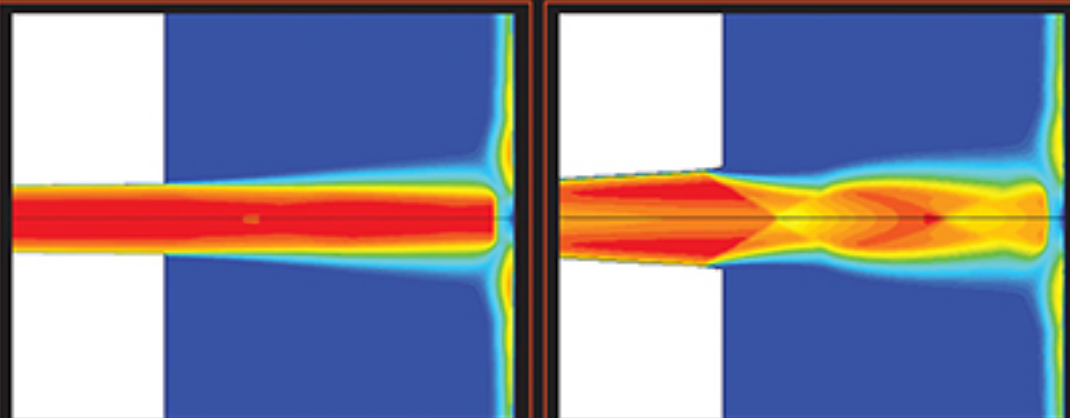


HIGH PRESSURE COLD SPRAY

PRINCIPLES AND APPLICATIONS



EDITED BY

C.M. KAY & J. KARTHIKEYAN

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Foreword

Cold Spray Technology Development at ASB Industries, Inc.

When I became a certified public accountant, the last thing on my mind was a career in manufacturing. However, when a client decided to sell ASB Industries in 1981, I could not resist the challenge; after all, I was quite familiar with the financial aspect of the operation. I bought the company, then modernized the plant and vowed to keep up with new technologies. The very next year, we bought a high-velocity oxygen fuel system, the first company in the United States to do so. ASB Industries was also the first to use natural gas, which is cheaper and safer than using high-pressure tanks. The compressor equipment may seem expensive, but natural gas is so much less expensive that we recovered the cost in just two years.

In February 1995, I read an article in the *NCTPC News* (National Center for Tooling and Precision Components) about Dr. Anatolii Papyrin, one of a group of Russian scientists who had developed cold spray in the mid-1980s at the Russian Academy of Sciences in Novosibirsk.

The article announced that Dr. Papyrin was to demonstrate the cold spray process in Toledo, OH. By that time, we were well acquainted with thermal spray but had never heard of cold spray. I wondered how it could work and if, in fact, it did work. To find out for myself, I went to the dem-

onstration in Toledo and watched as Dr. Papyrin sprayed cold copper particles onto a substrate. To my surprise, the particles had good adherence, and the coating had good properties. The technology appealed to us because of its potential to produce coatings that retained their original properties and also to use low-melting-point powders.

We could see that the process needed improvement in many areas, but we believed that it could ultimately produce high-quality coatings without flame and with less pollution at a reasonable cost.

At the time, Dr. Papyrin was under contract with the National Center for Manufacturing Sciences, but he joined ASB Industries in 1996 as a consultant, after his contract had ended. He did a great deal of development work on the technology for us but ultimately could not do everything himself.

By 1998, we needed help with nozzle development and controls. Dr. Christopher Berndt, who was at State University of New York at Stony Brook at the time, told us about Dr. Jeganathan Karthikeyan (“Karthi”), a young engineer who was working with him on nozzle development for plasma spray. Karthi had built nozzles for the thermal spray of liquids, had also developed various controls for temperature and pressure, and had worked on development of powder materials.

In addition to his experience, I soon learned that he was as enthusiastic as I was about the possibilities of cold spray technology. My vision was to develop the technology by improving nozzle design, controlling spray parameters, and improving coating materials. In Karthi, I was sure that we had found the dedicated engineer who could actually design and build the system. We hired him.

When Karthi first saw the system we had built, he began to realize the large nature of the project he had taken on. He told me that every component of the system had to be brought up to date. The nozzle was primitive, the temperature could be set but not controlled, the powder flow was erratic, and the pressure varied too much. In addition to the equipment, the powder particles had too much variability in size, shape, and chemistry. I told him he should do whatever was necessary. Little did I know that this was the beginning of a long and difficult journey but one that would ultimately become worth all the effort and expense.

To make our vision a reality, Karthi would need to develop a reliable system with controls and feedback loops. Such a system needed a specially designed nozzle, reliable temperature and pressure controls, a dependable powder-feed system, and powder feedstock that was consistent in chemistry, size, and shape. For the system to work, all these complex components had to work smoothly together. Despite these innumerable challenges, Karthi and ASB personnel set out to design and build all facets of the technology.

To have an idea of the challenges involved, here is a brief description of the process. In the cold spray system, powder is kept in the hopper, then fed through a hose into the nozzle. Conventional thermal spray processes

operate at 100 psi pressure, but in the first cold spray systems, the operating pressure was three times that, at 300 psi. Unfortunately, no powder feeder existed at that pressure. How could we proceed if this vital component did not exist?

We overcame that roadblock by working with a hopper manufacturer to develop a high-pressure powder-feed system, and we ended up with two different 300-psi powder feeders. In fact, today (2015) the cold spray systems operate at even higher pressures, up to 850 psi.

At the same time that we were discussing and deliberating over the high-pressure powder feeder, Karthi was busy inventing the first one-piece cold spray nozzle, for which we acquired a patent. He then installed temperature controllers, pressure regulators, flowmeters, feedback loops, and other controls. He and the ASB team built the rest of the system even as we waited for the first powder feeder to be delivered.

Then there was the fundamental problem with the Russian design. In the Russian system, the spray gun was mounted onto the large heater box. Carrier gas was heated in this large box and then entered the gun, where it was mixed with the powder and ejected through the nozzle onto the substrate. Because of this design, the substrate had to be moved across the nozzle, which remained stationary on the heavy box. Karthi and I agreed that this was not practical for spraying large surfaces and that we needed a flexible hose that could connect the heater with the gun, so that only the gun had to move. The hose would have to be made of materials that could withstand both high temperatures and high pressures yet be flexible enough to be easily manipulated by an operator.

Unfortunately, such hoses did not exist. Some were designed to function at high pressure but none at both high temperature and high pressure. Undaunted, we called on several hose manufacturers and told them what we needed: insulation to keep the heat in, strength for high pressure, and flexibility to allow ease of movement. They were ultimately successful in this development, and we then had an insulated hose 1 in. in diameter and flexible enough to spray large areas.

We also had to change the design of the gun, for which we received another patent. After two years of development, we thought we had made enough progress to announce the new technology at the 2000 International Thermal Spray Conference. I encouraged the audience to take on some research and design (R&D) projects, to join us in a vision of the future where everyone contributed to the success of the industry. I reasoned that if enough people took on R&D projects, the equipment and powders would improve and the number of applications would grow. However, to most of them the risks outweighed the potential benefits, and no one else was willing to take up the gauntlet.

Mark Smith of Sandia National Laboratories came to our plant and examined our system. We were happy to explain everything to him, and he went back to Sandia and built a system there.

We kept the vision, and in 2001 ASB Industries joined in a Cooperative Research and Development Agreement (CRADA) at Sandia National Laboratories that also included Pratt & Whitney, Alcoa, Ford Motor Company, Siemens Westinghouse Power Corporation, Praxair Surface Technologies, and Ktech Corporation.

This CRADA was formed to expedite the development and commercialization of cold spray technology for Sandia/ U.S. Department of Energy and the industrial partners. This collaboration allowed the partners and Sandia to pool technical expertise, funding, and other resources to jointly address some key issues related to process, equipment, and coating material characteristics. The work would provide Sandia and its partners with an improved fundamental understanding of the chemistry and physics of cold spray. This was an opportunity to jointly resolve critical technical and manufacturing challenges that needed to be addressed for successful commercialization.

Nozzle improvements were crucial to improving the economies of the cold spray process. The CRADA goals related to nozzle design were to produce the highest-possible particle velocity with the lowest-possible gas flow; greatly reduce helium use; minimize nozzle fouling with certain powders, such as aluminum; and acquire a more thorough understanding of nozzle modeling and particle velocity measurements.

To improve the quality of cold spray deposits, we needed to achieve a better understanding of the underlying process fundamentals. In other words, we needed a model that would allow us to predict coating properties from input parameters such as gas pressure and temperature. Work included determining critical velocities, investigating substrate-preparation effects, modeling deposit properties, establishing spray parameters and postspray treatments, and determining bonding mechanisms.

We contributed \$20,000 per year over the three-year span of the CRADA and were the smallest of the companies involved. We were willing to share what we had learned. During the program, Karthi improved a nozzle design that enabled the process to work much better.

The nozzle is the most important component in the system. It is where everything comes together: the process gas, the carrier gas, and the powder. It is sensitive to variations in particle size and shape and to temperature. When the temperature rose too high, sometimes particles would adhere to the sides and clog the nozzle. This was the problem Karthi tackled and solved by making the nozzle out of a polymer material. This new design and new material extended the life of the nozzle and allowed us to spray some high-melting-point materials that were not possible before.

Of course, this also increased the range of possible applications, which increased the potential for growth of the entire thermal spray industry! This has always been our vision.

It was at that point that research groups and companies from around the world began to take notice of us. They knew that we would be willing

partners, as I had never been reticent about expressing my belief that there should be no secrets. The way to grow the industry is to work continually to advance the technology. When that happens, applications will grow and the industry will grow, helping everyone in the business.

