin	+ 2,000 hours
4	IVD Al/Zinc-Tin	+ 2,000 hours

At the end of the 2,000 hours time limit, the panels were removed from the apparatus. However, several panels of IVD aluminum and zinc-tin were allowed to continue to 3,000 hours and were still free of red rust corrosion. At this point the test was stopped.

6.0 Summary

The zinc-tin material described in this paper was developed as a replacement for cadmium electroplated deposits. As such, we feel that the deposit has the ability to replace cadmium in its most important function: protecting steel base materials from corrosion.

Salt spray tests have shown the material can protect steel base metals from corrosion for over 2,000 hours. This far exceeds specifications for cadmium plating such as AMS QQ-P-416, cadmium brush plating; AMS 2451/4 and zinc alloy plating specifications such as AMS 2417 E for protective duration of these coatings in salt spray testing.

Zinc-Tin deposits also appear to be a good sacrificial coating that will protect bare steel that has been exposed because of scratches or nicks which can occur in the coating during use. This zinc-tin material was able to protect the exposed steel for over 1,000 hours in salt spray tests which again, exceeds the exposure limits listed in AMS QQ-P-416.

Hydrogen embrittlement is usually handled by employing a post plate bake. This zinc-tin solution has to eliminate this requirement. This solution is used for brush electroplating and it is necessary this for this solution to deposit a coating that does not induce hydrogen into the plating interface. Electrolytic plating specifications require post plate baking over high

strength or hardened steel test samples before hydrogen embrittlement tests are performed. The zinc-tin deposit was tested without a post plate bake and was still able to meet this process requirement. This performance characteristic is important in that components, regardless of the hardness can now be repaired in place with out the need for heat treating for embrittlement relief.

Adhesion of the zinc-tin deposit on a base metal and existing coatings is of prime importance if this material is to be used on these various metals. At this point, the zinc-tin has shown that the deposit is capable of bonding to steel, cadmium and IVD aluminum, as shown by the tape test and the 90° bend test.

The adhesion of this material is also a function of the preparation steps that are used in prepping the various materials for bonding to the zinc-tin. While the electrochemical process worked well for bonding zinc-tin onto bare steel, it is not recommended for plating onto areas with the existing corrosion protective metal coatings. The chemical/physical preparation procedure works well on static coatings and will prepare steel and existing electrodeposits of cadmium and zinc alloys but will not be thorough enough to prepare coatings such as IVD aluminum. The best all around prep procedure was the abrasive blast procedure, as it will prepare all of the substrates equally well.

Perhaps the most unique challenge in developing a solution such as this is to find a material that is compatible to various types of metal substrates. Zinc-Tin was examined because it was thought that the material would bond to steels, cadmium and other cadmium replacement deposits such as IVD aluminum⁷ without detrimental galvanic interaction that would reduce the quality and durability of the corrosion

protective coatings. The salt spray test of this zinc-tin coating on the various test panels showed that there was no galvanic interaction to adversely affect the bonding or the protective properties of the materials tested.

7.0 On Going Studies

Tests continue with this zinc-tin brush plating solution to determine its ability to replace cadmium electrodeposits. Several companies, most notably, The Boeing Company are presently conducting tests on this zinc-tin alloy. To date, tests performed for Boeing's J-Gap Low Strength Steel project have confirmed that the zinc-tin has good corrosion resistance on test panels and panels which have been scribed. Chromated Zinc-Tin coatings have been determined to provide good paint adhesion. In addition, the solution is easy to use and provides a consistent deposit for the testing personnel.

Tests involving IVD aluminum repair are ongoing. Previously described tests are being verified. However, Boeing has taken the tests further, This includes a bend to break test to check adhesion of the plated material. This test worked well on all but the IVD test coupons. Further studies will be required to find a coating that will better bond the zinc-tin deposit to meet this requirement. This may require the use of a pre-plate deposit to help the adhesion of the zinc-tin onto the IVD aluminum. This new pre-plate must have galvanic compatibility and not add hydrogen into the plating interface. Another test will begin to determine how different ratios of zinc and tin will affect the performance of the deposit when taking the salt spray testing beyond the 3,000 hours mark. Finally, non-chromate based post plate treatments are being investigated in order to provide the enhanced corrosion resistance while removing chromium compounds from this plating process. This removal of hexavalent chromium from this plating process will become increasingly important as environmental restrictions become ever tighter.

8.0 Conclusion

As a result of this testing, it appears that the zinc-tin metal described in this paper, while still under examination, can be useful as a replacement for cadmium in brush plating repair or production processes. This material has all of the properties that are required of such a replacement product. It is compatible with various base metals, has excellent corrosion protection, does not induce hydrogen into the plating area and has good adhesion to various metals that may be present in a repair area. In closing, this product can be used with existing brush plating equipment and requires no specialized equipment. The plating process of this zinc-tin is the same either in the field or in the plant and has the same plating characteristics of similar brush plating solutions such as zinc or cadmium.

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Posters

Hardening of Metallic Surfaces by Diffusion Processes (with and without Reaction)

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Abstract

Diffusion processes are used to obtain alloying coatings on metallic substrates in order to increase hardness. The coating layers obtained by two experimental methods are presented in this paper.

1. Coatings obtained from gaseous phase by using powder mixtures. The process temperature was between 1000-1200°C and diffusion elements were Cr, V, and Cr + V. The metallic substrates were Armco iron, mild steels with low carbon content (0.2% C) and cast iron

(FC200). The obtained coatings were solid solutions, chromium carbides + iron carbides, vanadium carbides + iron carbides or chromium-vanadium-iron carbides.

2. Coatings obtained by electrotransport of the diffusion elements (Be and Zr) through a molten bath (LiF-NaF-KF) with either BeF₂ or K₂ZrF₆, discharge on the surface cathode (Cu) and diffusion into metallic cathode. The process temperature was 700°C (Be-Cu) and 800°C (Zr-Cu).

Hardness of the coatings was higher than that of the metallic substrates. The hardness value is a function of the coating nature. The carbide layers have the highest hardness.

1.0 Introduction

Diffusion processes are largely used for obtaining alloying layers on metallic specimen surfaces when one tries to create a new category of materials whose utilization is based mainly on their surface properties, such as hardness, wear, friction and corrosion resistance. In many cases, chemically modified surfaces must resist mechanical and thermal stresses that imply a good adherence of the layer onto the base material and even more to ensure a coherence of the crystalline network at the interface of the two materials. A new task is thus added to metal alloying, as in this case the process starts from small depths (of the order of tens to hundreds of microns) from the specimen surface and therefore the diffusion laws are to be applied.

Our team has been involved in obtaining layers on metallic surfaces by using diffusion:

- i. Method for obtaining layers from the gaseous phase using a treatment medium made of powder mixtures¹⁻⁶ and
- ii. Method for obtaining layers by electrotransport of the diffusive element through molten salts and discharge onto the diffusion surface.⁷⁻¹⁰

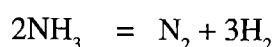
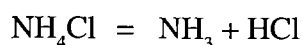
One of the objectives of our study has been the hardness enhancement of the metallic specimen surfaces by forming superficial layers.

2.0 Experimental Procedure

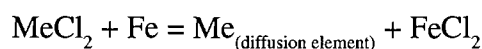
2.1 Method of Diffusion Metallization, Procedure of Powder Packing

This procedure consists in using some containers made of refractory steel sheet where specimens of Armco iron, steel and cast iron are introduced and packed in a cementing mixture and then submitted to a treatment at high temperature.

The cementing mixture is powders (particle size 0.3-0.5 mm) of diffusion metal or metals, pure or as ferroalloys, Al_2O_3 and NH_4Cl . Aluminum oxide is added in order to hinder the sintering of powder particles on the specimen surface. NH_4Cl is an activator as it contributes to forming the atoms of the diffusive element according to the reactions taking place at the process temperature:



One of reactions that takes place on the metallic surface and is responsible for releasing the diffusive element is:



The diffusion element or elements result in an activated state on the treated specimen surface. These diffuse from the surface towards the interior, leading to formation of diffusion layers with a structure more or less complex as a function of the substrate material nature, temperature and process duration.

The diffusion metallization treatment needs temperatures between 1000-1200°C and durations of 4-32 hours. The principles of the method were largely described elsewhere.³

The diffusion layers were studied by optical and electron microscopy, x-ray diffraction and microhardness.

Optical micrographs were obtained by means of EPYTIP and EPYQUANT optical microscopes and NEOPHOT metallographic microscope, all provided with photographing facilities.

Electron microscopy analysis was carried out with a JEOL JXA-5A microprobe. Composition images were obtained, over which characteristic x-ray intensity variation profile of studied elements were superposed. x-ray images of the diffusive elements were also obtained.

X-ray diffraction analysis was carried out by means of a TUR-M-62 diffractometer using wave length $\text{XK}\alpha$ of cobalt, $\lambda = 1.7889 \text{ \AA}$.

A Hanemann microhardness device provided with a diamond prism was used in Vickers microhardness trials. This device allows for recording indentation prints in very narrow sections. The following loads were used: 5, 10, 20, 40, 65, and 100 gf. At least 5 indentation prints were made for each load. Microhardness was computed with the following relationship:¹¹

$$\text{HV}_{(P)} = 1854.4 \frac{P}{\epsilon^2 d^2} \quad (1)$$

where P is penetration load in gf, ϵ is an device constant, d is diagonal of the indentation print in micrometric divisions, $\epsilon \cdot d$ is the diagonal length in μm .

2.2 Experimental Results

In the present contribution we discuss the experimental results obtained for the following couples: Fe-Cr, Fe-V, Fe-Cr-V, mild steel - Cr-V, 34 MoCN-15 steel - Cr-V and FC200 cast iron - Cr-V.

The working conditions and thicknesses of the layers obtained under the experimental conditions for diffusion chromization, vanadization and chromo-vanadization of Armco iron are listed in Table 1.

By a diffusion chromization treatment of Armco iron (Table 1), diffusion layers with large thicknesses

Table 1. Experimental Condition and Layer Thicknesses

System	Powder Mixture Composition, (wt.%) (Powder Granulation, mm)				$\frac{\text{Cr}}{\text{V}}$	Temp. (°C)	Time (Hours)	Layer Thickness (μm)
	Cr	FeV	Al_2O_3	NH_4Cl				
Fe-Cr	78 (98% Cr; <0.12% C) (0.3-0.5 mm)	-	20	2	-	1100	10	150
Fe-V	-	78 (79.9% V; <0.12% C) (0.3-0.5 mm)	20	2	-	1100	10	320
Fe-Cr-V	39.5 (98%Cr; <0.12% C) (0.3-0.5 mm)	48.5 (79.9% V; <0.12% C) (0.3-0.5 mm)	10	2	1/1	1100	10	450

(150 μm) were obtained, Figure 1. Due to chromium enrichment of the sample surface, a solid solution α with a cubic centered volume is formed, according to the phase diagram of Fe-Cr system.¹² The chromium concentration decrease indicated by the diffusion profile in Figure 2 determines the reach of the Cr solubility limit in phase α at a certain distance from its surface. Starting from this thickness, which increases with the diffusion time, the interior of the specimen is constituted at 1100°C, by a γ phase with a cubic network with centered faces. The diffusion rate in the two networks is different and the penetration profile shows a discontinuity, whose value has been established at a concentration $N_{\text{Cr}} = 0.14$ or 13 wt.%.² The interdiffusion coefficients calculated by Boltzmann-Matano and modified Grube methods in phase α at 1100°C vary with the concentration within the limits: $D = 0.217 \times 10^{-9} \text{ cm}^2/\text{s}$ ($N_{\text{Cr}} = 0.64$) and $D = 2.5 \times 10^{-9} \text{ cm}^2/\text{s}$ ($N_{\text{Cr}} = 0.14$).²

From the point of view of hardness, the layer is about two times harder than the Armco iron and the hardness decreases continuously from the surface along with the decrease in chromium concentration, Table 2 and Figure 3.

In the case of Fe-V couple, the layer obtained by vanadium diffusion in Armco iron is also of a type α solid solution (at 1100°C), with a continuous and uniform decrease of the vanadium content and with a cubic network with centered volume down to a concentration $N_{\text{V}} = 0.018$ or 1.64 wt.%.² Beyond this concentration, the solid solution γ with a cubic network with centered faces is formed. Under the same treatment conditions, temperature 1100°C and 10 hours Table 1, the obtained layer was thicker, 320 μm . This is explained by a higher diffusion rate for vanadium than chromium. The interdiffusion coefficients calculated in phase α at 1100°C by Boltzmann-Matano and modified Grube

methods vary with concentration between the limits: $D = 0.151 \times 10^{-8} \text{ cm}^2/\text{s}$ at $N_{\text{V}} = 0.326$ and $D = 0.565 \times 10^{-8} \text{ cm}^2/\text{s}$ at $N_{\text{V}} = 0.021$.^{2, 6} The layer hardness on the surface is approximately 3 times higher than that of Armco iron. Hardness decreases also for the Fe-V couple with a decrease of vanadium concentration in the layer Table 3.

The simultaneous diffusion of chromium and vanadium into Armco iron at 1100°C for 10 hours leads to layers of the type α solid solution with a body centered cubic network. The discontinuity values when α solid solution turns into γ solid solution with a face centered cubic network are the following: $N_{\text{V}} = 0.062$ (5.69 wt.% V) and $N_{\text{Cr}} = 0.0065$ (0.61 wt.% Cr).¹ The layer is thicker, 450 μm , Figure 4.

This fact is explained by the reciprocal influence of the two elements, Cr and V, on the diffusion rates.¹³ The concentration variation of the two elements with the distance from the surface is represented by the intensity profiles of characteristic X radiations for V and Cr in Figure 5. One can see that at the same distance from the surface, the vanadium concentration is higher than chromium. Although chromium has a diffusion rate lower than vanadium, it is the first which diffuses into iron and deforms the crystalline network and so eases the way for vanadium which accumulates at higher concentrations. The chromo-vanadized layers on Armco iron have hardnesses between those of chromized and respectively vanadized layers, Table 4.

The hardness decreases with distance as in the previous cases.

2.3 Chromo-Vanadizing of Steels

In the present paper, we deal with chromo-vanadization of two steels: (i) unalloyed steel with low

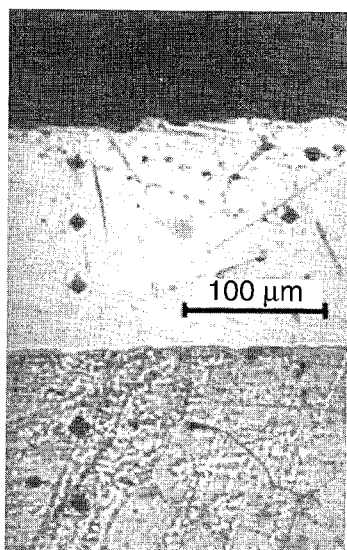


Fig. 1: Optical micrograph of Cr diffusion layer obtained in Fe-Cr system (1100°C; 10 hrs); cross section; indentation prints at a penetration load $P = 40$ gf; with metallographic etch Nital 2.5%.