The Armed Forces University in Munich sent representatives to visit us. After learning all they could about our system, they returned home and built their own. The first commercially available cold spray system was built by the Germans, based on our system. Then the university initiated a program in which students joined researchers who were developing cold spray. Students learned the technology, and now they are engineers working in the field. All of this R&D work in Germany is now coming to fruition. Over the years, this university has developed knowledgeable and experienced engineers who are doing work with excellent results. In one widespread application, a company in Germany produces induction-heated pots and pans coated by cold spray with an iron-base material.

Today (2015), we work with students from various universities, such as Michigan State University and State University of New York at Stony Brook. They come for various amounts of time, from one week to six months. They learn about cold spray, the challenges involved with the technology, and the physics-based models we use to find answers.

We work with customers to develop new technologies, which they can then patent. Thus, new technology can get into the marketplace, even if it is in a limited way. Our approach is that our customers fund us to do research, then they patent it. Some share these patents with us, and others keep the patents within their companies. In that way, we can attract high-tech companies such as Pratt & Whitney, Exxon Mobil, Siemens, and others. We develop the expertise, then they get and use the patent.

For example, metal foams for insulation were developed by Exxon. A cold spray process was developed by Pratt & Whitney for refurbishment of a rocket engine chamber. BMW uses cold spray for battery components in hybrid engines. Around the globe, cold spray has found many applications, but in this country, although there are some applications, they are secret. We need an open, mass-produced application. When cold spray becomes accepted as a standard coating method, I am convinced that the scope of its applications will rapidly expand.

What could these be? Well, for one thing, three-dimensional manufacturing. The future is going to be in additive manufacturing. At the 2014 AeroMat Conference, many presentations focused on additive manufacturing. Cold spray is ideal for this technology, because the powders retain their original microstructure.

As our experience at ASB Industries has shown, a vision that is based on R&D and the future can enable progress across the industry and, indeed, across the world. We invite the readers of this book to join us.

Albert Kay
ASB Industries

Preface

Cold spray refers to a material-deposition technique that uses a supersonic particle jet. In the high-pressure cold spray (HPCS) process, gas and powder are mixed upstream and expanded via de Laval nozzle to produce a supersonic particle jet, which produces coatings based on a wide selection of materials with superior characteristics and high deposition efficiency. Although some systems (low-pressure cold spray) use subsonic particles laden with a peening agent to process ductile materials with acceptable properties, these systems are not covered in this book.

In a short span of approximately 20 to 25 years, cold spray has moved from a scientific curiosity carried out in a few research establishments to an established and integral manufacturing process, adopted in multiple high-tech industries. Homemade spray systems have been replaced with a selection of vendor-supplied commercial systems. Special powders with specific characteristics, required for cold spray processing, are readily available.

Around the globe, scientists and engineers have taken up both basic and application research and development (R&D) activities in universities, national laboratories, and industries. These activities have resulted in advancements in all aspects of the technology, including basic science of gas/particle interaction, particle impact and coating generation, parameters/processing/properties relationships, and performance of coatings in various industrial environments. These advancements have led to a multitude of applications, from protective and performance-enhancing layers to repair and refurbishing of parts to fabrication of components by near-net shaping or additive manufacturing techniques. The number of industries adapting to cold spray technology is growing rapidly, from automobile to aerospace to turbine and power to defense to sputter targets and others.

Enormous growth in R&D activities has led to a huge databank in the form of publications in peer-reviewed journals and conference proceedings. However, consolidated information on all aspects of cold spray technology in book form is hard to find. This book covers the need for

consolidated information, with focus on applications in specific industries. Experts around the globe have contributed in their specific areas of specialties.

The basic science and modeling of the cold spray process are discussed in the first few chapters, which are followed by details of equipment and powder supply. The second half of the book concentrates on cold spray applications in various industries. Experts from each industry have written about applications in their specific industries.

We have tried to eliminate repetition of specific applications in multiple chapters. However, some applications present themselves in many industries. For instance, the defense, aerospace, and power-generation industries require repair/refurbishment of turbine components and are treated by industry experts in their respective chapters from their perspectives.

We offer our deepest thanks to all those who have contributed to this publication. The time, effort, and professionalism represented by the commitment to authoring these chapters is the culmination of relationships developed out of a shared passion for cold spray technology—relationships built at airports and conferences, via emails, in hotel lobbies, and through many joint development initiatives. It is both a professional and personal honor for us to work with those who are held in the highest regard for their expertise, sincerity, and time to contribute.

The reader will find this book a useful assembly of information. The substantial information provided by the authors will serve as a resource that may lead the reader in many directions, both in the principles of HPCS and in applications in which the unique properties of cold spray have developed by providing both exceptional surfacing solutions and additive manufacturing applications.

Our authors have focused on cold spray, a field in which their work has reached all corners of the world as a result of their knowledge and working relationships. Included within these chapters are references showing a cross section of true scientific research, from materials development to practical applications.

We acknowledge that these authors, in making their contributions to this book, have spent substantial amounts of time persevering in the task of documenting their knowledge. We believe the chapters contained within this book will easily demonstrate the truth of our acknowledgment and greatly add to the reader's knowledge of cold spray.

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Charles Kay is currently vice president of ASB Industries, Barberton, Ohio, and has been with ASB for over 29 years. ASB focuses on expanding the reach of thermal spray technology in new areas. Charles specializes in identifying new application areas in various industries such as steel, paper, power, etc. He has co-authored many technical articles on cold spray technology that have been published in various peer-reviewed journals and conference proceedings. He has served as president of the ASM Thermal Spray Society and is an active member of various ASM Thermal Spray Society committees.



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J. Karthikeyan, director of research and development at ASB Industries, earned his Ph.D. from Bombay University, India, and specializes in thermal spray and advanced material processing technology. He is one of the pioneers of cold spray technology and has carried out R&D on almost all aspects of the technology, from design and development of nozzles, guns and systems to engineered coatings for specific industries. He has authored over 100 publications, mostly in peer-reviewed jour-



nals. During the last 15 years, he has been leading industrial cold spray R&D and has authored over 50 peer-reviewed papers, contributed to *ASM Handbook*, Volume 5A, *Thermal Spray Technology*, and holds six patents in various aspects of cold spray technology.

He served as the conference chairman of ASM-sponsored Cold Spray 2004, Cold Spray 2007 and Cold Spray 2010 meetings in Akron, Ohio. He also organizes special symposiums on cold spray technology at international thermal spray conferences every year. He is a Fellow of ASM International and has served as a member of the ASM Thermal Spray Society Board (2008-11). He is a member of the International Board of Review of many prestigious journals such as *Journal of Thermal Spray Technology*.

CHAPTER 1

Introduction to Cold Spray

M.F. Smith, Sandia National Laboratories*

COLD SPRAY IS A PROCESS TECHNOLOGY that, for the first time, enables the rapid deposition of a wide range of metals and some other materials in the solid state at temperatures far below their melting points. It is fair to say that cold spray is a revolutionary technology. Before cold spray, in order to deposit metal coatings it was necessary to either dissolve the metals in a chemical bath (plating), melt them (thermal spray coating), or vaporize them (vapor deposition). Now, under the proper conditions, metals can be rapidly deposited in the solid state, and thus, undesirable changes are avoided in chemistry or phase composition commonly associated with the other deposition technologies just listed.

There are two major categories of cold spray process technologies, commonly referred to as high-pressure cold spray (HPCS) and low-pressure cold spray (LPCS). The LPCS process is not discussed in this book, but its differences from HPCS are briefly explained later in this chapter. Throughout the rest of this book, including the remainder of this chapter, the term *cold spray* will refer specifically to HPCS unless otherwise stated.

In the HPCS process (Fig. 1.1), small solid particles in the range of 5 to 100 μm in diameter are accelerated in a supersonic jet of heated gas to high velocities, typically on the order of 300 to 1200 m/s (1000 to 4000

*Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

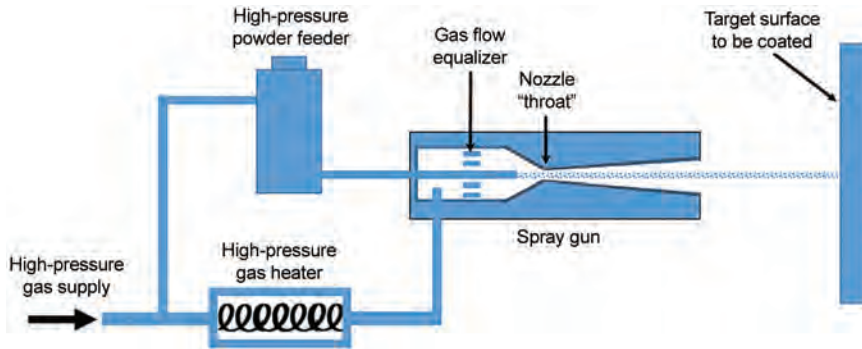


Fig. 1.1 The high-pressure cold spray process uses a high-pressure gas heater and a high-pressure powder feeder to inject the spray powder upstream of the nozzle throat. This provides the very high particle velocities that enable this process to deposit a wide range of metals and some other materials.

ft/s), and then sprayed onto a hard substrate surface; for example, a metal, ceramic, or glass. If the velocity is high enough and the material combination is suitable for the process, upon impact the particles undergo adiabatic heating and plastically deform at very high shear rates, causing them to flatten out and bond to the underlying surface (Ref 1.1, 1.2). This bonding mechanism is very similar to the adiabatic shear instability found in explosive welding; but, in this case, it occurs on a microscale.

The astute reader will note that the process gas in Fig. 1.1 is heated, yet the process is called “cold spray”. As is explained in more detail later in this chapter, the process gas is initially heated to increase the flow velocity of the gas in the spray nozzle and thus increase spray particle velocities. Although the gas may start out at moderately high temperatures, it cools very rapidly as it expands in the long diverging section of the spray gun nozzle, and the spray particle temperatures therefore remain well below the melting point. So, compared to conventional thermal spray, where the spray particles are melted or nearly melted during the deposition process, this is a comparatively low temperature spray process technology hence, the name *cold spray*.

As in explosive welding, to achieve good bonding in cold spray the impact velocity of the spray particles must exceed a critical minimum to produce a hydrodynamic shear instability at the bond interface that is essential for good bonding. If the impact velocity is too low, the particles will simply rebound and abrade the surface, much as in conventional sand blasting, or possibly some particles may become physically embedded in the surface, but without substantially deforming the surface or firmly bonding to it. In cold spray, the minimum impact velocity necessary to achieve the hydrodynamic shear instability is termed the critical velocity (V_{crit}). The deposition efficiency (i.e., the mass of material actually deposited as compared to the mass of material sprayed onto the surface) in-

creases dramatically as the average particle velocity moves beyond V_{crit} . The critical velocity varies significantly for different materials, and other factors, such as spray particle temperature, substrate temperature, and particle size, can also influence it.

In HPCS, the accelerating gas jet is created by passing high-pressure gas, typically in the range of 1 to 5 MPa (145 to 725 psi), through a converging-diverging nozzle (de Laval nozzle) to achieve supersonic flow. The diagram in Fig. 1.2 illustrates changes in gas pressure, flow velocity, and temperature in a converging-diverging nozzle. The small-diameter region of the nozzle that separates the converging and diverging sections, often called the nozzle throat, is a critical element of the nozzle geometry. If the pressure drop from the upstream end of the nozzle throat to its downstream end is at or above a critical minimum, the gas in that region will flow at exactly the local speed of sound, that is, sonic or Mach 1 flow. As the gas then expands in the subsequent diverging section of the nozzle, the gas density decreases and it cools and accelerates to supersonic velocity. To achieve the highest spray particle velocities, the solid particles are injected upstream of the nozzle throat, passing through both the sonic and supersonic sections of the nozzle. A diagram of an HPCS nozzle and calculated gas and particle velocities is shown in Fig. 1.3.

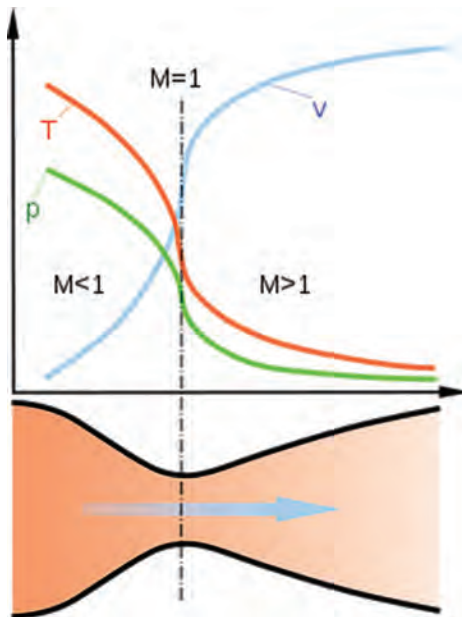


Fig. 1.2 Notional diagram illustrating changes in gas velocity, temperature, and pressure flowing through a converging-diverging (de Laval) nozzle. If the pressure decrease across the narrow throat of the nozzle is above a critical minimum, the flow velocity in the diverging section of the nozzle becomes supersonic (Mach > 1), and the gas temperature drops as the flow velocity increases.

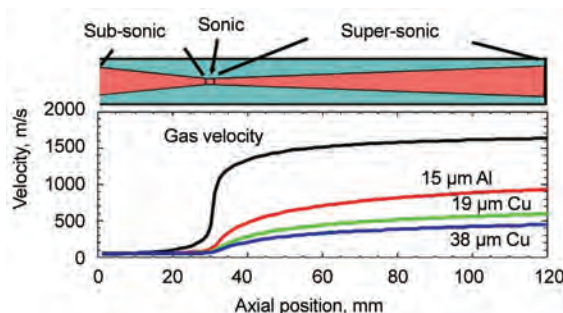


Fig. 1.3 Calculated gas and particle velocities in the converging (sub-sonic), throat (sonic), and diverging (supersonic) regions of a high-pressure cold spray nozzle. All particle velocities remain substantially lower than the gas velocity, but smaller (19 vs. 38 μm copper) and lighter (aluminum is lighter than copper) particles achieve comparatively higher velocities.

The sonic velocity in the nozzle throat and the resulting spray particle velocities are strongly dependent on the composition and temperature of the process gas supplied to the accelerating nozzle (Ref 1.3). Low-molecular-weight gases, such as helium, generally produce higher gas and particle velocities, and for this reason, most of the early cold spray systems operated primarily with pure helium or sometimes with mixtures of helium and nitrogen or helium and air. However, the high cost of helium and its limited availability in some regions of the world were a significant barrier for many potential cold spray applications.

Preheating the high-pressure process gas as it is fed into the system increases the sonic velocity in the nozzle throat, and higher particle velocities can therefore be achieved by preheating the gas. Systems were soon developed that used less expensive, readily available nitrogen gas preheated to increase the particle velocities. Today, gas temperatures in such systems can range up to 1100 °C (2010 °F or 1373 K). Despite the relatively high supply gas temperatures available in such systems, the gas does cool significantly as it expands in the diverging region of the nozzle. Therefore, the spray particles are exposed to high temperatures only for a relatively short time and still remain well below their melting point. Nevertheless, some heating of the spray particles can occur at relatively high gas temperatures. This particle heating may actually be beneficial, because it tends to depress the critical velocity and thus enhance deposition efficiency. However, if the particles are heated too much, there is a risk of causing some oxidation of the metal if the spraying takes place in an ambient air environment. Operating at relatively high gas temperatures, where there is some heating of the spray particles, is sometimes referred to as “warm spray”, although this term is not rigorously defined at present.

The LPCS process (Fig. 1.4) shares many features in common with the HPCS process just described, with a few subtle but very important differ-

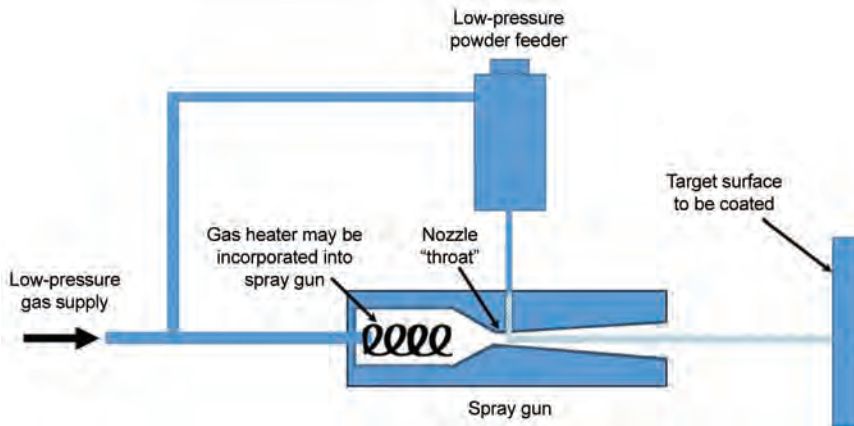


Fig. 1.4 The low-pressure cold spray process uses a low-pressure powder feeder to inject the spray powder downstream of the nozzle throat, directly into the supersonic diverging section of the nozzle. The system is lighter and less expensive but more limited in materials.

ences. In LPCS, compressed air or nitrogen at comparatively lower pressures, typically on the order of 0.5 to 1.0 MPa (75 to 140 psi) is preheated to temperatures ranging up to 550 °C (1022 °F or 823 K), then forced through a converging-diverging nozzle and accelerated to velocities ranging up to approximately 600 m/s (2000 ft/s). The smaller and lighter electric gas heaters in LPCS systems are frequently incorporated into a handheld spray gun assembly.

In contrast to HPCS, in the LPCS process the powder feedstock is introduced downstream of the nozzle throat directly into the supersonic diverging section of the nozzle. Injecting the powder downstream of the nozzle throat greatly reduces the complexity and cost of the powder-feeding equipment because the gas pressures in this region are much lower. However, a natural consequence of injecting the particles downstream of the nozzle throat and of using moderately heated compressed air or nitrogen as the working gas is that the maximum achievable particle velocities in such systems are lower. This means that the range of materials that can be deposited with LPCS is more limited. Nevertheless, these systems offer the advantages of compact size and portability as well as lower purchase and operating costs. This makes them well suited for applications such as spraying zinc- or aluminum-base anticorrosion coatings onto steel, for example, in repair shops or in the field. The development of special composite metal/ceramic powders for use in such systems has also expanded the range of materials that can be successfully deposited.

Cold Spray versus Thermal Spray. Compared to common thermal spray coating methods, some potential advantages of cold spray include less substrate heating, compressive residual stresses in the spray-deposited

material (which enables very thick deposits, ranging up to many centimeters), no heat-related chemistry or phase changes in the sprayed material, and, in most cases, little or no oxidation of the deposited material, even when sprayed in an ambient air environment. On the other hand, the range of materials that can be deposited and the range of suitable substrate materials are more limited with cold spray than with thermal spray. Cold spray works best with relatively ductile metals and with composite materials that include ductile metals, for example, cermets with a ductile metal matrix. It is less well suited to brittle metal alloys or pure ceramics; however, as noted later in this chapter, in recent years there has been some success with cold spray deposition of extremely fine ceramic powders. Cold spray also requires a substrate surface that is hard enough to deform the incoming solid particles. For example, attempts to cold spray metal directly onto a relatively soft substrate, for example, a plastic or a fiber-reinforced composite, will most likely result in significant damage to the substrate because the substrate is simply not strong enough to withstand the impact of the high-velocity metal particles.