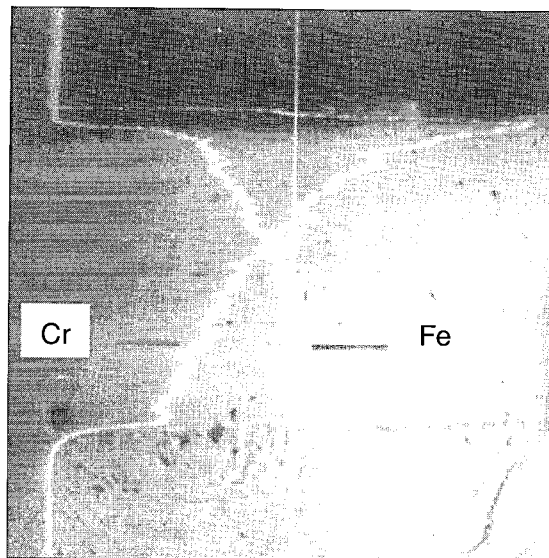


Fig. 2: Electron micrograph; composition image and variation profiles of X characteristic intensity for Cr ($K\alpha$) and Fe ($K\alpha$); magnification $\times 150$.

Table 2. Hardness Variation With Distance from the Surface (Fe–Cr System)

Distance from the Surface (μm)	23	67	110	200	255
HV _(40 gf) (Kgf/mm ²)	214	178	154	116	112

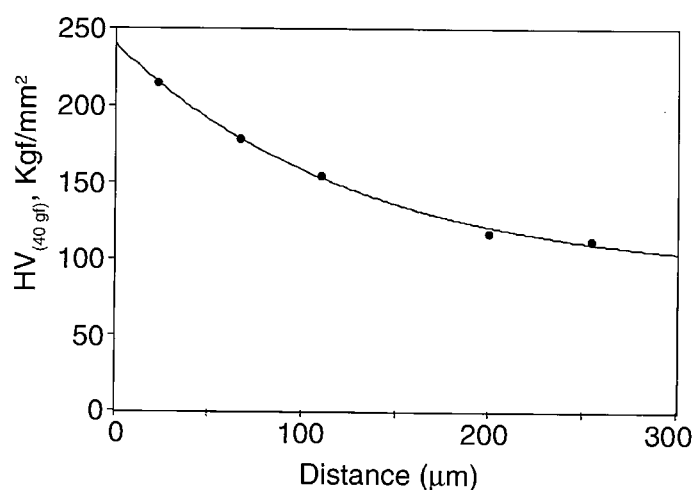


Fig. 3: Variation of layer hardness with distance from the surface in Fe-Cr system.

Rank 1 Eqn. 8002 (Exponential) $y = a + b\exp(-x/c)$,
 $r^2 = 0.99616296$ DF Adj $r^2 = 0.98465185$,
 FitStd Error = 3.763005, Fstat = 259.61766,
 $a = 89.458324$, $b = 150.00786$, and $c = 126.25684$.

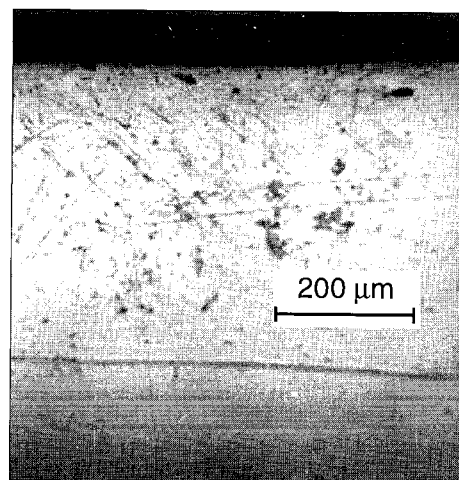


Fig. 4: Optical micrograph of chromo-vanadized layer in Fe-Cr-V system (1100°C; 10 hrs); cross section; with metallographic etch Nital 2.5%.

Table 3. Hardness Variation with Distance from the Surface (Fe–V system)

Distance from the Surface (μm)	20	150	275	400
HV _(40 gf) (Kgf/mm ²)	302	241	149	117

Table 4. Hardness Variation with Distance from the Surface (Fe–Cr–V System)

Distance from the Surface (μm)	20	100	300	375	500
HV _(40 gf) (Kgf/mm ²)	284	245	167	155	113

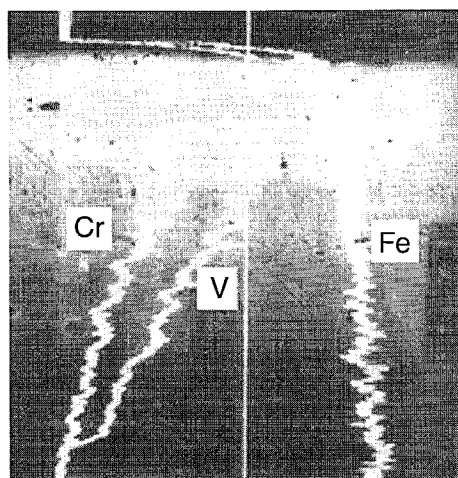


Fig. 5: Electron micrograph; image of composition + intensity profiles of x-characteristic radiations $K\alpha$ of Cr, V and Fe; magnification $\times 150$.

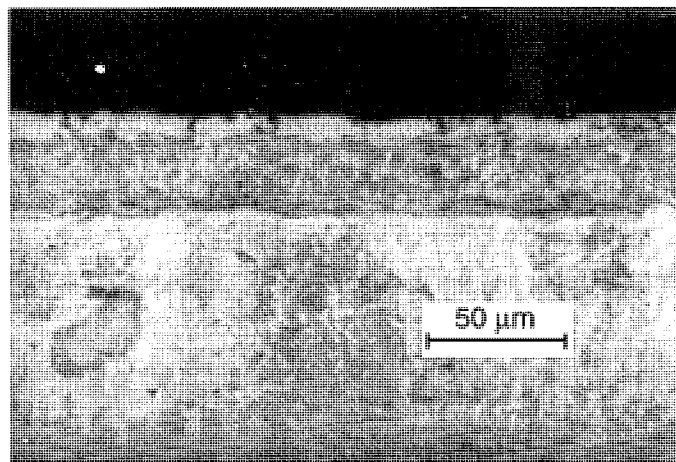


Fig. 6: Optical micrograph of a chromo-vanadized layer on OL37 steel, under treatment conditions listed in Table 5, with metallographic etch Nital 2.5%.

carbon content (max. 0.19 wt.% C) OL 37 and (ii) alloyed steel 34MoCN-15 having a low carbon content (0.30-0.38 wt.%).

These two steels were initially carburized approximately 1 wt.% C for a depth about 1 mm. After the carburizing, these steels were chromo-vanadized in the conditions from Tables 5 and 6. Chromium and vanadium are two elements that form carbides. So on the surface of the superficial carburized steels a thin layer of mixed carbides of Cr, V, and Fe is formed. The layer containing carbides are very thin, because the diffusion of Cr and V through a carbide layer is much slower, of the order 10^{-18} cm²/s. The carbide layers are formed by diffusion with reaction.

OL 37 steel was carburized with carburizing agents (charcoal and Na₂CO₃) introduced in the chromo-vanadizing powder mixture, Table 5. The layer obtained under the experimental conditions, although very thin, 35-40 μm, is continuous, uniform and follows the sample contour, Figure 6. The electron microscopy images show the different nature of this layer. At the exterior is a higher vanadium concentration, while chromium concentration is lower, Figures 7b and c. Within the layer, some vanadium-rich islands are formed. Chromium has a solid solution distribution under the carbide layer. By x-ray diffraction analysis, some mixed V, Cr, and Fe carbides were identified, chromium and iron concentration being smaller. The islands within the layer are constituted of VC formed by the faster diffusion at the grain boundaries. The layer hardness is very high:

$$HV_{(100\text{ gf})} = 1790 \text{ Kgf/mm}^2$$

and that of OL37 steel core is:

$$HV_{(100\text{ gf})} = 94 \text{ Kgf/mm}^2$$

The composition of the 34MoCN-15 steel is: C = 0.30-0.38, Mn = 0.40-0.70, Si = 0.17-0.37, Cr = 1.4-1.7, Ni = 1.4-1.7, Mo = 0.15-0.30, P_{Max} = 0.35, and S_{Max} = 0.35 wt.%. This low carbon content steel was initially carburized approximately 1 wt.% for a depth 1 mm. Experimental conditions are given in Table 6.

These layers have very thin, 20-25 μm, thicknesses but they are uniform, continuous and compact. From electron microscopy analysis, one can see that the layer was formed by diffusion with reaction of chromium and vanadium. In this case, chromium is concentrated as carbides on the layer surface, Figures 8a and d, while vanadium diffuses towards the interior at the grain boundaries and replaces iron almost entirely, Figures 8a-c. The layer hardness is very high, similar to that of carbide layers:

$$HV_{(100\text{ gf})} = 1441 \text{ Kgf/mm}^2$$

X-ray diffraction analysis on the sample surface showed the presence of the following carbides: Cr₂₃C₆, (Cr, Fe)₇C₃, VC_{0.88}, V₈C₇, and V₂C.

2.4 Chromo-Vanadizing of Cast Iron

The cast iron used by us was FC200 (gray cast iron having a carbon content higher 2.11 wt.%). The experimental conditions of superficial chromo-vanadizing cast iron are listed in Table 7.

The layers obtained in FC200 cast iron chromo-vanadization are very thin (~20 μm), and their thicknesses do not increase significantly even at very

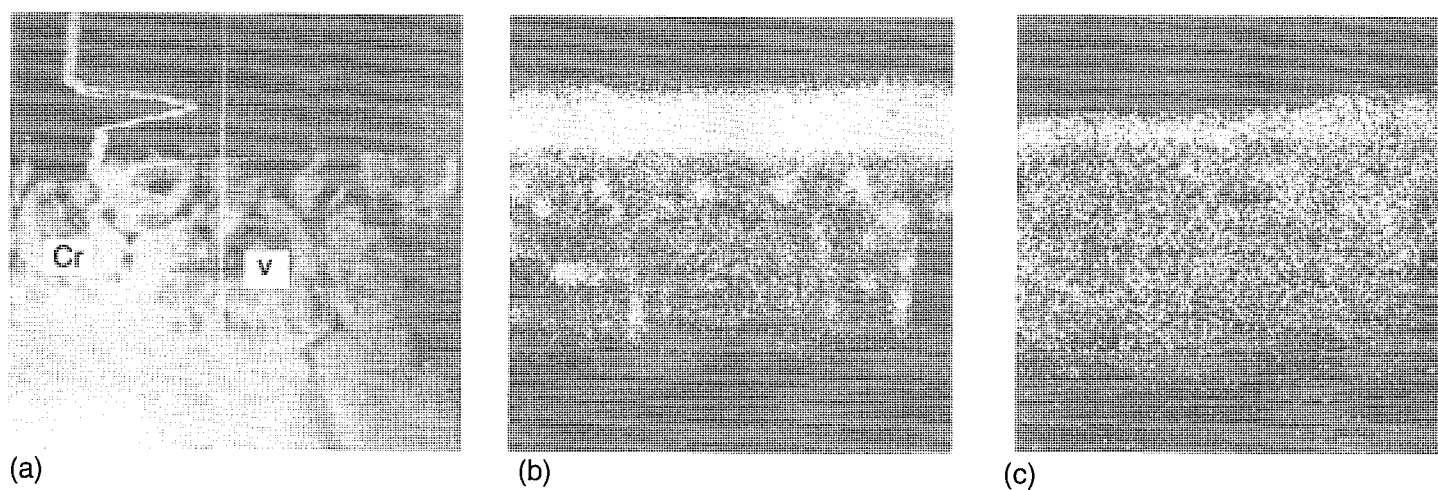


Fig. 7: Electron micrographs: (a) composition image + variation profiles of X characteristic radiations CrK α and VK α , (b) x-ray image VK α , and (c) x-ray image CrK α , magnification x 600.

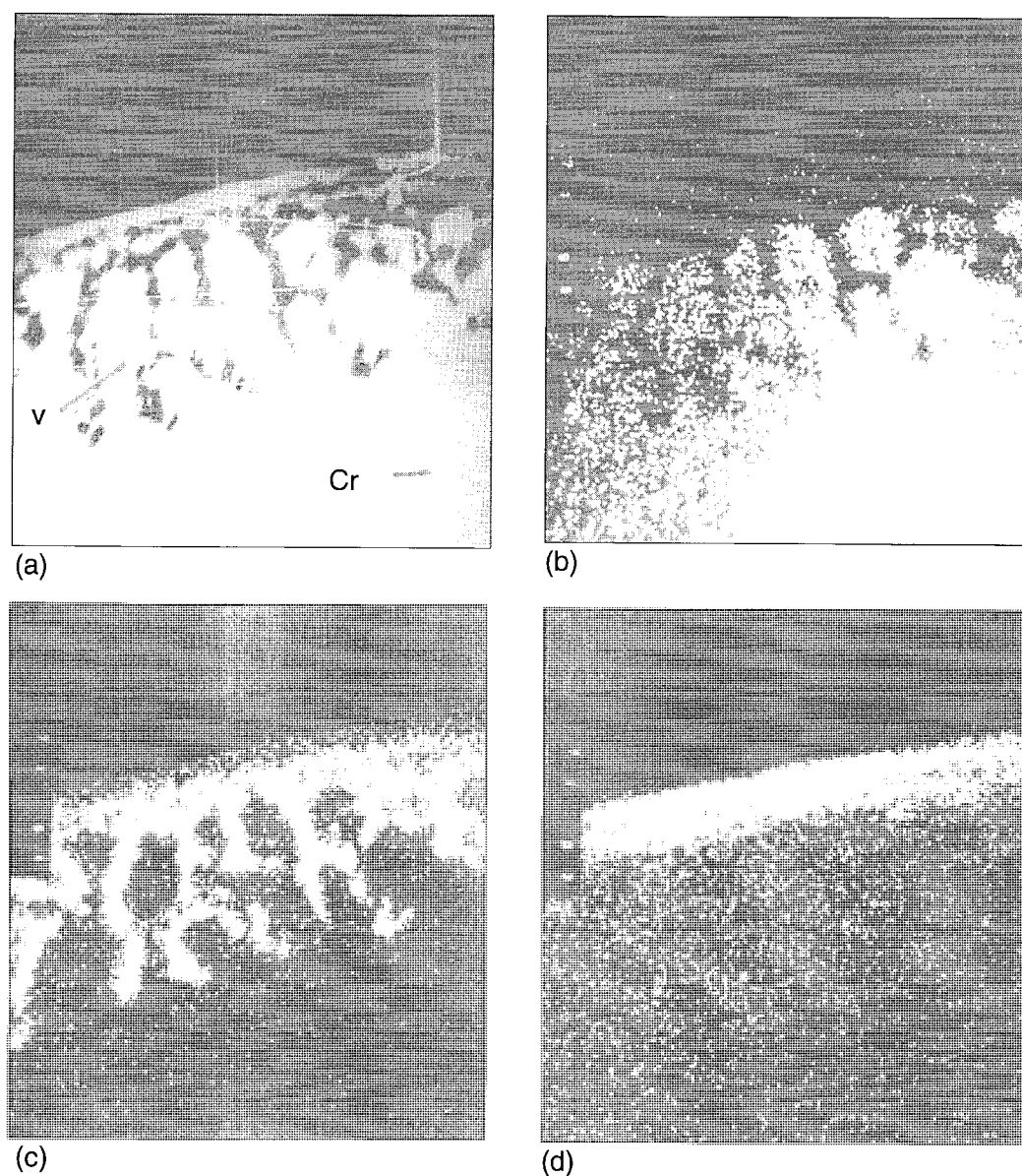


Fig. 8: Electron micrographs: (a) composition image + profile variation CrK α and VK α characteristic x radiations, (b) x-ray image FeK α , (c) x-ray image VK α , and (d) x-ray image CrK α , magnification x 600.