Each thermal spray process and each cold spray process has its own unique advantages and limitations. There is no one “best” process for all applications, and it is better to think of the various processes as different tools for different jobs. For those unfamiliar with the many different spray deposition technologies and their respective advantages and limitations, it is highly recommended that expert advice be sought when considering a potential new coating application. Success or failure of a given application depends strongly on selecting the correct spray deposition process.

1.1 Early History of Cold Spray

Although it is widely accepted that the cold spray process as we know it today began with research done in Russia in the 1980s, there are a few interesting patents that employed some of the individual elements that were later combined in our modern cold spray systems. None of these early efforts led to any significant commercial success, probably because they were limited to spraying only relatively soft, highly ductile metals.

More than 100 years ago, in August 1902, Samuel H. Thurston was granted U.S. Patent 706,701, entitled “Method of Impacting One Metal on Another” (Fig. 1.5). The process description in this patent refers to “metal particles driven by pneumatic pressure against the surface to be coated with such force as to embed the metal of the said particles into the surface of the metal against which they are driven and incorporate the two together, thus forming a stable and efficient metal coating.” This concept is similar to modern cold spray, but the information in the patent indicates that the working gas was unheated compressed air and that there was no converging-diverging nozzle, two factors that would have severely restricted the achievable particle velocities. So, this process was undoubt-

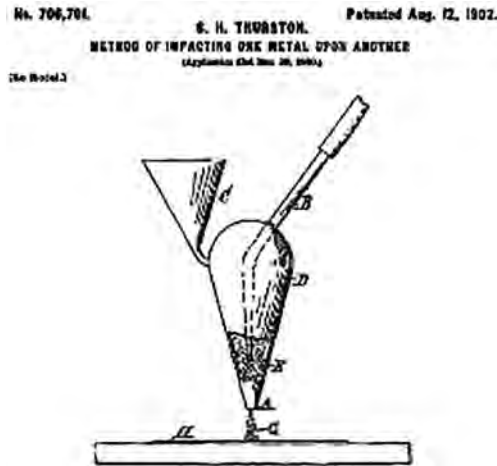


Fig. 1.5 Thurston patent, “Method of Impacting One Metal on Another,” 1902

edly limited to relatively soft, highly ductile metals. Indeed, in the patent Thurston notes, “The metals I have so far employed for this purpose are copper and aluminium as a coating upon iron and steel.”

The Swiss inventor Max Schoop, widely recognized as the founding father of modern thermal spray technology, also filed an early patent somewhat similar to Thurston’s patent. In U.S. Patent 1,128,059, issued in February 1915, Claim 1 describes “the process of producing coherent metallic coatings, which consist of projecting finely-divided, unmolten metal and metal oxide onto a surface to be coated with sufficient force to form a non-porous, homogeneous coating on said surface” (Fig. 1.6). The Schoop patent describes particle heating and flow upon impact due to kinetic energy. More importantly, it adds new features not found in Thurston’s patent, such as heating the gas in the spray device as well as preheating the particles somewhat to improve deposition. However, Schoop apparently did not employ a converging-diverging nozzle. Therefore, the particle velocities that Schoop could achieve would again limit this process to the softer, more ductile metals. Indeed, this patent mostly discusses metals such as lead-tin alloys, aluminum, and copper.

Several decades later, in 1963, yet another U.S. Patent, 3,100,724, was issued to Charles Rocheville. In this patent, a supersonic nozzle is described for the first time. Indeed, Rocheville used a somewhat complex sequential pair of converging-diverging nozzles to accelerate solid particles in his spray device (Fig. 1.7). Although the supersonic nozzle design was undoubtedly a step forward, Rocheville used unheated compressed air as his working gas, which would again limit the maximum particle velocities that he could achieve. His patent discusses only relatively thin metal coatings and states, in part, that the outcome of the process is “to



Fig. 1.6 Schoop patent, “Method of Plating or Coating with Metallic Coatings,” 1915

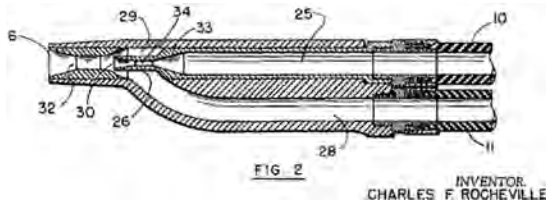


Fig. 1.7 Rocheville patent, “Device for Treating the Surface of a Workpiece,” 1963

cause said materials to adhere in the pores of the part, and in some instances to fuse thereon.” Once again, even with this relatively elaborate nozzle system, some of the key elements that have led to success in modern cold spray systems were missing.

Although these early patents certainly set the stage for the modern cold spray process, they failed to achieve widespread acceptance and impact, most likely because of the limitations already described. It would be another couple of decades before researchers, who did not initially set out to develop a coating process, inadvertently discovered what has now become the commercially successful cold spray technology that we use today.

The origin of our modern cold spray process is generally attributed to researchers working at the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences in Novosibirsk, Siberia, in the mid-1980s. The research team in Novosibirsk was conducting supersonic wind tunnel experiments, studying gas flow around solid models of various shapes. To help visualize the flow around the models, the flow stream was seeded with small metal particles that could be tracked with laser diagnostics. The researchers observed that as the flow velocity was progressively increased, there was a dramatic change in the interaction of the particles with the solid models. At lower impact velocities, the particles abraded the surface of the models, bouncing off and pitting the surface in a manner similar to sand blasting, and, in some cases, particles also became embedded in the surface, similar to the results of some of the early patents (Fig. 1.8a). However, as the flow velocity in-

creased beyond a certain point, which is now called the critical velocity, the particles began to adhere to the surface of the model and rapidly build up a coating (Fig. 1.8b). Others may well have observed this phenomenon in prior wind tunnel studies, but these researchers realized its potential as an important new coating technology and dubbed it the “cold gas dynamic spray method” (Ref 1.4). The U.S. Patent 5,302,414 for this process was eventually issued to Anatolii Alkimov, Anatolii Papyrin, Vladimir Kosarev, Nikolai Nesterovich, and Mikhail Shushpanov in 1994, followed quickly by a European patent in 1995.

The original Russian academy team completed a considerable amount of process development work before the process started to take hold outside of Russia. Figure 1.9 shows a very early prototype “gas dynamic spray method” coating system that combined for the first time all of the essential elements that enabled them to successfully deposit a much wider range of metals. Specifically, their new system employed heated process gas, a supersonic converging-diverging nozzle, and lower-molecular-weight gas, such as pure helium or helium mixed with nitrogen or air. This early cold spray system was used to successfully deposit a wide range of pure metals, metal alloys, and even some composite materials. It was also used to complete some early experimental work to better understand the fundamental science of the process. Figure 1.10 shows some early experimental results illustrating that deposition efficiency (DE) increases rapidly as the average particle velocity moves beyond the critical velocity. The “S” shape of the DE curves in Fig. 1.10 is related to the particle size distribution of the spray powder. As the flow velocities increase, smaller powder particles at the low end of the powder size distribution reach the critical velocity first and begin to deposit, forming the bottom curve of the “S” in the DE plot. As the gas flow velocity is further increased, progressively larger particles in the feedstock powder reach critical velocity and, because most of the powder particles fall somewhere toward the middle of the size distribution, the DE now rises quickly, creating the steeper middle part of the “S.” Finally, the flow velocity becomes high enough that the larger particles at the high end of the powder size distribution begin to deposit, completing the top of the “S” in the DE-versus-flow-velocity plot.

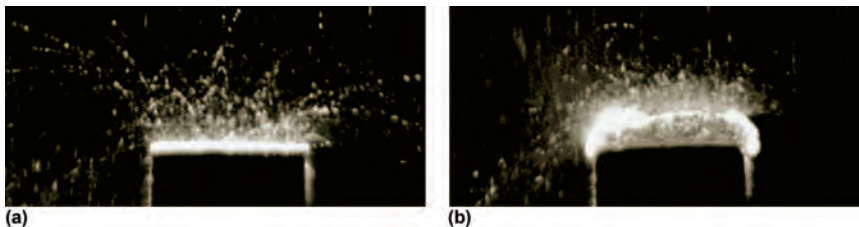


Fig. 1.8 Early Russian wind tunnel experiments show that (a) at 250 m/s (820 ft/s) impact velocity, the copper particles entrained in the flow rebound and do not adhere, but (b) at 900 m/s (2950 ft/s), a coating is rapidly built up. Courtesy of Anatolii Papyrin

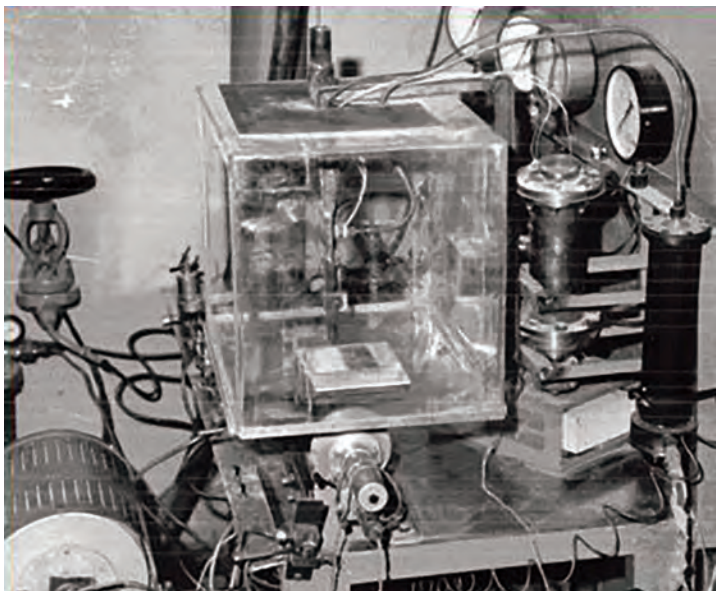


Fig. 1.9 Early Russian cold gas dynamic spray system used to deposit a wide range of metals and some ceramic-metal composites. Courtesy of Anatolii Papyrin