Table 5. Working Conditions for Chromo-Vanadization of OL37 Steel

System	Powder Mixture Composition, (wt.%) (Powder Granulation, mm)						$\frac{\text{Cr}}{\text{V}}$	Temp. (°C)	Time (Hours)
	Cr	FeV	Al ₂ O ₃	NH ₄ Cl	Charcoal	Na ₂ CO ₃			
OL37-Cr-V	35 (98% Cr; <0.12% C) (0.3-0.5 mm)	50 (48% V; <0.12% C) (0.3-0.5 mm)	5	5	4.5	0.5	$\frac{1.4}{1}$	1050	6

Table 6. Experimental Conditions for Obtaining Cr-V Diffusion Layers on 34MoCN-15 Steel

System	Powder Mixture Composition, (wt.%) (Powder Granulation, mm)				$\frac{\text{Cr}}{\text{V}}$	Temp. (°C)	Time (Hours)
	FeCr	FeV	Al ₂ O ₃	NH ₄ Cl			
34MoCN-15 Steel (carburizing ~ 1% C on ~ 1 mm)	45 (58% Cr; <0.12% C) (0.3-0.5 mm)	33 (79.9% V; <0.12% C) (0.3-0.5 mm)	20	2	1/1	1100	10

Table 7. Experimental Conditions for Chromo-Vanadization of Cast-Iron

Substrate	Powder Mixture Composition, (wt.%) (Powder Granulation, mm)				$\frac{\text{Cr}}{\text{V}}$	Temp. (°C)	Time (Hours)
	FeCr	FeV	Al ₂ O ₃	NH ₄ Cl			
Cast-Iron FC200	49 (59.5% Cr) (0.3-0.5 mm)	39 (74% V) (0.3-0.5 mm)	10	2	1/1	1020	8; 16; 32

long durations of the process (32 hours). They are uniform, compact and follow well the specimen contours, Figures 9a and b).

The layers are made of chromium and vanadium carbides. Under the carbide layer, a perlite zone is formed which ensures the passage from the hard carbide layer to the mild ferrous core of the cast iron. It is worth mentioning that perlite structure of the cast iron core suffered a ferritizing process during the chromo-vanadization process. Close to the hard carbide layer, the perlite remained untransformed, being stabilized by a chromium which diffused inwards.

Hardness measurements led to the following values:

$$\text{Layer: } \text{HV}_{(100 \text{ gf})} = 2392 \text{ Kgf/mm}^2$$

$$\text{Cast iron inward: } \text{HV}_{(100 \text{ gf})} = 225 \text{ Kgf/mm}^2$$

The great difference between hardnesses in the layer and the core can be also seen from the indentation print magnitude, Figure 9b.

2.5 Method of Diffusion Metallizing by an Electrotransport of the Diffusive Element in Molten Salts and Discharge on the Diffusion Surface

This procedure consists in a galvanic cell with molten electrolyte, in our case fluorides of alkali metals (LiF, KF, and NaF), the cathode is a metallic specimen made of copper on which the diffusion layer is formed

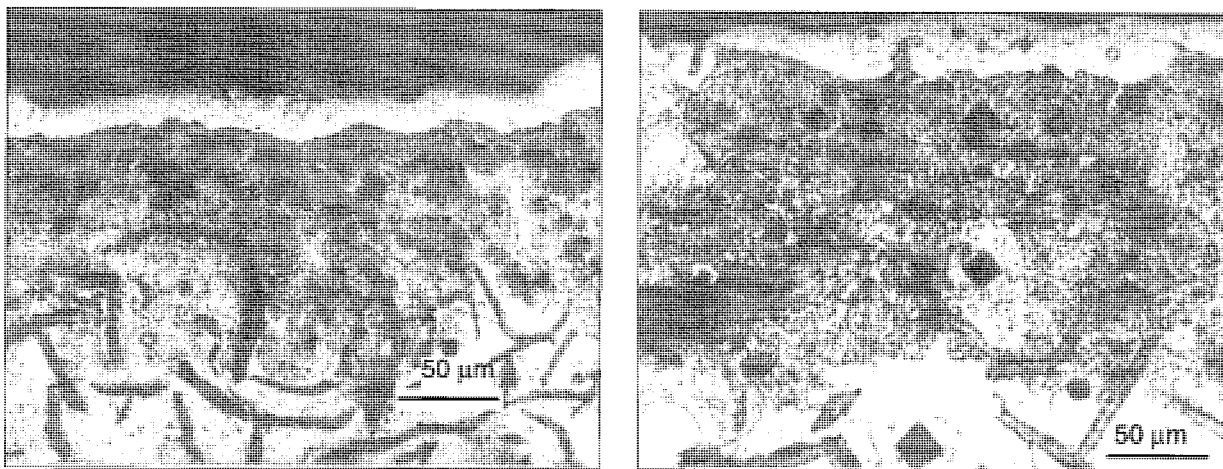


Fig. 9: Cross section optical micrographs of a sample cast iron chromo-vanadized under the experimental conditions in Table 7 (duration 16 hours), (b) indentation prints obtained at a penetration load $P = 100$ gf, metallographic etch Nital 2.5%.

Table 8. Experimental Conditions for Surface Zirconizing of Copper

System	Electrolytic Bath	Anode	Cathode	Temp. (°C)	Time (Hours)	CCD (mA/cm ²)
Cu - Zr	Ternary Eutectic (LiF, KF, NaF) + 3 mole% ZrF ₄	Zr rod (99%)	Cu Rods and Springs (99.99%)	800	3	5 - 38

and the anode is made of the diffusive elements (Zr and Be). During the process, the anode dissolves in the electrolytic bath releasing the diffusive element ions which reach the cathode surface where are electrolytic reduced becoming atoms in an active state. At the high process temperature (700-800°C), the atoms reduced on the clean surface of the cathode diffuse into its bulk and form on the surface an alloy layer which is compact and metallurgically attached to the substrate. This procedure allows for independent handling of the factors determining the process chemistry in the electrolyte (composition, temperature and cathodic current density) and therefore the cathodic deposition rate, as well as factors (temperature, duration) determining the diffusion process of the metal deposited deeply into the base metal bulk. The obtained layers can be formed of solid solutions or of a succession of phases. In all cases, due to the fact that diffusion conditions are ensured by dissolution of oxides from the metallic substrate surface into electrolytic bath, coherent and very compact layers were obtained.

The experimental set up and a detailed description of processes are presented elsewhere.⁷⁻⁹

2.6 Copper Zirconizing

The experimental conditions for obtaining Zr-Cu layers are given in Table 8.

A diffusion layer obtained at a cathode current density (CCD) of 25 mA/cm² is presented in Figures 10 a to c.

In this case, diffusion with reaction takes place. A quantitative analysis in several layer zones by electron microprobe method showed the existence of three compounds: Cu₄Zr, Cu₃Zr, and CuZr₂. Zones formed by the three compounds are seen clearly defined when one follows the variation profiles of characteristic ZrL α and CuK α X intensity radiations, Figure 10a. The steep jumps of profiles when passing from a zone to another are also clearly noticed.

Hardness at a load of $P = 40$ gf was 791 Kg/mm², while in the case of copper core it was 80 Kg/mm² at

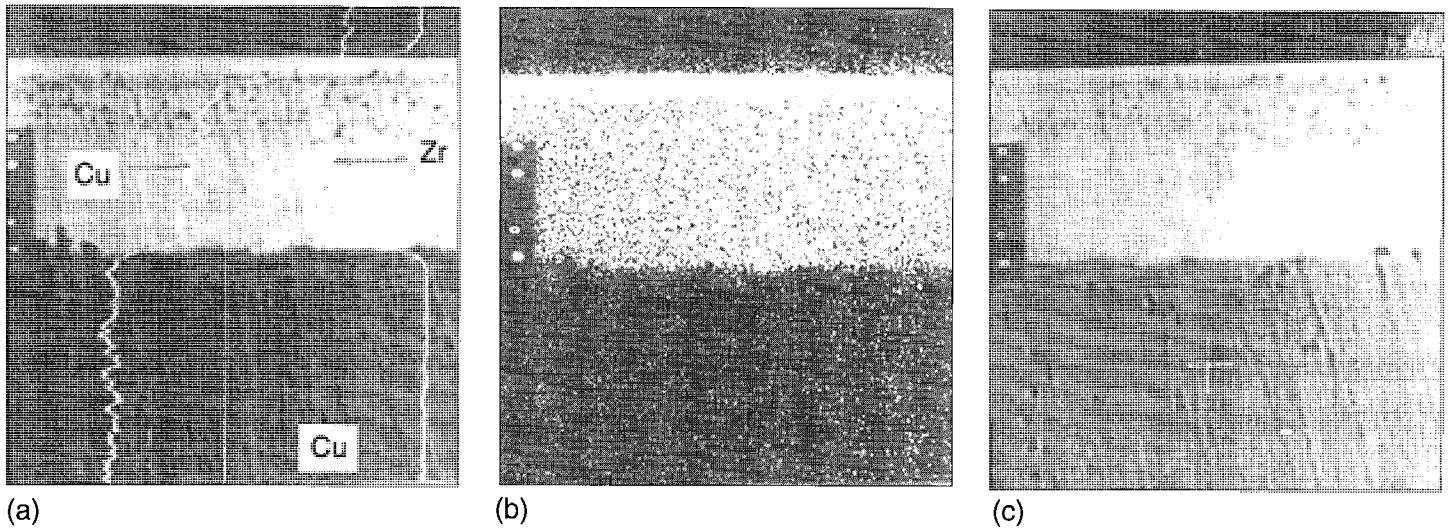


Fig. 10: Electron micrographs: (a) composition image + profiles of characteristic ZrL α and CuK α x-ray intensities, (b) x-ray image ZrL α , and (c) composition image with the marked points where analysis was made; magnification x 600.

Table 9. Experimental Conditions for Obtaining Beryllided Layers

System	Electrolytic Bath	Anode	Cathode	Temp. (°C)	Time (Hours)	CCD (mA/cm ²)
Cu - Be	Ternary Eutectic (LiF, KF, NaF) + BeF ₂ (10-30 mole %)	Be Rod (99.9%)	Cu Rods, Springs and Plates (99.99 %)	700	3 and 6	12 - 30

the same load. Due to a higher Zr concentration, hardness is still higher at the exterior in the zone of CuZr₂. As this zone was very thin, no exact measurements could be carried out. Thickness of the entire layer was ~ 40 μ m.

2.7 Copper Berylliding

The experimental conditions of this process are listed in Table 9. The beryllium diffusion into copper starts with α solid solution formation, which is very thin and then continues with formation of a layer of composition Cu₂Be, called β phase. Under the conditions of a greater Be contribution, a zone corresponding to CuBe, called γ phase, is formed at the exterior. In Figure 11, a layer obtained at a 20 mole% BeF₂ concentration in the electrolytic bath, CCD = 14 mA/cm², temperature 700°C and a duration of 3 hours is depicted.

A layer of 90 μ m of Cu₂Be was obtained. The constant of the variation profile of characteristic CuK α

x-ray intensity is a proof that this layer is formed of a single phase whose composition does not vary.

Layer hardness, the same over the whole thickness, is HV_(40 gf) = 447.4 Kg/mm². Indentation prints maintain their size, Figure 12. In the case of solid solutions, the indentation prints became larger, when the diffusive element concentration decreased.

In Figure 13, the image of a layer presenting two zones is given. The constant of the variation profile of characteristic CuK α x ray intensity over the entire thickness of the two zones is proof that these are formed of compounds: the outer zone corresponds to γ phase, CuBe, while the inner one to β phase, Cu₂Be.

Diffusion in the two phases is different. Diffusion coefficient of Be is higher in β phase: $D\beta^{Be} = 20 \times 10^{-8}$ cm²/s and lower in γ phase: $D\gamma^{Be} = 11.5 \times 10^{-8}$ cm²/s.¹⁴ Therefore, γ phase is thinner, 11 μ m, than β phase, 55 μ m. Hardness of beryllium rich γ phase is HV_(40 gf) $\cong$ 600 kgf/mm². The measurements in this zone

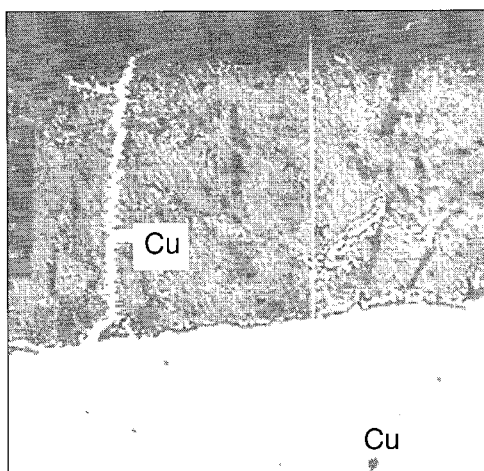


Fig. 11: Electron micrograph; composition image + profile of characteristic X-ray $\text{CuK}\alpha$, magnification $\times 300$.

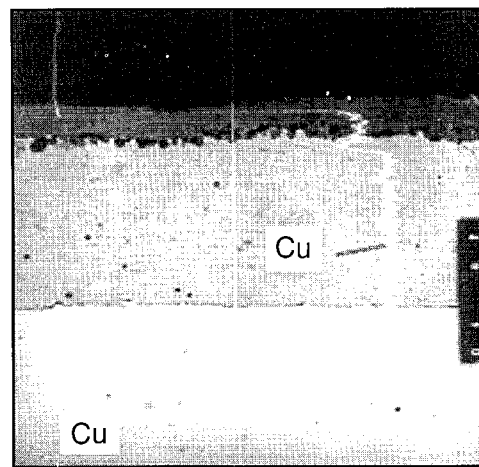


Fig. 13: Electron micrograph of a cross section in Be-Cu sample beryllized in the following conditions: 20 mole% BeF_2 , 700°C , 3 hours, $\text{CCD} = 20 \text{ mA/cm}^2$, composition image + variation profile of characteristic $\text{CuK}\alpha$ x-ray intensity, magnification $\times 300$.

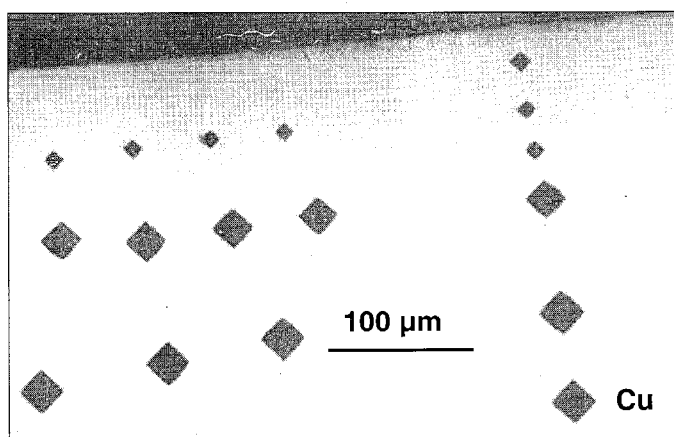


Fig. 12: Cross section optical micrograph of a Cu-Be sample (2 mm thick plate) beryllized under the following conditions: 25 mole% BeF_2 , 700°C , 3 hours, $\text{CCD} = 12 \text{ mA/cm}^2$, indentation prints obtained at a load $P = 40 \text{ gf}$, no metallographic etch.

were not accurate enough because the zone was too small.