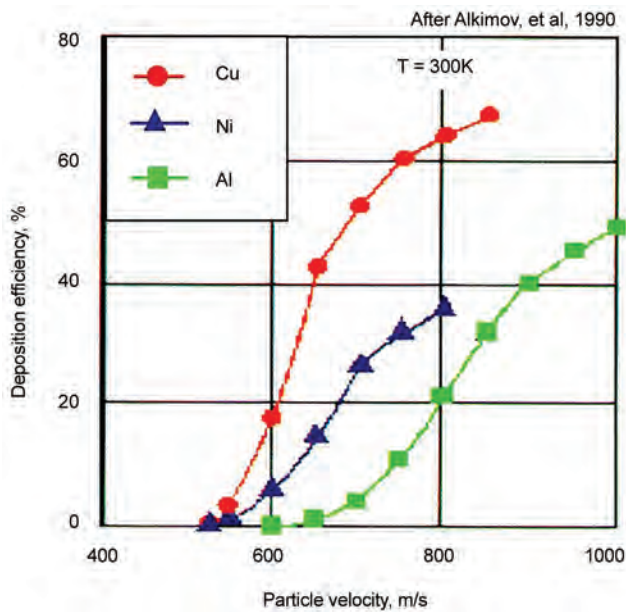


Fig. 1.10 Early Russian experimental results show that deposition efficiency increases dramatically above a given velocity and that this critical velocity varies for different materials. For example, in this plot the critical velocity for aluminum is higher than that for nickel or copper. Source: Ref 1.4

Figure 1.10 also shows that the critical velocity varies somewhat for different metals. In addition to these process studies, the early Russian investigators also explored some potential commercial applications for cold spray, such as building a pilot-scale cold spray system to deposit anticorrosion coatings onto steel pipe.

1.2 Growing International Interest in Cold Spray

In the summer of 1993, Dr. Robert McCune, a researcher at Ford Motor Company in Dearborn, MI, became aware of the Russian cold gas dynamic spray technology as a result of a visit to the former Soviet Union by a group of technologists from CMI, a Michigan metal casting company originally called Cadillac Malleable Iron. The CMI team, including company founder Ray Witt, brought back film footage of a high-velocity deposition process showing rapid metal deposition without melting the spray particles. After some investigation, McCune learned that Dr. Anatolii Papyrin, one of the principal researchers of this technology, was to visit the United States in 1994 as part of a delegation from Russia. Arrangements were made for Dr. Papyrin to come to Ford Motor Company to make a presentation explaining this process to a multicompany thermal spray coating group operating under the auspices of the National Center for Manufacturing Sciences (NCMS), located in Ann Arbor, MI. Members of this NCMS coating group included Ford Motor Company, General Motors Corporation, Pratt and Whitney Division of United Technologies Corporation, General Electric Aircraft Engines, Tubalcain Company, and Flame Spray Industries.

In 1994, the NCMS group began supporting Dr. Papyrin to conduct a cold spray demonstration project at the University of Toledo. There, Papyrin set up the first cold spray system in the United States and conducted the first cold spray research in the United States, creating several early technical reports on the process. These reports included one of the first English-language open-literature publications on the cold spray process, which was presented at the Eighth National Thermal Spray Conference in September 1995 (Ref 1.5). It was at this conference that Dr. McCune first presented a temperature-versus-velocity plot comparing cold spray to various thermal spray processes (Fig. 1.11). Over the years, the origin of that plot was somehow lost, but McCune's comparative plot has since been reproduced in various forms in numerous books, articles, and presentations about cold spray. The NCMS group also established a second U.S. cold spray research system at the General Motors Technology Center in Warren, MI. A General Motors' research team continued to pursue cold spray research with this system even after the formal NCMS cold spray effort ended in 1997.

While Anatolii Papyrin was working with NCMS, he issued the first U.S. license for the cold spray process to ASB Industries (Barberton, OH),

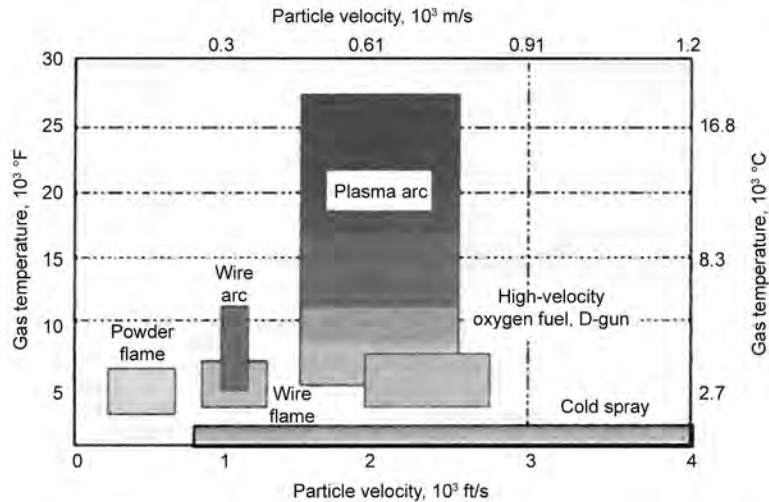


Fig. 1.11 Temperature-versus-velocity plot comparing cold spray with traditional thermal spray process technologies. Source: Ref 1.5

which operates a large thermal spray coating and finishing facility. Al Kay, President of ASB, was an early adopter and strong proponent of cold spray. He soon hired Dr. Jeganathan “Karthi” Karthikeyan, to begin a vigorous research and development (R&D) effort on cold spray. When the NCMS program concluded in 1997, Dr. Papyrin spent a brief period of time working with ASB Industries before taking a position at the Applied Research Laboratory of the Pennsylvania State University, to assist with building a cold spray program there.

At approximately the same time, another Russian research group was developing LPCS. This group founded the Obninsk Center for Powder Spraying in Russia in 1992 and developed a “low-pressure gas dynamic spray process,” later trade named Dymet. This low-pressure technology flowed into North America in the mid-1990s via researchers at the University of Windsor in Ontario, Canada, led by Roman Maev and Emil Strumban. A Canadian company, CenterLine Windsor Ltd. started specializing in this low-pressure technology, and they subsequently hired Dr. Julio Villafuerte to further develop and refine the technology. The result has been a great commercial success, and CenterLine has developed many customers for its portable, cabinet, and robotic spray systems in industries such as automotive, mass transit, aerospace, and defense.

The original HPCS effort at NCMS led to other U.S. interests in this emerging technology. Dr. Mark Smith, a thermal spray researcher at Sandia National Laboratories, had served as a technical advisor to the NCMS coating group in the mid-1990s and became intrigued with the cold spray process. Sandia is a U.S. Department of Energy National Laboratory that

has a large Thermal Spray Research Laboratory (TSRL) located in Albuquerque, NM. Dr. Smith and his colleague, Dr. Richard Neiser, started an internally funded cold spray R&D effort at Sandia's TSRL in 1997. With guidance from Papyrin, the Sandia research team designed and built its own heavily instrumented cold spray system. They also teamed with Sandia gas-dynamics experts, including Dr. Ronald Dykhuizen, to carry out the first gas-dynamics studies of the process in the United States, resulting in a widely cited paper, "Gas Dynamic Principles of Cold Spray," published by Dykhuizen and Smith in 1998 (Ref 1.3). Interestingly, in addition to process R&D, the Sandia system was also used early on for a time-critical repair of a Sandia metal component that was to fly on an earth-orbiting satellite. This is believed to be the first cold-sprayed item to be launched into space (Fig. 1.12).

Interest in cold spray technology began to grow very rapidly in the late 1990s. An impromptu cold spray panel discussion organized by Dr. Smith at the 2000 International Thermal Spray Conference in Montreal, Canada, drew a large international audience, quickly overflowing the meeting room. By this time, researchers in Europe were also becoming very active in cold spray R&D, and interest in the process was beginning to emerge in Asia as well.

In 2000, when the internally funded Sandia R&D effort was completed, Dr. Smith formed a consortium of interested companies, including some of the former NCMS partners, to continue precompetitive development of cold spray technology. The member companies in the Sandia consortium were Alcoa Aluminum Company, ASB Industries, Daimler Chrysler, Ford

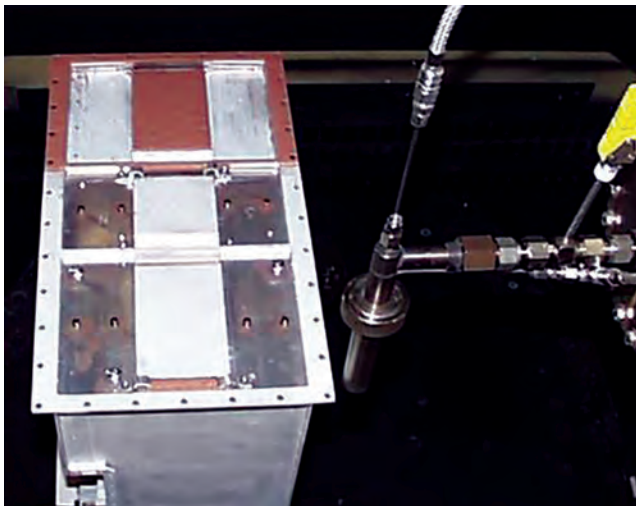


Fig. 1.12 Early cold spray repair of a Sandia satellite housing. Out-of-tolerance surface was built up with cold spray and then remachined to meet specifications. This is believed to be the first cold-sprayed part to be launched into space. Courtesy of Sandia National Laboratories

Motor Company, Jacobs Chuck Manufacturing Company, Ktech Corporation, Pratt & Whitney Division of United Technologies Corporation, Praxair, and Siemens Westinghouse. During the course of this consortium, which ran until 2003, Dr. Papyrin left Pennsylvania State University and began working at Ktech Corporation, a Sandia consortium member company located in Albuquerque, NM. While at Ktech, Dr. Papyrin spent significant time working with the cold spray research team at the Sandia TSRL, supporting consortium cold spray R&D. The Sandia consortium research included experimental and computational modeling studies of the process as well as investigations of materials properties and bonding mechanisms, process economics (including an experimental helium recycling system provided by Praxair), and the development of process improvements to resolve early production-readiness issues, such as rapid nozzle fouling when spraying aluminum. Numerous technical papers were published as a result of this early, precompetitive R&D.

From the early 2000s on, interest and activity in cold spray technology grew at a very rapid pace. For example, a cold spray symposium held in Albuquerque, NM, in 2002 attracted 75 participants, of which 15 were from foreign countries (Ref 1.6), while a follow-on cold spray symposium held in Akron, OH, in 2004 attracted 151 participants from 14 countries (Ref 1.7), double the number of participants compared to just two years earlier. While a full accounting of activities from this time forward is beyond the scope of this early history overview, there are a few noteworthy post-2000 highlights that deserve brief mention.

In 2000, a cooperative effort including German partners The Linde Group (Linde AG), CRP Automationstechnik AG, and Germany's University of the Federal Armed Forces along with ASB Industries Inc. in the United States began a substantial joint industry/university cold spray effort. In a relatively short time, a newly founded German company, Cold Gas Technology GmbH (CGT), working in close cooperation with these partnering organizations, developed and began to market commercial-duty, production-ready systems for cold spray, with ASB Industries as its sole U.S. distributor.

By the end of 2002, the first commercially produced automotive components, copper coatings cold sprayed onto aluminum heat sinks, began to be manufactured. In 2003 and again in 2006, the research group at the University of the Federal Armed Forces (UFAF), located in Hamburg, Germany, and under the leadership of Professor Heinrich Kreye, published a couple of landmark papers on the hydrodynamic instability in cold spray and its relationship to the critical velocity and associated process parameters (Ref 1.1, 1.2). The ready availability of commercial-grade spray systems from CGT, combined with an enhanced understanding of the process and its optimization provided by the UFAF research, laid an important foundation for further growth and commercialization of HPCS technology.

Beginning in approximately 2006, researchers in Japan began to publish papers describing successful cold spray deposition of extremely fine ceramic powders (Ref 1.8). Because of the nature of the cold spray process, up to that time it had generally been accepted that cold spray was not suitable for the deposition of brittle materials, such as ceramics. However, when ultrafine ceramic powder particles were used, success was achieved, although the bonding mechanism for ceramics is thought to be somewhat different compared to metals (Ref 1.9). The capability to cold spray ceramics could open the door for important new commercial applications.

In 2007, the U.S. Army Research Laboratory established the Center for Cold Spray Research and Development under the direction of Victor Champagne at its Aberdeen Proving Ground in Maryland. Working jointly with United Technologies Research Center, a cold spray repair process was soon developed to reclaim millions of dollars worth of corroded and worn magnesium gearbox housings for UH-60 Black Hawk helicopters and other military hardware.

Magnesium gearbox housings are very lightweight, but they are also highly susceptible to fretting wear and corrosion, especially in marine environments, resulting in significant unscheduled maintenance costs and high replacement costs, ranging up to more than \$800,000 per unit. The Army and Navy reportedly spent \$17 million in one year for UH-60 main transmission and tail rotor gearbox housing assemblies, so the capability to repair and reclaim many of these damaged housings using cold spray represented a major economic benefit for the U.S. military. In 2008, the U.S. Department of Defense issued military specification MIL-STD-3012, “Cold Spray Manufacturing Process Standard,” to support the use of cold spray for defense applications.

From early efforts to spray deposit solid particles more than 100 years ago, cold spray technology has continued to evolve and improve. Although still not as widely used as most commercial thermal spray technologies, commercial applications and use of cold spray are increasing. Today, the range of equipment and applications for HPCS continues to expand. An example includes the relatively recent development of a high-pressure, portable, handheld system that is part of an emerging line of U.S.-built commercial cold spray equipment being designed and marketed by ASB Industries. No doubt, further technology developments will appear in the years to come as researchers and commercial users worldwide continue to refine and improve cold spray technology for an ever-expanding range of applications.

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CHAPTER 2

Process Science of Cold Spray

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IN HIGH-PRESSURE COLD SPRAYING, or kinetic spraying, generally powder particles accelerate in a supersonic gas stream and deposit on surfaces to produce dense coatings or bulk parts. The basic mechanism for adherence of metallic particles is their plastic deformation upon impact, which creates sufficient heat for solid-state welding. Consequently, a metallurgical bond forms between particle and substrate. Interestingly, high-strength metal alloys and hard-phase composites have also been successfully built up as coatings by cold spraying, and even the deposition of ceramic phases has been reported. The interdisciplinary science behind cold spraying includes topics from fluid dynamics, high-strain-rate mechanics, materials science, and engineering. In this chapter, materials science is primarily considered. This chapter reviews the current understanding of kinetic spraying for different materials, covering widely accepted general mechanisms for particle deposition and the processes and parameters involved. For more complex deformation and interaction of some engineering alloys and dissimilar materials, particular mechanisms are also discussed, some of which are still under investigation in current research.

First the mechanisms of bonding are reviewed, and an overview is given of the optimization of the critical process parameters for improving coating qualities. A separate section deals with bonding between different materials, addressing influences on adhesion to the substrate as well as the cohesion between dissimilar coating constituents. The knowledge of the

basic science and mechanisms finally allows for discussion of the requirements for suitable cold spray equipment and of the parameter sets needed for successful coating deposition.

Chapter 3, “Modeling and Simulation of Cold Spray,” in this book then gives the theoretical background for these critical parameters and mechanisms, leading to a general procedure for optimization, and gives preconditions regarding suitable spraying facilities. These findings are validated with some generic examples.

2.1 Introduction

Anatolii Papyrin and his team invented cold gas spraying prior to 1986, and since then, extensive lab experiments have yielded fundamental insights into the process, which have been documented in numerous patents, several textbooks, and more than a thousand scientific publications (Ref 2.1–2.9). Currently, cold spraying is a reliable industrial technology with several interesting applications and opportunities (Ref 2.10–2.13). The term cold spraying is attributed to particles that impact in the solid state onto the substrate. Thus, warm spraying (Ref 2.14–2.18) and aerosol spraying (Ref 2.19–2.22) are related processes.

As compared to conventional thermal spray technology, cold spraying is relatively simple to implement. A pressurized gas, typically nitrogen or helium, is preheated and reaches supersonic velocities after passing through a converging/diverging de Laval nozzle. Through a separate gas line, a fluidized powder feedstock is fed into the gas stream. The powder is accelerated by the expanding gas and impacts the substrate at high velocities of up to 1200 m/s (4000 ft/s) (Ref 2.7, 2.23–2.26). The gas velocities are determined by the gas type, the gas temperature, and the expansion ratio of the spray nozzle. Particle impact velocities depend on the acceleration in the surrounding gas jet, which is governed by the gas velocity, the related drag forces by the gas density or pressure, the nozzle length, and the powder mass. The particle temperature upon impact depends on various factors, such as the gas temperature, the gas density or pressure, the heat capacity of the gas, the nozzle design, and the heat capacity of particles, and can range from room temperature to more than 1000 K. In contrast to conventional thermal spraying, bonding in cold spraying does not require melting and is facilitated through particular heat-generating processes in the solid state during the high-velocity impact (Ref 2.1, 2.7, 2.9, 2.25, 2.26). The comparatively low process temperatures, the very short time scales for the exposure to the process gas, and the use of more or less inert process gases make the cold spray process particularly suitable for applications in which it is vital to avoid oxidation and to retain properties of the powder feedstock in the sprayed deposits (Ref 2.10–2.12, 2.27). To illustrate the benefits achievable beyond those of thermal spraying, Fig. 2.1 shows typical microstructures of copper coatings as prepared

by arc spraying and cold spraying. For the arc-sprayed coating, there is an oxygen content of 1.5 wt%, resulting in 30% lower electrical conductivity as compared to the initial high-conductivity oxygen-free copper powder (Ref 2.28). In contrast, the cold-sprayed coating has an oxygen content of less than 0.05 wt%, which is almost as pure as the powder feedstock. Under ideal conditions, functional properties such as the electrical conductivity and the thermal conductivity can reach up to approximately 90% of those of bulk material (Ref 2.29). As a result of the plastic deformation of spray particles during the impact, cold-sprayed coatings usually have a high hardness comparable to that of highly work-hardened bulk material, as, for example, in cold rolling treated to more than 90% thickness reduction (Ref 2.28). Because of shot peening effects, cold-sprayed coatings typically show compressive stresses (Ref 2.30). In practice, usually no phase transformations are observed, because of the short residence time (a few milliseconds) in the hot gas stream, the short deformation process