3.0 Conclusions

1. Coating layers obtained on both ferrous (Armco iron, steels and cast iron) and non-ferrous (copper) metallic substrates are formed during some processes implying diffusion either with or without reaction.

2. Layers of solid solution are harder than the substrate material, and their hardness decreases with the decrease in the diffusive element (elements) concentration.
3. Layers constituted of compounds are much more harder than the metallic substrate and their hardness remains constant over the entire thickness of phases forming a layer.
4. The hardest layers are the carbide-containing ones.

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Vitroceraamic Oxidic Systems as Coatings on Pure Titanium (Biomedical Substrates)

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Abstract

Two frits of the following compositions were prepared: $\text{SiO}_2\text{-CaO-B}_2\text{O}_3\text{-Na}_2\text{O-TiO}_2$ and $\text{SiO}_2\text{-CaO-B}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O-Li}_2\text{O-P}_2\text{O}_5\text{-MgO-TiO}_2$ which subsequently were used to compound slips (barbotines) for covering the titanium plates used as metallic substrates. The covering procedure was enameling. In order to achieve a better adherence between the vitroceraamic layer and metallic substrate, some titanium powder of dimensions comparable with those of the frit ($< 20\text{ }\mu\text{m}$) was added in the frit powder. The quantity of added

pure titanium powder was 0.1-0.2 wt.%. The vitroceraamic – titanium systems were characterized by means of optical and electron microscopy, x-ray diffraction and microhardness trials. The studied systems are interesting because they can be used in implantology.

1.0 Introduction

Titanium and its alloys as well as some steels with high chromium and nickel contents are widely employed in implantology due to their biocompatibility and good

Table 1. Compositions and Mechanical Properties of Bioactive Ceramics Used in Implantology⁵

Oxide	Composition, (wt.%)					
	Bioglass® 45S5	S53P4	Glass-Ceramic Ceravital®	Glass-Ceramic Cerabone A-W	Glass-Ceramic Imaplant® L1	Glass-Ceramic Bioverit®
Na ₂ O	24.5	22.6	5 - 10	0	4.6	3 - 8
K ₂ O	0	0	0.5 - 3.0	0	0.2	3 - 8
MgO	0	0	2.5 - 5.0	4.6	2.8	2 - 21
CaO	24.5	21.8	30 - 35	44.7	31.9	10 - 34
Al ₂ O ₃	0	0	0	0	0	8 - 15
SiO ₂	45.0	53.9	40 - 50	34.0	44.3	19 - 54
P ₂ O ₅	6.0	1.7	10 - 50	16.2	11.2	2 - 10
CaF ₂	0	0	0	0.5	5.0	3 - 23
B ₂ O ₃	0	0	0	0	0	0
Phase*	Glass	Glass	Apatite Glass	Apatite β-Wollastonite Glass	Apatite β-Wollastonite Glass	Apatite Phlogopite Glass
Density (g/cm ³)	2.6572	-	-	3.07	-	2.8
Vickers Hardness (HV)	458 ± 9.4	-	-	680	-	500
Compressive Strength (MPa)	-	-	500	1080	-	500
Bending Strength (MPa)	42 (Tensile)	-	-	215	160	160
Young's Modulus (GPa)	25	-	100-150	118	-	70-88
Fracture Toughness K _{IC} (MPa · m ^{1/2})	-	-	-	2.0	2.5	1.0
Slow Crack Growth (n)	-	-	-	33	-	-

* Apatite = Ca₁₀(PO₄)₆(OH, F)β-Wollastonite = CaO · SiO₂Phlogopite = ((Na, K)Mg₃(AlSi₃O₁₀)F₂)

mechanical properties.¹⁻⁴ Nevertheless, in time, metallic implants produce inconveniences at the place where they are fixed because the occurrence of a fiber tissue capsule that insulates the implant material from the bone. Therefore their replacement becomes necessary. That is so due to a bioactivity lack of the metallic implants. In 1969, it was discovered that some glass and vitroceramic compositions partially crystallized from the oxidic system Na₂O-CaO-P₂O₅-SiO₂ were able to form strong bonds with the living bone, Table 1.⁵

Biocompatible and bioactive vitroceramic materials are used to manufacture small implants which do not take important mechanical stresses. For making the implants capable to resist to high mechanical stresses, the common solution is to coat a biocompatible metal with a bioactive vitroceramic layer. There are many efforts world-wide in this directions.⁶⁻¹¹ The most delicate problem in making a good vitroceramic coating on a metallic substrate is the adherence between the two

completely different materials. The main condition to be fulfilled for a good adherence is that the two materials have equal, or at least close to each other, thermal expansion coefficients. Once the metallic substrate was chosen, one cannot intervene anymore in modifying its thermal expansion coefficient. In the case of vitroceramics, these coefficients are calculated with several relations where one has to take into account the nature of oxidic materials and their proportion in the mixture as well. Therefore, in order to obtain a good adherence we have the possibility to chose an oxidic composition with a coefficient as close as possible to that of the metallic substrate. But this problem is not that simple, because coating temperature has to be taken into consideration as well.

Too high a temperature can lead to either contamination of the coating layer with metallic atoms or a modification of the metallic crystalline network. One has to observe also the vitroceramic bioactivity

Table 2. Thermal Expansion Coefficients of Titanium

Temperature, (°C)	Thermal Expansion Coefficients, (α) $\times 10^7$ (/°C)
100	88
200	91
400	94
600	97
800	99

Table 3. Oxidic Compositions of Frits

Oxide	Frit D1			Frit D03		
	Mole %	wt.%	Thermal Expansion Coefficient (α) $\times 10^7$ (Calculated)	Mole %	wt.%	Thermal Expansion Coefficient (α) $\times 10^7$ (Calculated)
SiO ₂	46.65	45.80	139.2	50	48	104
CaO	14.20	13.00		11	10	
Na ₂ O	27.36	27.70		7	7	
B ₂ O ₃	11.33	12.90		12	13.2	
TiO ₂	0.46	0.60		1	1.3	
K ₂ O	-	-		5	7.5	
Li ₂ O	-	-		6	2.9	
P ₂ O ₅	-	-		3	6.8	
MgO	-	-		5	3.3	

which is ensured by some oxidic compounds. Our team has been lately involved in obtaining vitreoceramic coatings on different metallic substrate with applications in implantology.^{12, 13}

2.0 Experimental Procedure

The procedure we use for obtaining coating layers on biocompatible metallic substrates is enameling. Pure titanium (VT1 - 00) (having the following impurities: 0.05% C, 0.20% Fe, 0.08% Si, 0.10% O, 0.04% N, and 0.008% H in wt.) has been chosen as substrate and its thermal expansion coefficients are listed in Table 2.¹⁴

Other mechanical properties of the pure titanium are: Young's module: 108.5 GPa,¹⁵ ultimate strength (resistance to rupture): $R_m = 225\text{--}230$ MPa,¹⁵ fracture toughness: $35\text{--}42$ MPa $\times$ m^{1/2}.¹⁶ At 882°C, titanium changes its crystallization form: from compact hexagonal α Ti it turns into cubic centered β Ti. Taking into account the thermal expansion coefficient of titanium at 800°C,

values in Table 2 and temperature of transformation of titanium network, we have chosen two oxidic compositions which fulfill the required conditions, (Table 3).

The raw materials used were: SiO₂ of optical purity and CaCO₃, Na₂CO₃, borax, TiO₂, K₂CO₃, Li₂CO₃, P₂O₅, and MgO, all p.a. reagent grade. The stoichiometrically weighed mixtures were melted at 1100°C (Frit D1) and respectively 1200-1250°C (Frit D03) and maintained for 30 minutes at that temperature level. Frits were obtained in water at room temperature and then ground in an agate mortar and then sifted. Only powders with dimensions between 20 and 80 μ m were chosen for slip (barbotines) preparation by mixing them with either of the two solutions: (i) 1 : 10 triethanol amine : ethylic alcohol and (ii) 5% kaolin – distilled water.

The metallic substrate were titanium plates of 10 : 10 : 2 mm. Surfaces were sand or steel ball blasted and then ultrasonically cleaned in acetone for two rounds of 10 minutes. Slips (barbotines) prepared from powder

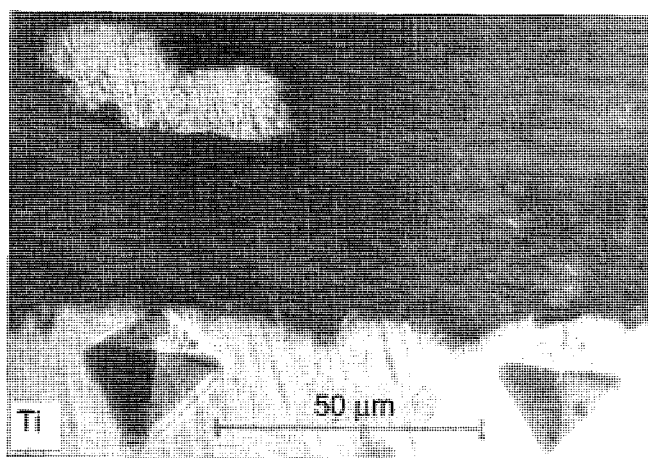


Fig. 1: Cross-section optical micrograph for (Frit D1 + 0.2 wt.% Ti) - metallic titanium substrate couple, microhardness imprints at $P = 100$ gf, no metallographic etch.

frits (particle size 20-80 μm) with added liquid medium (either triethanol amine + ethylic alcohol or kaolin + distilled water) were applied to titanium plates by immersion or painting. The coating temperatures did not exceed 710°C.

In order to improve the adherence and mechanical properties of the vitroceraic layers, ~ 20 μm Merck pure titanium powder (0.1-0.2 wt.%) was added to the powder frits.

The vitroceraic layer-metallic substrate systems were studied by optical and electron microscopy, X-ray diffraction and microhardness trials.

Optical micrographs obtained on transverse sections were taken by means of two microscopes, EPYTIP and M.C.1.M., both provided with photographic facilities.

Electron micrographs were obtained on a Philips 515 scanning microscope provided with analysis systems for energy (EDS) and wave length (WDS).

A TUR-M-62 with $\text{CoK}\alpha$ wave length and iron filter was used for X-ray diffraction analysis.

Vickers microhardness measurements were made on a Hanemann microhardness device provided with a diamond prism at penetration loads $P = 5, 10, 20, 40, 65$, and 100 gf. For each penetration load, at least 10 imprints were recorded. The imprint diagonals were measured with micrometric accuracy, as well as the length of the cracks starting from imprint corners in order to determine hardness and fracture toughness.

3.0 Experimental Results

We report here only the most conclusive experimental results from among those obtained on a greater number of vitroceraic layer-titanium substrate couples.

3.1 Vitroceraic Layer (Frit D1) – Metallic Substrate (Pure Titanium) System

Simple vitroceraic layers¹³ and 0.1-0.2 wt.% titanium powder consolidated ones were prepared. In both cases, the layers were uniform, porous, adherent on the metallic substrate and had thickness of up 70 μm . X-ray diffraction analysis evidenced the presence of $\text{Na}_2\text{CaSi}_3\text{O}_8$. An optical micrograph on cross section of the couple (Frit D1 + 0.2 wt.% Ti powder) - titanium substrate is presented in Figure 1. The couple was subjected to a thermal treatment at 450°C for 30 minutes. The microhardness imprints on the interface at a penetration load $P = 100$ gf are deformed; they are smaller towards the layer and larger towards the metallic substrate. The layer does not peel off and there are no cracks along the interface, fact that indicates a good adherence of the layer on the substrate. Titanium particles are well fixed into the vitroceraic matrix.

The following microhardness values were obtained:

Vitroceraic layer	: $\text{HV}_{(100 \text{ gf})}$	= 928 Kgf/mm ²
Interface	: $\text{HV}_{(100 \text{ gf})}$	= 416 Kgf/mm ²
Metallic substrate	: $\text{HV}_{(100 \text{ gf})}$	= 361 Kgf/mm ²
(pure titanium)		

3.2 Vitroceraic Layer (Frit D03) - Metallic Substrate (Pure Titanium) System

The vitroceraic layers were prepared with a slip (barbotine) made of Frit D03 (Table 3) and a liquid binder formed of 5% kaolin and distilled water. The couple was held at to 700°C for 2 minutes following a thermal treatment at 450-480°C for 30 minutes. The layers were uniform, porous, adherent to the metallic substrate and had thickness of about 90 μm . Such a layer is presented in Figure 2 in cross section. The microhardness imprints are also deformed, smaller towards the layer and larger towards the metallic substrate. This proves that an interdiffusion at the interface took place so that a zone with intermediate properties between those of vitroceraic and metal has formed. The electron micrographs, secondary electron images, Figures 3a and b are very interesting because the imprint deformation at the interface is clearly seen, without the peeling the layer. Moreover, the fragile character of the vitroceraic

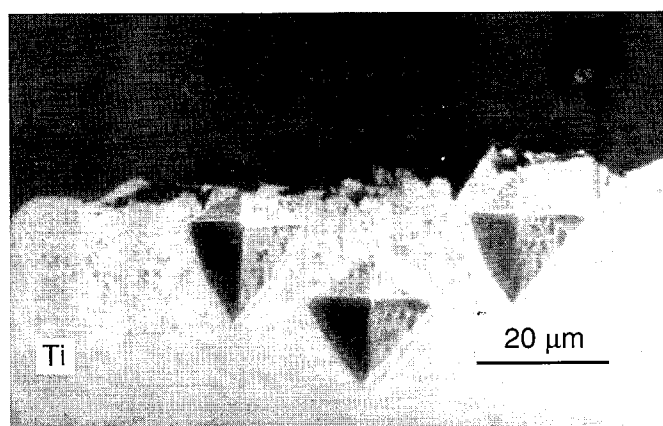


Fig. 2: Cross section optical micrograph of vitroceraamic layer (Frit D03) - metallic substrate (pure titanium) couple, microhardness imprints at a penetration load $P = 100$ gf, no metallographic etch.

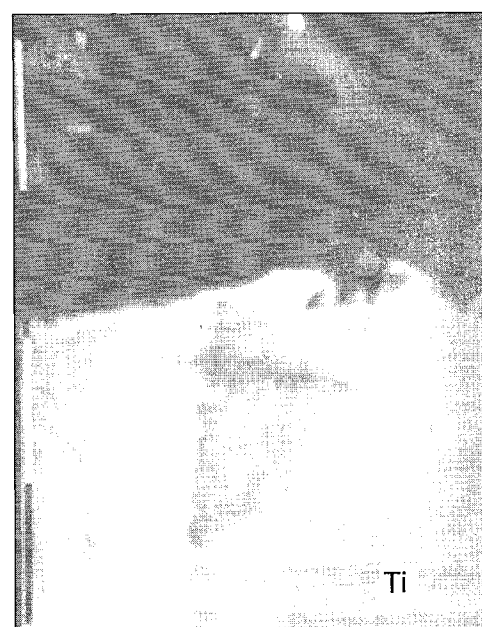
layer is also evidenced by the cracks that start only from the imprint corner situated in the layer, perpendicular direction and not along the interface. Microhardness at the interface is $HV_{(100\text{ gf})} = 571.1 \text{ Kg/mm}^2$. When cracks propagate perpendicularly to the layer and not along the interface, then the layer adherence is very good.¹⁷

X-ray diffraction analysis of the vitroceraamic layer evidenced the existence of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Vitroceraamic layers obtained on metallic substrate used in implantology must be porous. They either contain hydroxyapatite or are able to form it when enter in contact with the human body fluids. In Figure 4, one can observed that pores are present in the layer.

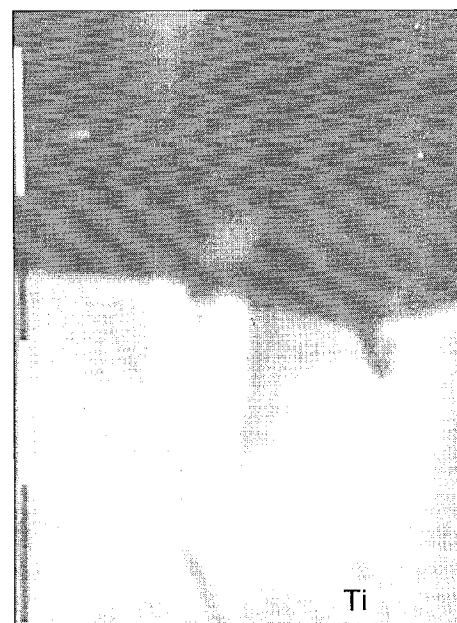
3.3 Composite - Type Vitroceraamic Layer (Frit D03 + 0.1 wt.% Ti Powder) - Metallic Substrate (Pure Titanium) System

Such a layer was obtained by using a slip (barbotine) formed from frit D03 (particle size $25 \mu\text{m}$), a liquid medium (5% kaolin + distilled water) and Merck pure titanium powder (particle size $25 \mu\text{m}$). The binding temperature was 700°C for 3 minutes, no thermal treatment. The obtained layers were uniform, porous, adherent to the metallic substrate and had thickness between $80\text{--}100 \mu\text{m}$, Figure 5.

The layer adherence is very good. Microhardness imprints obtained at the interface are similar to those in the previous cases, that is smaller towards the layer and larger towards the metallic substrate. There are no cracks



(a)



(b)

Fig. 3: (a and b) Electron micrograph, secondary electron images for vitroceraamic layer (Frit D03) - titanium couple; magnification $\times 2500$.

along the interface, but only perpendicular to the layer, Figure 6.

The following microhardness values were obtained:

Composite		
vitroceraamic layer	: $HV_{(100\text{ gf})}$	= 921 Kg/mm^2
Interface	: $HV_{(100\text{ gf})}$	= 556 Kg/mm^2
Metallic substrate (titanium)	: $HV_{(100\text{ gf})}$	= 384.4 Kg/mm^2

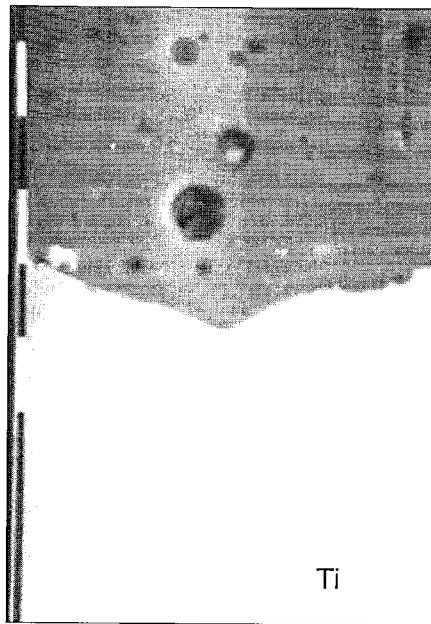


Fig. 4: Electron micrograph, secondary electron image, magnification x1250.

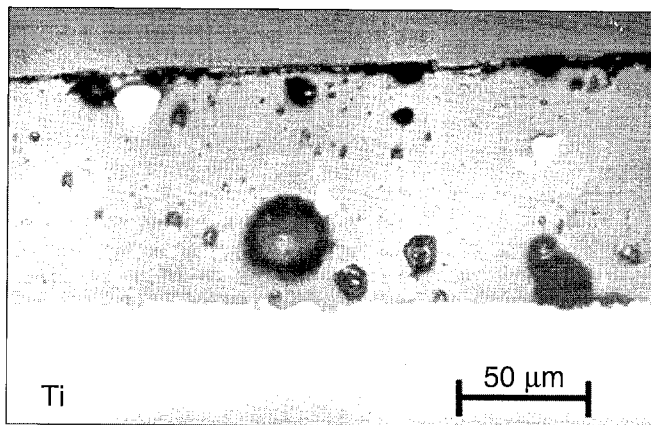


Fig. 5: Cross section optical micrograph for composite - type vitroceraamic layer (Frit D03 + 0.1 wt.% Ti) - metallic substrate (pure titanium) couple, no metallographic etch.

Titanium particles were uniformly distributed within the layer to act as a reinforcing network. Due to the fact that vitroceraamic and titanium have close thermal expansion coefficients ($\alpha_{(Ti)} = (97 - 99) \times 10^{-7}/^{\circ}C$ and $\alpha_{(vitroceraam)} = 104 \times 10^{-7}/^{\circ}C$), no cracks are noticed in the proximity of the titanium particles. These are very well fixed into the vitroceraamic matrix and can not be

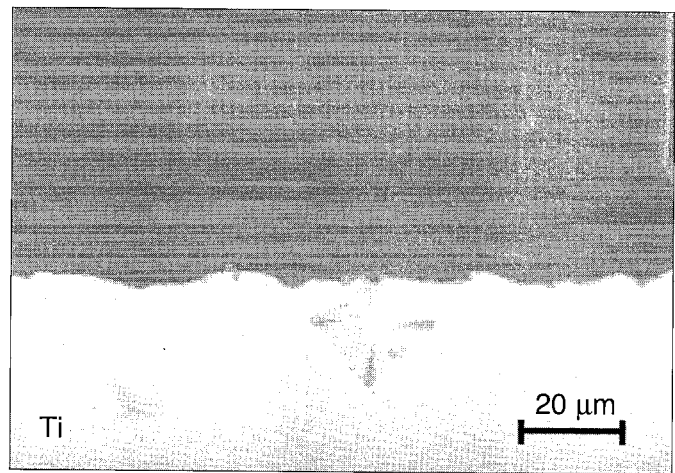


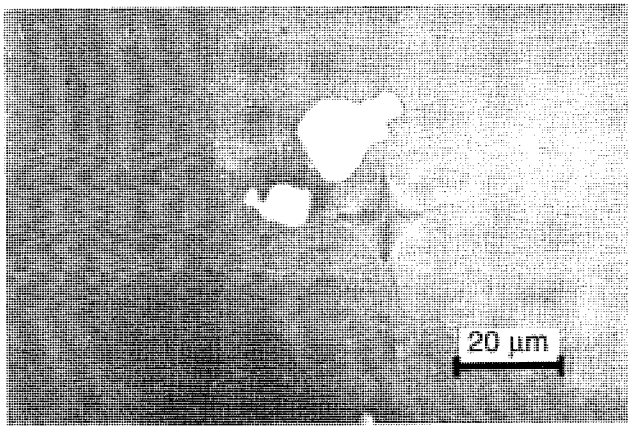
Fig. 6: Cross section optical micrograph for composite vitroceraamic layer (Frit D03 + 0.1 wt.% Ti) - metallic substrate (pure titanium) couple, imprint at load $P = 100$ gf, no metallographic etch.

dislodged when imprints are taken in their next vicinity. The imprints presented cracks which propagated from their corners, but the particles remained in their initial positions, Figures 7a - c. One can see in Figure 7c how two titanium particles placed close to a pore remained unmoved and the microhardness imprint broke. From measurements of imprint diagonals and lengths of the cracks propagated from imprint corners as well as from their centers, the fracture toughness, K_{IC} , could be determined with the relationship (1).¹⁷⁻¹⁹

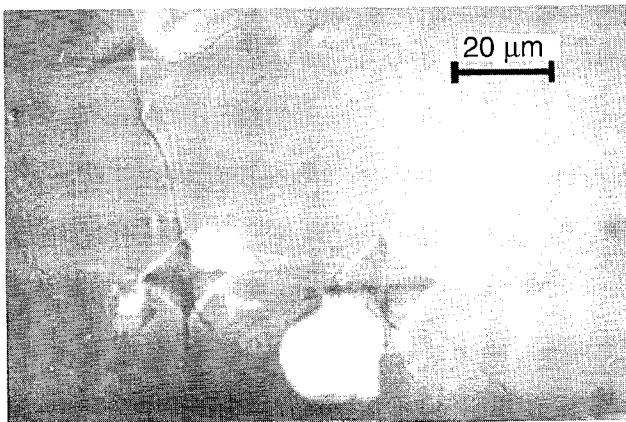
$$K_{IC} = 0.0638 \frac{P}{dl^{1/2}} \quad (1)$$

where P is penetration load in N; d is the length of the imprint diagonal in m and l is the length of cracks propagated from the imprint corners in m. For $P = 100$ gf (1 N), one obtains a fracture toughness $K_{IC} = 1.45 \text{ MPa} \times \text{m}^{1/2}$.

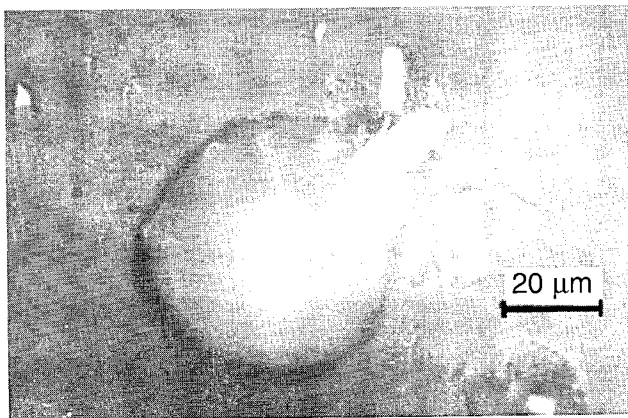
In the following, we present one layer obtained also with Frit D03 but using as liquid medium 1 : 10 triethanol amine : ethylic alcohol as binder. The layer was composite type when 0.1 wt.% Ti powder (particle size 25 μm) was added to the the slip (barbotine). Some samples were submitted for 30 minutes to a thermal treatment at 450 $^{\circ}C$. We obtained in all cases composite-type layers which were uniform, adherent to the metallic substrate and had thicknesses around 100 μm . In Figure 8, a composite vitroceraamic layer kept at 690 $^{\circ}C$ for 3 minutes and thermally treated at 450 $^{\circ}C$ for 30 minutes is depicted.



(a)



(b)



(c)

Fig. 7: Optical micrograph in the vitreoceramic layer of the couple (Frit D03 + 0.1 wt. % Ti) - metallic substrate (pure titanium), no metallographic etch: (a) titanium particles and an imprint at a load $P = 100$ gf, (b) titanium particle and 3 imprints at $P = 100$ gf, and (c) pore, titanium particles and an imprint at $P = 100$ gf.

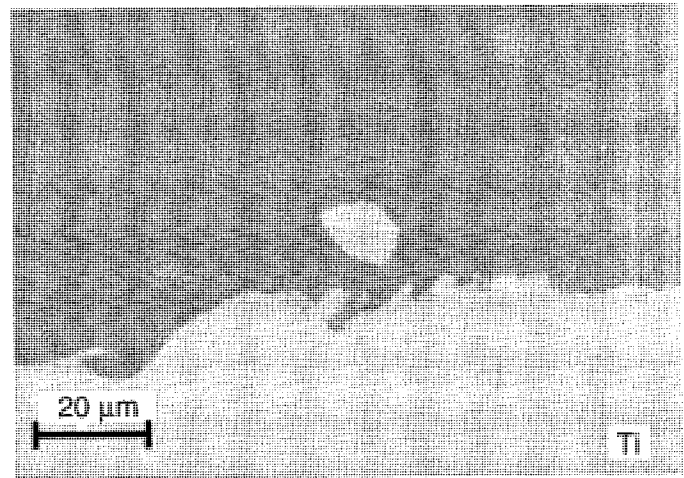


Fig. 8: Cross section optical micrograph for a composite-type vitreoceramic layer (Frit D03 + wt.% powder titanium + triethanol amine + ethylic alcohol) - metallic substrate (pure titanium) submitted to a thermal treatment, imprints at a load $P = 100$ gf, no metallographic etch.

The following microhardness values were obtained:

Composite		
vitreoceramic layer	: $HV_{(100\text{ gf})}$	= 939 Kgf/mm ²
Interface	: $HV_{(100\text{ gf})}$	= 568.4 Kgf/mm ²
Metallic substrate		
(pure titanium)	: $HV_{(100\text{ gf})}$	= 411 Kgf/mm ²

For the fracture toughness was obtained the value $K_{IC} = 1.62 \text{ MPa} \times \text{m}^{1/2}$. ($P = 1 \text{ N}$).

3.4 Composite-Type Vitreoceramic Layer (Frit D03 + 0.2 wt.% Ti) - Metallic Substrate (Pure Titanium System)

The vitreoceramic layers obtained with slip (barbotines) having a higher powder titanium content (0.2 wt.%), were also very adherent to the metallic substrates, uniform, porous and do not present cracks. As concern the hardness this was higher:

Composite		
vitreoceramic layer	: $HV_{(100\text{ gf})}$	= 1125.2 Kgf/mm ²
Interface	: $HV_{(100\text{ gf})}$	= 627.1 Kgf/mm ²
Metallic substrate		
(pure titanium)	: $HV_{(100\text{ gf})}$	= 414.4 Kgf/mm ²

The fracture toughness calculated at a penetration force $P = 1 \text{ N}$ was: $K_{IC} = 1.61 \text{ MPa} \cdot \text{m}^{1/2}$.

4.0 Conclusions

1. Oxidic systems $\text{SiO}_2\text{-CaO-Na}_2\text{O-B}_2\text{O}_3\text{-TiO}_2$ and $\text{SiO}_2\text{-CaO-Na}_2\text{O-B}_2\text{O}_3\text{-TiO}_2\text{-K}_2\text{O-Li}_2\text{O-P}_2\text{O}_5\text{-MgO}$ used as the coating layers of metallic substrate made from titanium resulted in uniform, adherent and porous covers.
2. Composite vitroceramic layers obtained by adding of powder titanium (0.1–0.2 wt. %) has better adherence to the metallic substrate (titanium). The cracks started from the indentation prints, obtained at the interface composite vitroceramic layer – titanium substrate, propagate perpendicularly to the layer and not along the interface.
3. The hardness of the layer increases with the powder titanium concentration.
4. X-ray diffraction analysis made on the coating layers proved the existence of the compound $\text{Na}_2\text{CaSi}_3\text{O}_8$ formed in the oxidic system $\text{SiO}_2\text{-CaO-Na}_2\text{O-B}_2\text{O}_3\text{-TiO}_2$ and the hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ formed in the oxidic system $\text{SiO}_2\text{-CaO-Na}_2\text{O-B}_2\text{O}_3\text{-TiO}_2\text{-K}_2\text{O-Li}_2\text{O-P}_2\text{O}_5\text{-MgO}$.