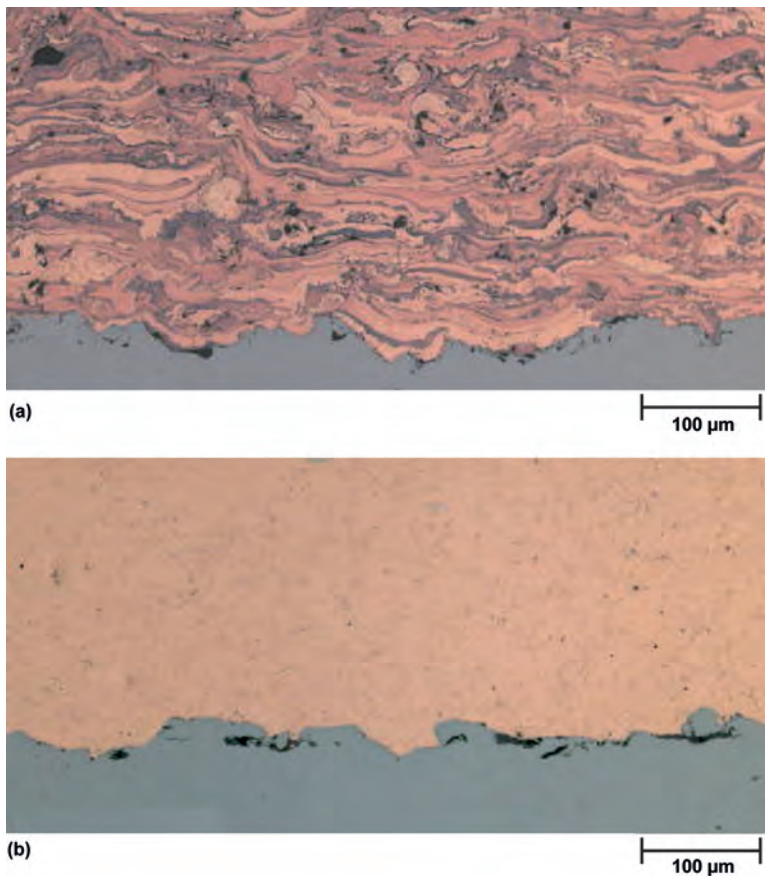


Fig. 2.1 Optical micrographs of copper coatings prepared by (a) arc spraying and (b) cold spraying

upon impact, and the fast cooling rates (approximately 10^8 K/s) (Ref 2.23). Only for a few cases, polymorphous crystal structure transformations were observed (Ref 2.31, 2.32). The conditions of severe compressive stress upon impact could favor the formation of phases with higher density.

To optimize the process and to achieve the best coating qualities, however, all process parameters must be fine-tuned with respect to the spray material and powder size range. Before dealing with the influence of particular parameters on the coating quality, the bonding process itself and the mechanisms involved need to be elucidated.

2.2 Basic Bonding Mechanisms

The basic bonding mechanisms in cold spraying of ductile metals have been presented and discussed in several publications (Ref 2.23, 2.33–2.35). For successful bonding, powder particles must impact on the substrate at very high speeds, exceeding a material-dependent critical velocity (Ref 2.24). Figure 2.2 illustrates the concept of critical velocity. At lower powder velocities, the particle impacts result in abrasion of the substrate surface by fatigue and fracture. By exceeding the critical velocity (v_{crit}), particular thermomechanical conditions are reached, under which material can be deposited as a result of high-kinetic-energy impacts. It is shown later how this critical velocity depends on material strength, density, melting temperature, heat capacity, and impact temperature. At velocities above the erosion velocity ($v_{erosion}$), material is removed from the substrate by hydrodynamic effects.

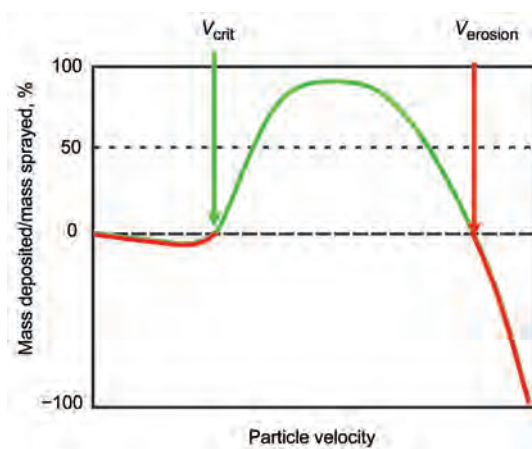


Fig. 2.2 Schematic of the mass change respective to the deposition efficiency with particle impact velocity, illustrating the concept of critical velocity. v_{crit} denotes the velocity above which deposition takes place; $v_{erosion}$ marks the transition to hydrodynamic effects that cause material removal.

The basic mechanisms of bonding require processes within the material that convert the impact energy into heat, thus increasing temperature and facilitating bonding. Because possible spray materials behave differently, influences on bonding mechanisms are discussed in separate sections. Bonding of ductile metals is well understood and described by current models, as explained subsequently. Alloys with limited deformability show more complex deformation and softening behavior, which restricts successful bonding. Brittle materials usually fail under the impact. For one special agglomerate of submicron particles, layer formation by high-pressure cold spraying has been reported (Ref 2.36, 2.37). All these cases are discussed subsequently; topics of current research are also addressed.

Metallic Materials with Ductile Deformation Behavior. For ductile particles, the shear stress upon impact leads to plastic deformation and large strains at extremely high strain rates of 10^9 s^{-1} (Ref 2.23). This plastic deformation may involve any microscopic deformation processes particular to a given material, for example, regular dislocation gliding and twinning (Ref 2.38). Thus, the high kinetic energy is transformed into thermal energy (Ref 2.39). The heat generation can be associated with the recombination of dislocations and related microscopic stress release. The generated heat causes material softening, which facilitates further plastic deformation and heat generation (Ref 2.40). The heat is predominantly produced in the zone of highest shear stress, that is, at particle-substrate or particle-particle interfaces. Because the heat cannot dissipate within the short time frame of approximately 50 ns, the plastic deformation and the temperature rise remain highly localized. Critical conditions for bonding are achieved if the thermal softening overcompensates the strain hardening and strain-rate hardening of the material, resulting in so-called adiabatic shear instabilities (ASI) (Ref 2.23, 2.34, 2.41). Temperatures close to the melting point of the material can then be attained, resulting in viscous flow of the material and eliminating the stress. Under these conditions and at these temperatures, excellent metallurgical bonding to the substrate or between adhering particles is obtained. As sketched in Fig. 2.3, loading a sphere under compression results in a Hertzian stress distribution in the substrate and the sphere. Plastic deformation then occurs along the planes of highest shear stress. For a particle impacting onto a flat substrate, the highest shear stress is obtained along a cone that is based with an angle of 45° around the circumference of the common contact zone, which so far has been only elastically deformed. By dislocation activation and gliding, particle and substrate plastically deform, resulting in material flow. The common contact zone enlarges and, concomitantly, so does the cone of highest shear stress.

Figure 2.4 shows respective modeling results for a single copper particle impacting onto a copper substrate and the resulting temporal development of temperature and stress of a certain point at the interface between particle and substrate reaching conditions for bonding. The occurrence of ASI is evident by the fast rise in temperature and the drop in stress after

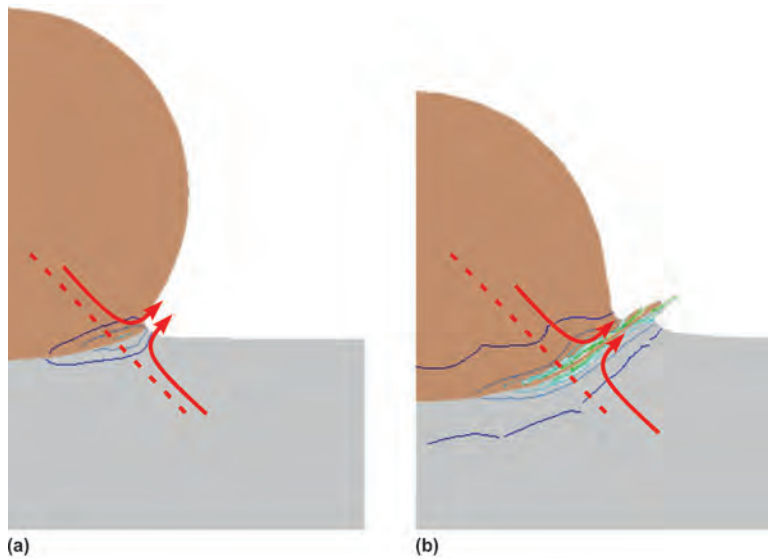


Fig. 2.3 Schematic of stress distribution and deformation upon impact of a sphere onto a flat surface, after different impact durations (a,b). The dashed line indicates the Hertzian cone of highest shear stress within particle and substrate; the arrows indicate the direction of material flow.

the time that is needed for the required plastic deformation to reach this point at the interface. As a result of the highest stress gradients (compare also to Fig. 2.3), the material flow occurs within the particle and substrate rather parallel to the interface. Substrate and particle exert high compressive stress at the common interface, and the only way for stress relief to occur is by an outward flow in the direction of the interface. Microscopically, such a 90° change in flow direction for shearing perpendicular to the interface would activate any gliding system, creating dislocations for plastic deformation. Thus, more heat is produced directly at the interface than deeper within the particle or substrate. Particle and substrate deform together under high compressive stress, and the material flow in the interface can reach speeds that are higher than the original impact velocity (Ref 2.23). The highly strained and thus heated material in the flow is subject to additional deformation by the still-moving particle, creating further stress. Plastic strain and thus temperature accumulate with the material flow along the interface. In other words, the material flow transfers hot material (i.e., heat) toward the outer rim of the enlarging contact zone, where, under the ongoing deformation, more strain and more heat are generated. Thus, the deformation of each cell in the interface profits from the previous deformation of adjacent cells closer to the point of first contact, and heat is continuously accumulated, increasing the local temperature. Above a certain temperature, thermal softening will more than counterbalance the hardening effects, and ASI will develop, resulting in a second,