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Modification of Oxide Thermal Barrier Coatings Deposited on a Superalloy by Laser-Beam Radiation

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Abstract

This work describe the influence of laser treatment on structure and some properties of Al_2O_3 , $\text{Al}_2\text{O}_3 + 5\%\text{Ni}$, $\text{Al}_2\text{O}_3 - (95\%\text{Ni} + 5\%\text{Al})$, $\text{Al}_2\text{O}_3 + 5\%\text{Ni} - (95\%\text{Ni} + 5\%\text{Al})$, and $\text{Al}_2\text{O}_3 + 5\%\text{Ni} + \text{CrAl}$ layer oxide ceramic coatings of about $100\ \mu\text{m}$ thickness deposited by air plasma spraying on a heat resistant alloy on nickel matrix. It has been stated that laser remelting of power density $0.01 - 0.2 \times 10^9\ \text{W m}^{-2}$ and scanning rate within $5 - 7\ \text{m min}^{-1}$ ensures good quality of ceramic coatings in comparison with not-remelted coatings. Ceramic coatings under laser treatment have better thermal conductivity

than as deposited layers. As proved in model calculations, after laser treatment they show smaller temperature drop in certain thickness. Erosion resistance of the coatings, however, is greater after laser treatment.

1.0 Introduction

Oxide aluminum coatings and their compounds formed by air plasma spraying (APS), due to chemical stability, oxidation resistance, electric insulation and anti-wear have many in engineering applications.

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Table 1. Chemical Composition, Phase and Particle Size and Morphology of Mixed Powder Particles

Powder	Mixture Contents (wt.%)	Phase Constitution	Granularity (μm)	Morphology
Al_2O_3	98 Al_2O_3 0.5 SiO_2 0.5 Fe_2O_3 1 TiO_2	Phase α Trigonal Lattice Phase β Hexagonal Lattice	90/54	Melted, Crashed Irregular
NiAl	Ni $\geq$ 93, Al 4-4.5	Nickel, Aluminum	90/45	Nickel Coated Spherical
$\text{Al}_2\text{O}_3 + \text{Ni}$	95 Al_2O_3 , 5Ni	Phase α Trigonal Lattice Phase β Hexagonal Lattice	90/45	Spherical Coated

They are used for covering parts of the machines and devices in motor industry (hot parts of engines), aviation (blades), conventional power engineering (elements of turbines) and nuclear power engineering (tokamak, stellarator).¹⁻⁵ The cause of coating deterioration is among others, thermal stresses connected with different thermal expansion of the ceramics and metal substrates and phase changes occurring both in the ceramics and the substrates. In order to diminish stresses, before placing a ceramic coating on a metal substrate, a plasma sprayed layer is deposited which has an intermediate thermal expansion coefficient, or a diffusive treatment is applied that improves the connection between different materials. Fast solidification connected with rapid cooling of sprayed material remelted particles, which occurs in plasma spraying, causes formation of metastable phases e.g. formation of γ Al_2O_3 metastable phase at room temperature in the presence of α Al_2O_3 , a phase which results from not fully remelted particles while plasma spraying. Each Al_2O_3 allotropic form features different physical properties and different molecule sizes.⁶ Structure changes connected with diminishing or enlarging the cell volume cause formation of micro-cracks and pores, which lead to changes of physical properties, particularly thermal conductivity. Previous studies⁷⁻⁹ analyse structure changes and thermal conductivity of plasma sprayed coatings of Al_2O_3 . For pure α Al_2O_3 , thermal conductivity is $30 \text{ W m}^{-1}\text{K}^{-1}$, and in heat treatment processes, it can reach $0.8 \text{ W m}^{-1}\text{K}^{-1}$. It should be noted that in air plasma spraying, not all particles are remelted, and changes of shape occur - they can be flatten. Generally, the coating has a lamellar structure. Non-continuity of structure is formed, and that reaches a few microns - channel pores,

interlamellar micro cracks of a few submicrons, interlamellar gaps. Slot new sentence stratification strongly depends on plasma spraying conditions. Quality of coatings can be better by applying laser treatment. Porosity disappears, density improves, and corrosion resistance is better. Structural changes occurring on the boundary of the ceramic coating - substrate improve the coating and matrix relationship. A CO_2 laser was chosen for performing laser remelting.¹⁰⁻¹⁴ This paper presents influence of laser treatment on single and double layer Al_2O_3 , $\text{Al}_2\text{O}_3 + \text{Ni}$, $\text{Al}_2\text{O}_3/\text{NiAl}$, $\text{Al}_2\text{O}_3 + \text{Ni}/\text{NiAl}$, $\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$ ceramic coatings on a metal substrate. On the basis of performed experiments, quality and usability of examined materials were described.

2.0 Experimental Details

Mixed powder particles from Sulzer-Metco were used to form surface layers. Chemical composition, phase, particle size and morphology of the particles are presented in Table 1.

Single and double layer coatings were placed on sand-blasted substrates of roughness coefficient $R = 5 \pm 2 \mu\text{m}$, made of a heat-resistant alloy (EI868). Properties and chemical composition of this alloy are given in Table 2. METCO 7MB plasma gun with a GHI nozzle diameter $\Phi 6.5 \text{ mm}$ was used.

In order to obtain coatings of different porosity, the distance between the nozzle and the substrate was changed from 0.10 to 0.16 m.

For given spraying conditions, single layer coatings of $90 \mu\text{m}$ thickness and double layer coatings of $90 \mu\text{m}$ (ceramic coating $60 \mu\text{m}$, relaxation layer $30 \mu\text{m}$) were obtained. The intermediate relaxation NiAl layer between the sample surface and ceramic

Table 2. Chemical Composition and Some Physical Properties of Substrate Material

Alloy Symbol	Chemical Composition (wt.%)	Density in 293 K (kg m^{-3})	Roughness (μm)	Thermal Conductivity in 293 K ($\text{Wm}^{-1}\text{K}^{-1}$)	Thermal Expansion in 293 K (K^{-1}) $\times 10^{-6}$
El 868	0.1 C 24-26 Cr 14-16 W 0.3-0.7 Ti 5Fe, Ni bal	8911.5	9.2	9.64	12.7

Table 3. Plasma Spray Parameters

Current Intensity (A)	Voltage (V)	Flow H_2 (lh^{-1})	Flow Ar (lh^{-1})	Ar Powder Mixture Carrier (lh^{-1})	Shift Rate (m min^{-1})	Powder Consumption (kg h^{-1})	Substrate Temperature (K)
500	80	520	1620	1080	30	1.8-1.9	323

Table 4. Experimental Conditions for Laser Remelted Ceramic Coatings

Coating Type	Power Density ($\times 10^9 \text{ W m}^{-2}$)	Scanning Rate (m min^{-1})	Kind of Gas and its Usage (l min^{-1})
Al_2O_3	0.1761	7	10
$\text{Al}_2\text{O}_3 + \text{Ni}$	0.0095	6	10
$\text{Al}_2\text{O}_3/\text{NiAl}$	0.0095	7	10
$\text{Al}_2\text{O}_3 + \text{Ni}/\text{NiAl}$	0.0786	6	10
$\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$	0.2536	5	10

coating was applied in order to improve adherence and lower the stresses caused by different thermal expansion of the substrate and ceramics. Single layer $\text{Al}_2\text{O}_3 + 5\%\text{Ni}$ coatings were made for the same reason. Some of the samples with Al + 5%Ni coating undergoing additional chromoaluminizing by a pack cementation method.¹⁵

A CO_2 laser with maximum power 1.2 kW was used to carry out the laser treatment. The best quality coating was obtained by varying the power density $0.004\text{--}1.3 \times 10^9 \text{ W m}^{-2}$ and scanning rate from 7 to 0.5 m min^{-1} in steps 0.25 m^{-1} as well as changing the substrate temperature, shroud gas and its flow speed.

In order to ensure the required quality of coatings, laser treatment was done on elements heated to a temperature dependant on the substrate material. Lowering the temperature gradient, and at the same time thermal stresses, reduces the cracking tendency of the coatings.¹⁶

Table 4 presents laser treatment conditions of plasma sprayed Al_2O_3 , $\text{Al}_2\text{O}_3 + \text{Ni}$, $\text{Al}_2\text{O}_3/\text{NiAl}$, $\text{Al}_2\text{O}_3 + \text{Ni}/\text{NiAl}$, $\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$ coatings, established on the basis of surface morphology observation and microstructure analysis.

With the help of scanning EDAX microscopy, observation of surface morphology and analysis of point

and surface element distribution were performed. In order to perform fractographic analysis, the metal part of the samples was cut and then broken.

Microstructure of coatings was defined with the help of light microscopy on polished microsections with the use of diamond pastes, with and without electrolytic etching (metal matrix), cut perpendicularly to the coatings.

Microhardness was measured with microhardness tester DUH 202 (Vickers method), at 1962 mN loading.

Thermal conductivity measurement from room temperature to 700°C was done for fixed flow of precisely stabilised heat flux by determining heat flux density on the basis of measured temperatures and element thickness. Firstly heat resistance, was taken for consideration, from that contact resistance, was determined then the thermal conductivity of thin ceramic coatings was calculated. On this basis temperature distribution in a coating and substrate could be determined. Calculation was done on the example of temperature distribution in a steel block of 30 cm height with 1 mm ceramic coating with one side at 700°C and the other side at 20°C environment. Elementary balance method, based on preparing balance for differential elements at fixed heat flux flow, was used.

Evaluation of erosion resistance was done on the basis of mass loss for an elemental surface unit under the air flow with qualified abrasive EB 120 in. the form of Al_2O_3 electrocorundum, 100 μm grain size from a 4 mm diameter nozzle at 0.3 MPa pressure. Velocity of the abrasive stream was about 20 g min^{-1} , and its mass on the sample was each time equal 80 kg. Each sample underwent 3 cycles of testing, during which 240 kg of abrasive was used. Other parameters of the test were: distance from nozzle to sample surface 25 mm, glancing angle of the flux to sample surface 30°.

3.0 Experimental Results and Discussion

Macroscopic observations of laser treated zones showed that air remelted ceramic coatings placed during that process on the heated substrate do not flake or chip. They are more rough than laser not-remelted ones and their rough coefficient grows from 7.3 to 10.5 μm .

Metallographic microscopic tests showed that plasma sprayed coatings feature equal thickness and changeable contrast due to the presence of different crystalline Al_2O_3 phases in the matrix of amorphous Al_2O_3 show a Figure 1. Ceramic coatings Figure 2,

plasma sprayed on Ni + 5% Al base show a less uniform structure and thickness, because the sub-layer, under the influence of high temperature plasma, melts and partly vaporizes; then during the cooling process it crystallises to metal base. Thus the boundary surface between the base and ceramic layer is strongly developed. Metallographic examinations presented in Figures 3, 4, and 5 showed that laser beam melting of the ceramics causes outflow of the ceramics between consecutive paths. After laser remelting the surface becomes less smooth, and sometimes stratification between the ceramic coating and the base occurs. It happens mostly in the case of single-layer Al_2O_3 coatings. On the outer surface of Al_2O_3 + Ni coatings small microcracks and small unevenness can be observed after laser melting. It is most probably connected with evaporation of melted Ni grains. Al_2O_3 , Al_2O_3 + Ni coatings and Ni + 5% Al placed on the metal base show after laser remelting good connection with the metal base and in some places dark spheres similar to cracks, placed perpendicular to the base (Figure 4). Observation of microsections in the dark area do not show cracks in these spheres (Figure 5). The most compact structure and good connection with the base feature Al_2O_3 + Ni coatings which prior to laser remelting undergo chromoaluminizing. In that case, under remelted ceramic-metal coating and the base, a metallic sphere is formed which has the structure of plate mixture. Quantitative metallographic analysis with the use of a computer picture analyser showed that laser remelting causes a decrease in closed porosity in relation to the not-remelted state of about 25% in case of Al_2O_3 coatings and of 3% in case of Al_2O_3 + Ni coatings. Al_2O_3 + 5%Ni ceramic samples which after plasma spraying undergo chromoaluminizing, before laser remelting feature porosity comparable to that of plasma sprayed Al_2O_3 + 5%Ni coating, which after remelting have 2.5% porosity.

Measurement of Vickers microhardness showed that laser remelted coatings in comparison to plasma sprayed ones feature higher microhardness than those not laser remelted. The microhardness of a laser remelted Al_2O_3 + Ni/NiAl coating is 1850 HV, and for non-remelted 1420 HV. The biggest growth in hardness after laser remelting is in Al_2O_3 /NiAl - 1925 HV coatings, and the smallest one Al_2O_3 + Ni + CrAl - 370 HV coatings.

The analysis of composition by the EDAX method in different places of microsection with a laser remelted Al_2O_3 + Ni coating showed that the ceramic layer shows a composition relevant to Al_2O_3 oxide, metal substrate EI868 alloy composition, in some places with higher W concentration, whilst the sphere between the substrate and the ceramic layer has a composition of a mixture

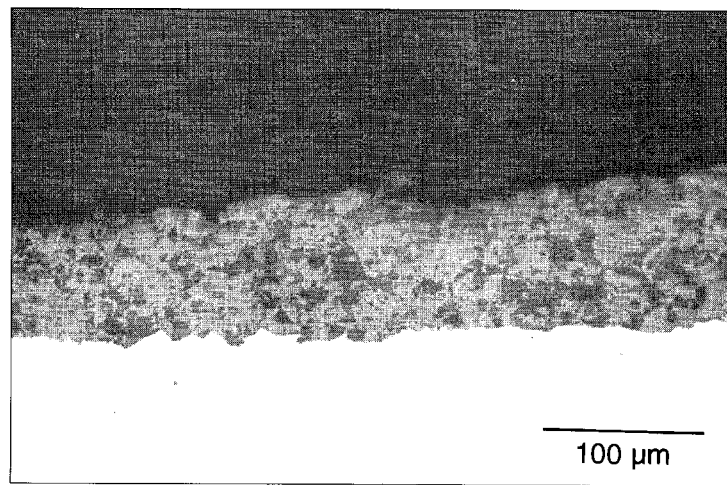


Fig. 1: Structure of plasma sprayed Al_2O_3 coating magnification 200x.

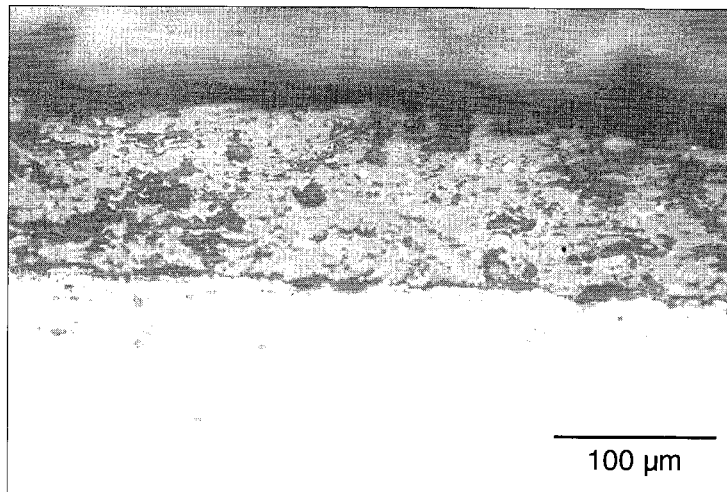


Fig. 2: Structure of plasma sprayed $\text{Al}_2\text{O}_3 + \text{Ni}$ coating magnification 200x.

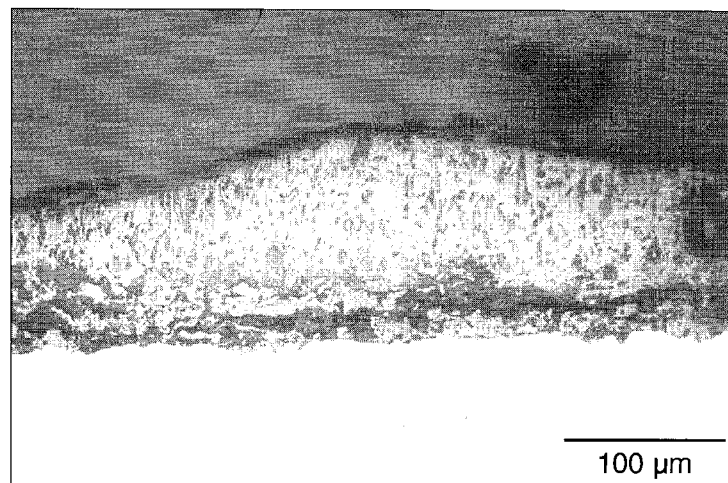


Fig. 3: Structure of laser remelted Al_2O_3 coating, scanning rate 7 m min^{-1} , magnification 200x.

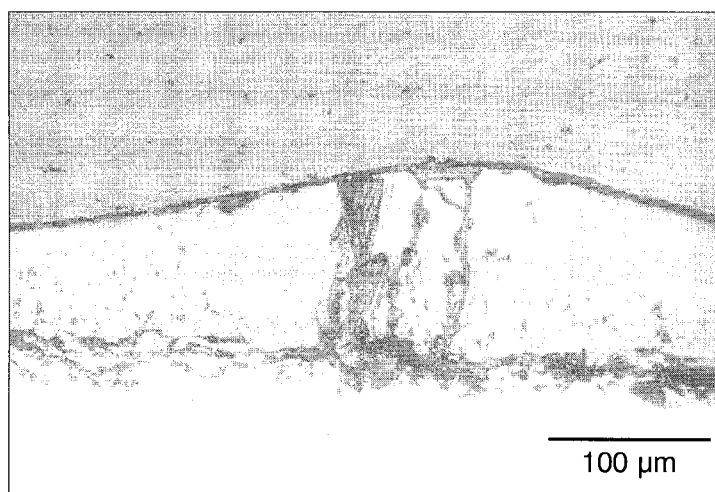


Fig. 4: Structure of laser remelted $\text{Al}_2\text{O}_3 + \text{Ni/NiAl}$ coating, scanning rate $6 \text{ m} \cdot \text{min}^{-1}$, magnification 200x.

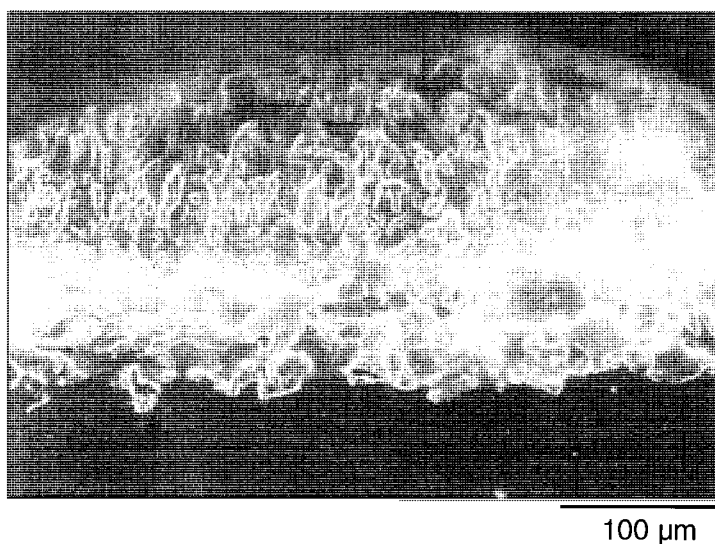


Fig. 5: Structure of laser remelted $\text{Al}_2\text{O}_3/\text{NiAl}$ coating, scanning rate $7 \text{ m} \cdot \text{min}^{-1}$, contrast phase, magnification 200x.

Al_2O_3 and Cr_2O_3 and a alloy matrix. The fractographic examination showed that $\text{Al}_2\text{O}_3 + \text{Ni}$, $\text{Al}_2\text{O}_3/\text{NiAl}$, $\text{Al}_2\text{O}_3 + \text{Ni/NiAl}$ coatings after plasma spraying have better developed fracture surface than the coatings after laser remelting (Figures 6a and b). Not much developed fracture surface of remelted coatings is caused by the influence of texture in a crystalline phase growth and the presence of an amorphous phase Al_2O_3 .¹⁷

Areas in the form of small bulges and hollows correspond to the cracks after grain boundaries - crystalline phases Al_2O_3 . Similar observation were done in case of laser remelted Al_2O_3 coatings that underwent chromoaluminizing obtained by pack cementation method.

Measurements and calculations of metal substrate density and a coating obtained by thermal spraying method and after laser remelting (Table 5) showed that laser remelting causes small growth in the density connected with reduction of close and open porosity and changes in phase composition¹⁷.

The biggest density growth after laser remelting show $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings, whilst $\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$ coatings show the smallest density growth.

Figures 7a-e show thermal conductivity in temperature function for a few chosen coatings. Al_2O_3 coatings obtained by APS method (Figure 7a) have the lowest thermal conductivity at temperature 600°C - about $1 \text{ W} \cdot \text{m}^{-1}\cdot\text{K}^{-1}$; after laser remelting it reaches $1.4 \text{ W} \cdot \text{m}^{-1}\cdot\text{K}^{-1}$.

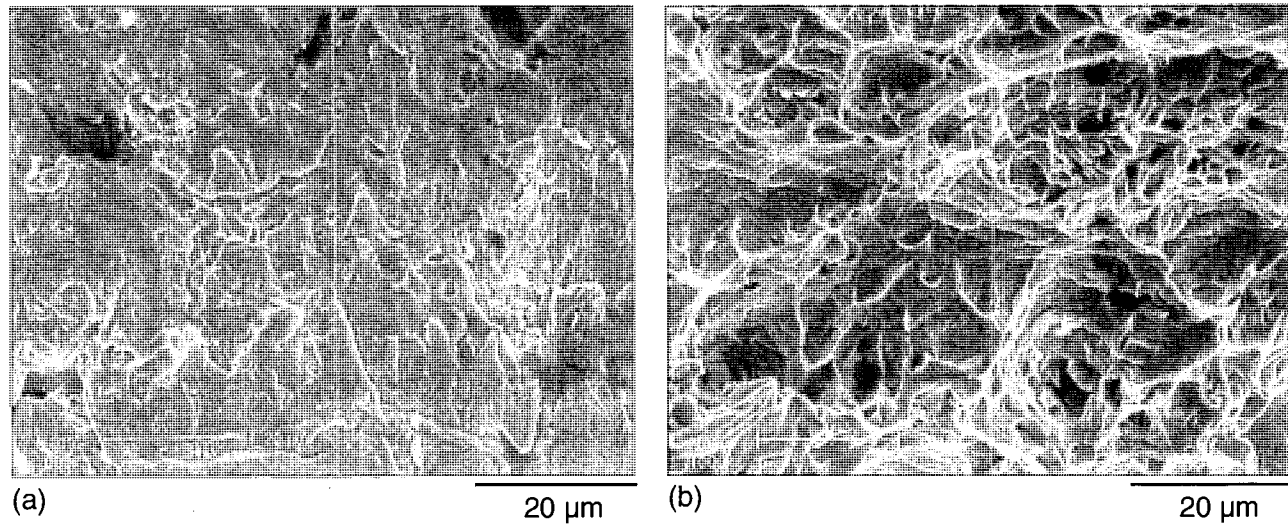


Fig. 6: Surface of coating fracture (a) fracture surface after plasma spraying and (b) fracture surface after laser remelting, magnification 1000x.

Table 5. Density of Plasma Sprayed Coatings Before and After Laser Remelting

Coating Type	Density [kg m^{-3}]	
	Not Laser Remelted	Laser Remelted
Al_2O_3	3971.21	4035.22
$\text{Al}_2\text{O}_3 + \text{Ni}$	4096.35	4177.64
NiAl	4885.25	4945.73
$\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$	6880.31	6906.80

The difference in thermal conductivity between non-remelted and laser remelted coatings is caused by the transfer of amorphous phase and crystalline phase β and $\gamma\text{Al}_2\text{O}_3$ into $\alpha\text{Al}_2\text{O}_3$ and also by a partial loss of pores.¹⁷ $\text{Al}_2\text{O}_3 + \text{Ni}/\text{NiAl}$ coatings (Figure 7b) have similar thermal conductivity in tested temperature range to $\text{Al}_2\text{O}_3/\text{NiAl}$ coatings (Figure 7c), both after plasma spraying and laser remelting. This is the result of almost identical phase structure of these coatings in both states.¹⁷ The presence of 5% nickel in Al_2O_3 coating (Figure 7d) causes only small changes in thermal conductivity $1.4 \text{ W m}^{-1}\text{K}^{-1}$ at the temperature 600°C , and after laser treatment up to $1.6 \text{ W m}^{-1}\text{K}^{-1}$. Such a small growth of thermal conductivity is due to small changes in the structure of $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings after laser remelting. In that state they have slightly smaller participation of an

amorphous phase and crystalline phases β and γ than directly after plasma spraying.¹⁷

The highest thermal conductivity in a tested temperature range have $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings which after plasma spraying undergo chromoaluminizing. The presence of metal phases in such coatings decides that at temperature 600°C , after plasma spraying their thermal conductivity is $1.7 \text{ W m}^{-1}\text{K}^{-1}$ and after laser remelting is $2.4 \text{ W m}^{-1}\text{K}^{-1}$.

Diversified thermal conductivity of tested coatings decides upon their different effectiveness as thermal barriers. According to the calculations (Figures 8a and b), the biggest temperature drop of about 10°C in 0.1 mm thickness and at temperature 600°C have the coatings of the lowest values of thermal conductivity i.e. Al_2O_3 after thermal spraying. This temperature drop becomes

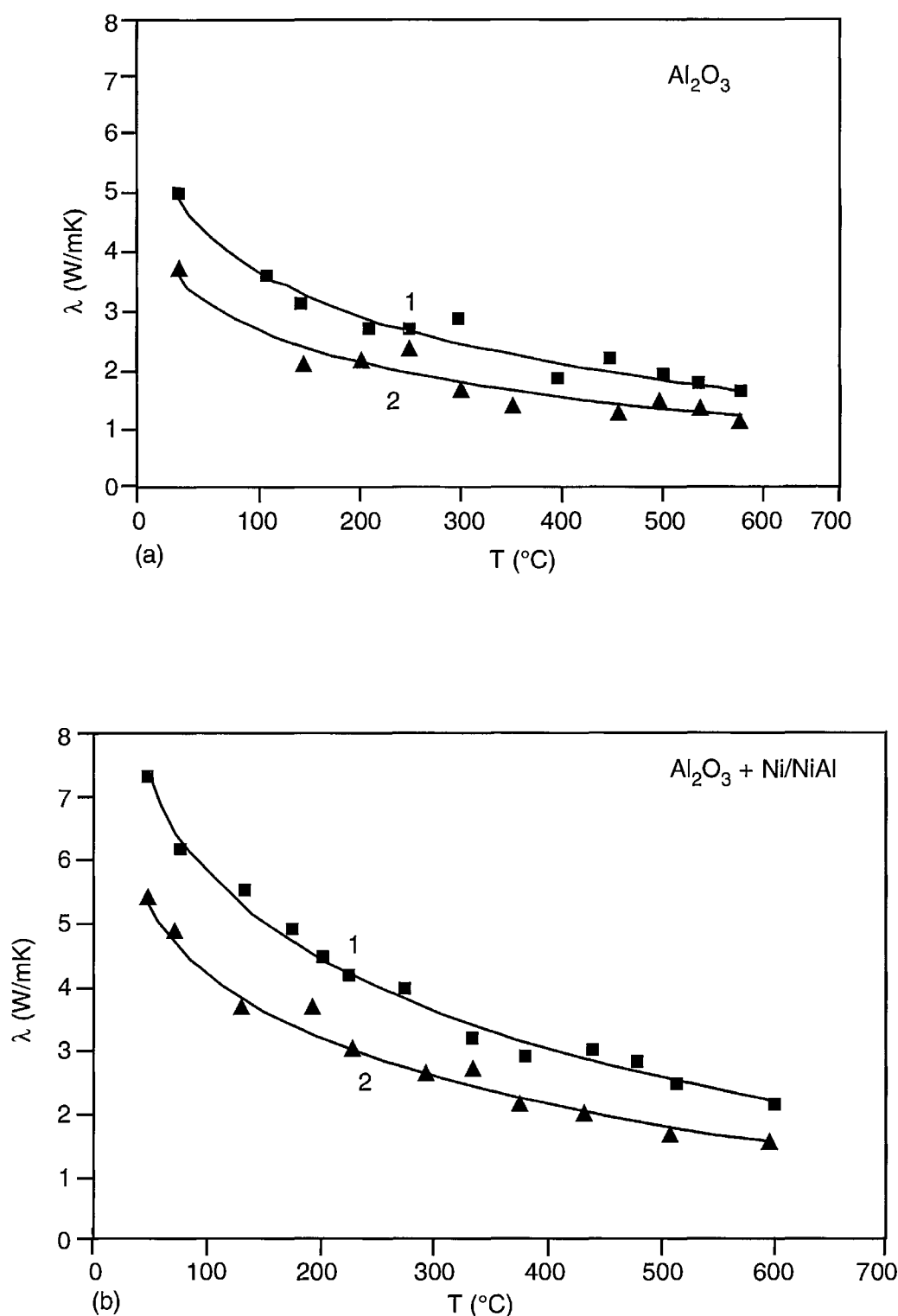


Fig. 7: Values of thermal conductivity (1) laser remelted and (2) plasma sprayed ceramic coatings as a function of temperature, (a) Al_2O_3 , (b) $\text{Al}_2\text{O}_3 + \text{Ni/NiAl}$, (c) $\text{Al}_2\text{O}_3/\text{NiAl}$, (d) $\text{Al}_2\text{O}_3 + \text{Ni}$, and (e) $\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$. (See c, d, and e in next page).

smaller to 6°C after laser remelting. The smallest temperature drop in 0.1 mm thickness and at temperature 600°C have $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings undergoing chromoaluminizing. Other Al_2O_3 and $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings deposited on NiAl sub-layer show intermediate values of temperature drop in a given thickness both after

plasma spraying and after laser remelting. The temperature drop in a given thickness of tested coatings will be bigger in high temperature as their thermal conductivity decreases in temperature function.

Testing erosion resistance (Table 6) in air flow with the abrasive EB120 in the form of alundum 100 μm grain

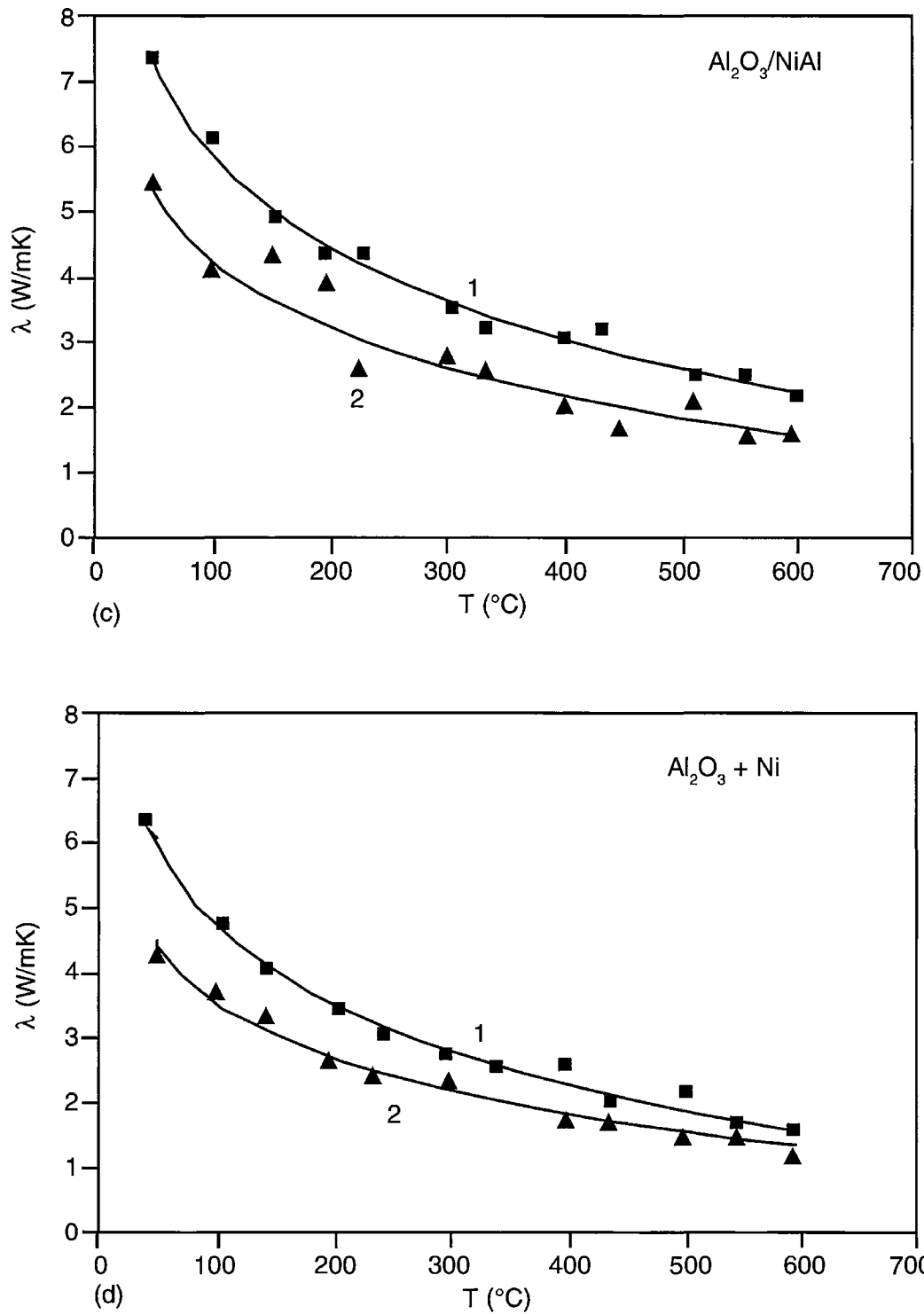


Fig. 7: Continued.

size showed that loss of volume and mass and unitary loss of mass in three consecutive examinations for particular coatings is diversified. Laser remelted coatings feature considerably higher erosion resistance than after plasma spraying $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings. The highest erosion

resistance have $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings which underwent chromoaluminizing, especially after laser remelting. Laser remelted $\text{Al}_2\text{O}_3 + \text{Ni}$ and Al_2O_3 coatings on a NiAl sub-layer have intermediate erosion resistance. The smallest erosion resistance is shown by Al_2O_3 . $\text{Al}_2\text{O}_3 + \text{Ni}$ coatings

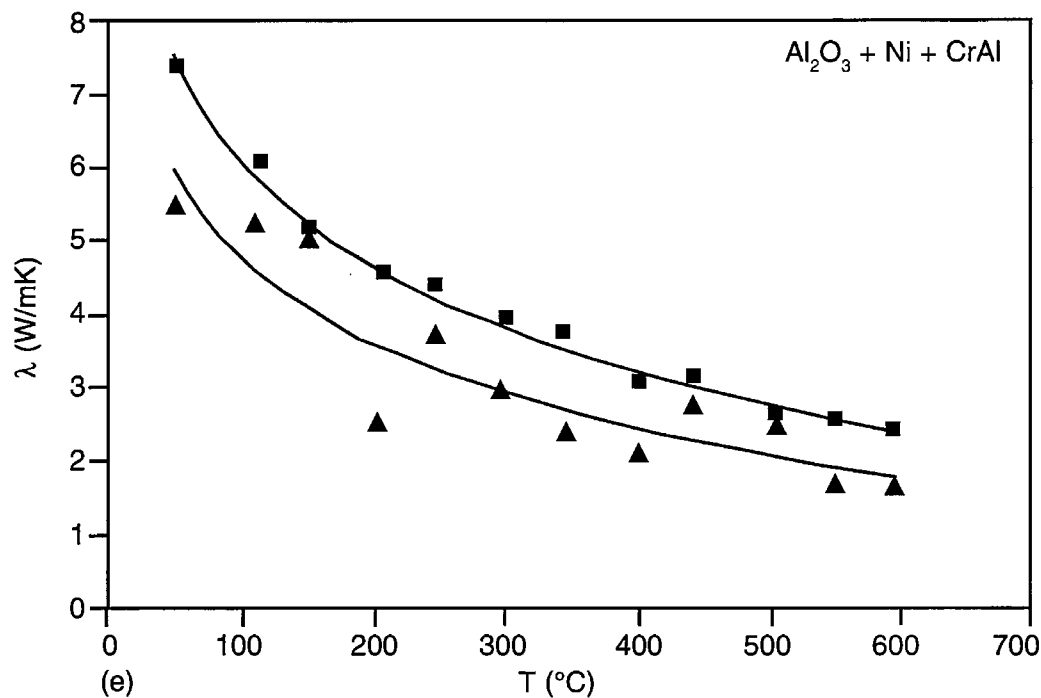


Fig. 7: Continued.

Table 6. Results of Erosion Examination

Coating Type	M_0	$M_1/80 \text{ g}$	$M_2/160 \text{ g}$	$M_3/240 \text{ g}$	$S [\text{cm}^2]$
Al_2O_3^*	5.5092	5.4848	5.4778	5.4778	5.70
$\text{Al}_2\text{O}_3/\text{NiAl}$	6.8263	6.7811	6.7506	6.7324	6.20
$\text{Al}_2\text{O}_3/\text{NiAl}^*$	7.0320	7.0220	7.0124	7.0030	6.24
$\text{Al}_2\text{O}_3 + \text{Ni}$	6.2914	6.2652	6.2474	6.2361	5.85
$\text{Al}_2\text{O}_3 + \text{Ni}^*$	6.4285	6.4070	6.3800	6.3780	5.85
$\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$	5.6171	5.6029	5.5995	5.5967	5.25
$\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}^*$	7.4233	7.4177	7.4155	7.4144	6.75
$\text{Al}_2\text{O}_3 + \text{Ni}/\text{NiAl}$	6.5016	6.4661	6.4368	6.4156	5.70
$\text{Al}_2\text{O}_3 + \text{Ni}/\text{NiAl}^*$	6.7786	6.7668	6.7645	6.7463	6.00
El 868	4.5395	4.5358	4.5328	4.5296	6.00

*Laser remelted

after plasma spraying, and after placing on a NiAl sub-layer also have the smallest resistance.

4.0 Conclusions

1. Obtaining ceramic coatings resistant to flaking and chipping calls for application of powder ceramic materials of required quality and proper choice of plasma spraying and laser remelting conditions.
2. Microstructure observation of laser remelted ceramic coatings shows deterioration of surface smoothness and connection between the coating and metal base. It concerns mainly coatings with a sub-layer and those which underwent chromoaluminizing. Less porosity in relation to the not-remelted state can be also observed, as density of remelted coatings increases.
3. Structure changes connected with laser remelting cause considerable increase of thermal conductivity of the coatings, depending on their kind, and thus they become less effective as thermal barriers.
4. Erosion examination showed that single and double layer ceramic coatings obtained by plasma spraying

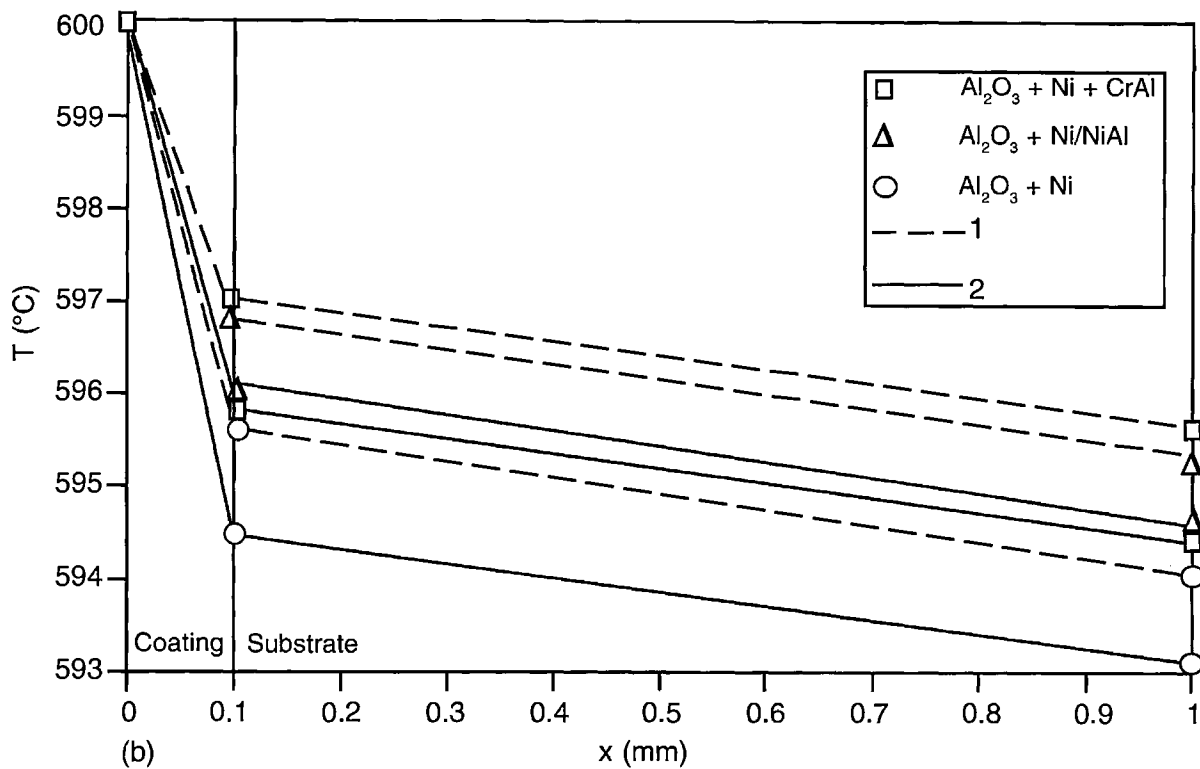
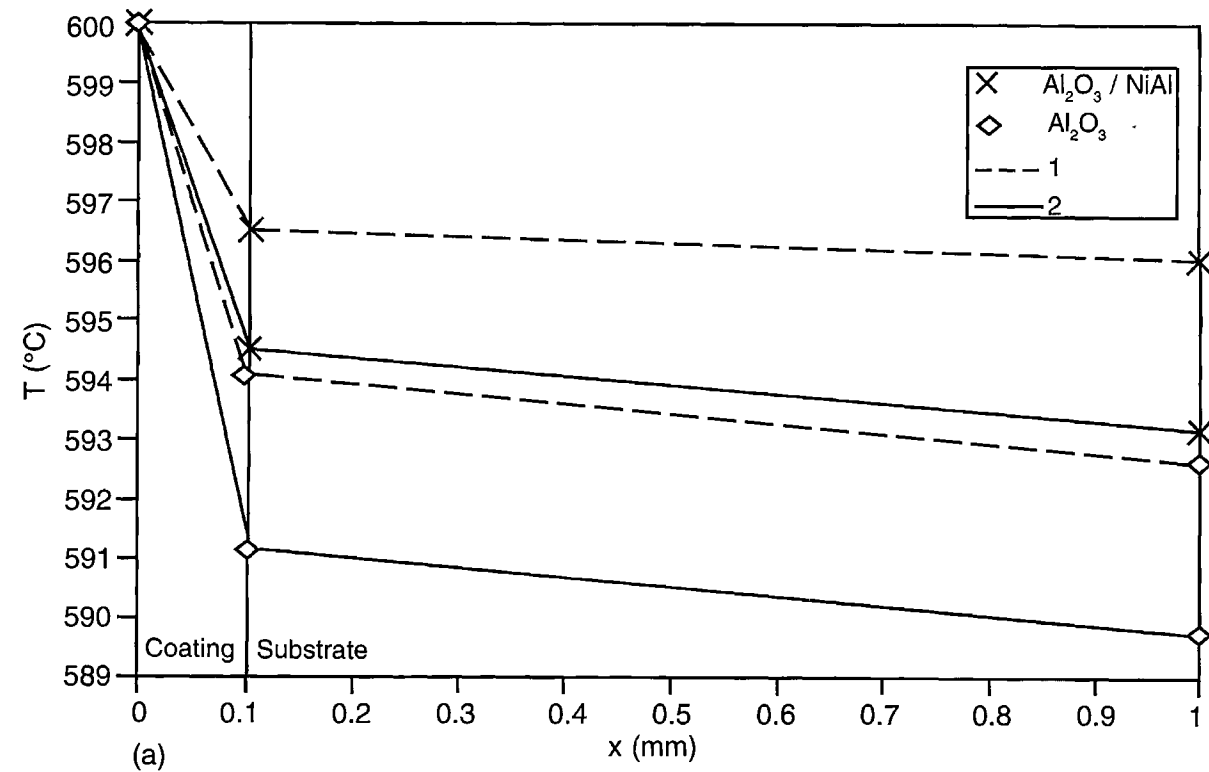


Fig. 8: Temperature changes of multi-phase structure surface as a function of thickness of plasma sprayed ceramic coatings (1) remelted and (2) not remelted, (a) Al_2O_3 and $\text{Al}_2\text{O}_3/\text{NiAl}$ and (b) $\text{Al}_2\text{O}_3 + \text{Ni}$, $\text{Al}_2\text{O}_3 + \text{Ni}/\text{NiAl}$ and $\text{Al}_2\text{O}_3 + \text{Ni} + \text{CrAl}$.

and laser remelting feature higher erosion resistance in the remelted state than after plasma spraying.

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