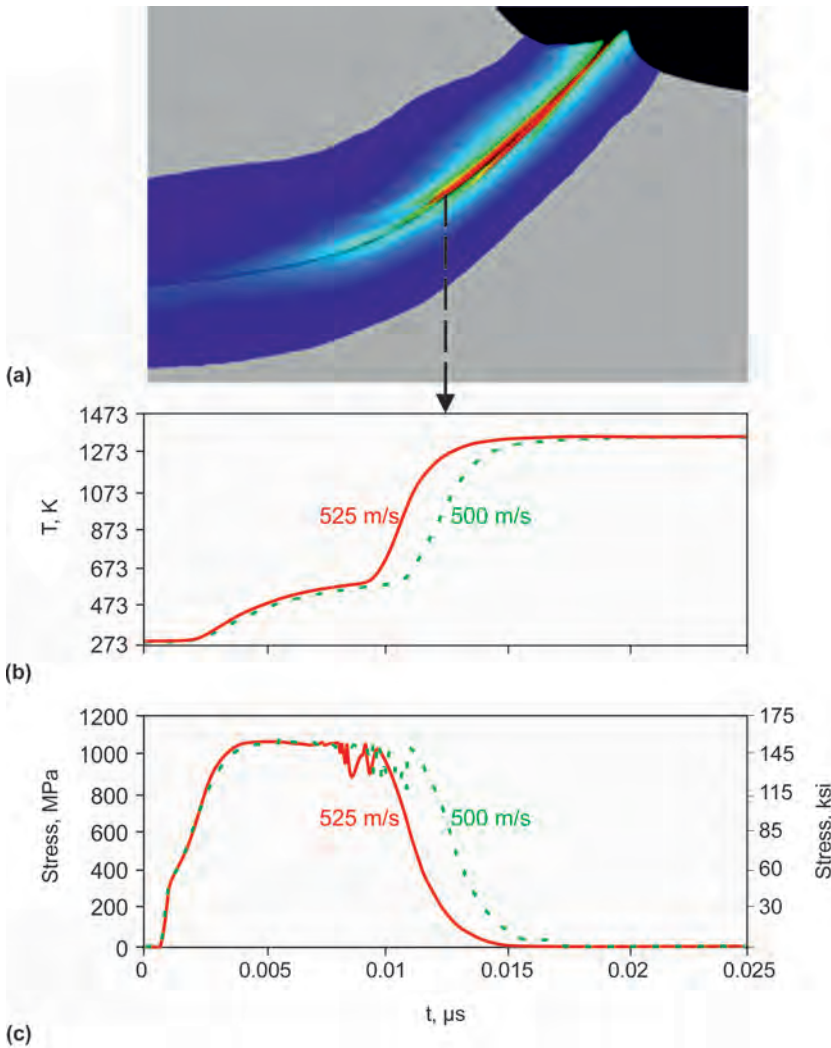


Fig. 2.4 (a) Snapshot of a finite-element impact simulation after 10 ns for the temperature distribution of a single copper particle impacting onto a copper substrate as well as (b) the temperature rise and (c) the stress development over time for a certain point at the interface between particle and substrate for particle impact velocities of 500 and 525 m/s (1640 and 1720 ft/s), which is above the critical velocity for formation of adiabatic shear instabilities (ASI). The point is chosen to be in the region of ASI. The temperature profile along the interface in (a) in principle also resembles the time behavior, that is, schematically; a similar diagram as depicted in (b) could also be drawn with the x-axis denoted as interface distance from point of first contact.

sudden increase of deformation and heat, ultimately leading to viscous flow of the material at a temperature close to the melting point. Any over-critical point within the interface shows a temperature evolution mostly identical to the one depicted in Fig. 2.4(a), only shifted on the time scale, according to the respective distance from the point of first contact.

Alternatively, strain or temperature development along the particle or substrate surface can be assessed, as shown in Fig. 2.5 (Ref 2.42). In Fig. 2.5, the maximum temperature reached during the full impact duration is plotted over the weighted distance from the area of initial contact (the “south pole”), showing the accumulation of heat. From such data, the onset point and the extent of ASI zones can be extracted. The results shown in Fig. 2.5 also demonstrate that even under high impact velocities, the south pole region does not reach conditions for ASI. This fact is also shown in Fig. 2.6, showing simulation results for copper impacting onto copper at a velocity of 600 m/s (2000 ft/s) (Ref 2.41). Despite the rather high impact velocity, the interfaces around the point of initial contact are not bonded by ASI. Location of areas of highest shear stress varies with impact angle or local surface geometries, for example, in the case of impact onto mainly rough surfaces or already adhering layers of particles. Thus, ASI could also occur on areas around the south pole, leaving less-well-bonded areas at other locations (Ref 2.34).

If the accumulation of heat during the plastic flow from the point of first contact to the outer rim is not sufficient, no ASI will occur, and thus the particle will remain nonbonded. As a rule of thumb, a minimum of 10 to 15% plastic strain (under quasi-static test conditions) is needed for any material to be able to develop ASI upon cold spraying.

The formation of ASI is also supported by increased initial temperatures, which then reduce the critical velocity. Consequently, for conditions

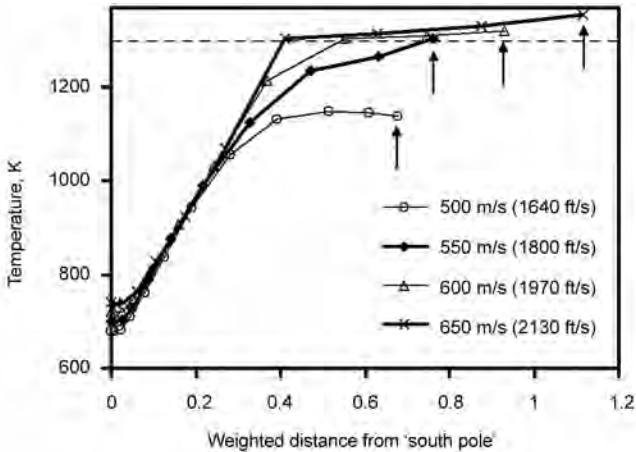


Fig. 2.5 Calculated temperature profiles along a meridian path on a copper particle surface impacting onto a copper substrate, for different impact velocities. The distance from the south pole has been weighted in a way to scale with the corresponding contact area. The arrows indicate the edge of contact area between particle and substrate. The dashed line indicates the threshold of shear instability. Source: Ref 2.42

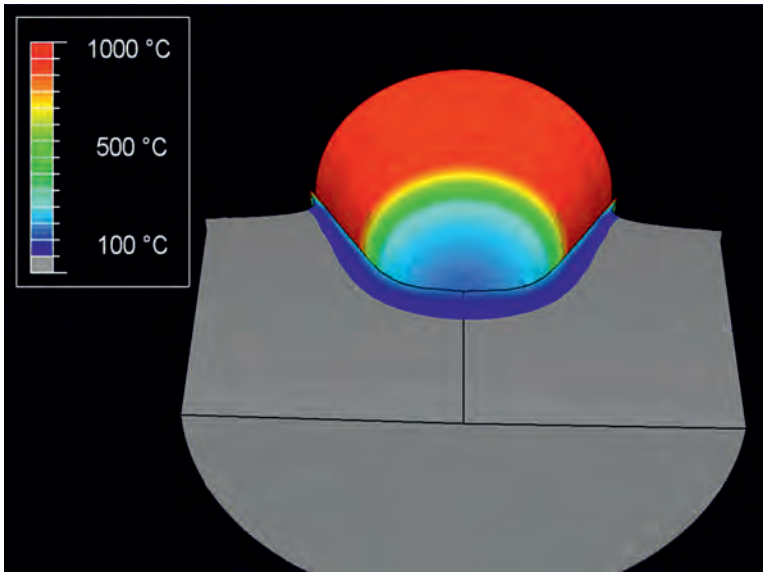


Fig. 2.6 Modeling results showing the interface temperatures under impact of copper onto copper at a velocity of 600 m/s (2000 ft/s). The results clearly show that the “south pole” area around the point of initial contact does not reach conditions for adiabatic shear instabilities. Source: Ref 2.34

slightly above the critical velocity, the maximum temperature or strain is always achieved only at the outer rim. For any further excess impact energy, critical conditions for bonding are already achieved at ring-shaped zones closer to the point of first contact, increasing the bonded area and the macroscopic tensile strength. Keeping the axis in Fig. 2.4 and 2.5 constant, higher impact velocities will compress the curve with respect to the x -axis, and ASI will appear sooner and closer to the point of first contact. Also, higher impact temperatures will shift the onsets to the left. For a higher starting temperature, less deformation is needed to create a threshold heat, and ASI will again appear sooner and closer to the point of first contact. The larger the area of ASI, the higher the tensile strength of the coating will be, approaching bulklike behavior for maximum reduction of the unbounded south pole region.

The high plastic strains obtained in cold spraying will result in ultrahigh dislocation densities and quite a number of associated phenomena, such as dynamic recrystallization (Ref 2.43) and the condensation of point defects (Ref 2.44). Low-temperature resistivity measurements indicate that cold-sprayed copper coatings contain significantly more defects than deformed bulk copper (Ref 2.43). This phenomenon can be explained by dislocation climbing, introducing interstitials and vacancies in ultrahigh densities in the crystal lattice. Unfortunately, no reports about the introduced point defect densities in cold spraying have been published so far. However, it

can be assumed that by dynamic defect creation and annihilation, their local concentration will temporally be significantly higher than in thermal equilibrium, approaching 10^{-4} , which would correspond to melting. In any case, locally higher point defect densities support viscous flow and the formation of ASI, in addition to thermal softening. Thus, a formalism solely based on thermal softening may be treated as a lower estimate of the necessary conditions for bonding.

The results from modeling concerning the extent of ASI can be experimentally verified by evaluating single-impact phenomena and subsequent testing under external loads. Figure 2.7(a) and (b) show a surface with bonded single Ti-6Al-4V particles before and after ultrasonic cavitation erosion. Obviously, a few particles are ripped out of the substrate and leave ring-shaped defects behind, as illustrated in Fig. 2.7(c). Figure 2.7(d) exhibits the contact zone of such a removed particle. The central area of the particle can be seen clearly, and it was obviously not bonded to the substrate. The ring-shaped outer area is still covered by substrate material (pure titanium), indicating that the strength of the interface between

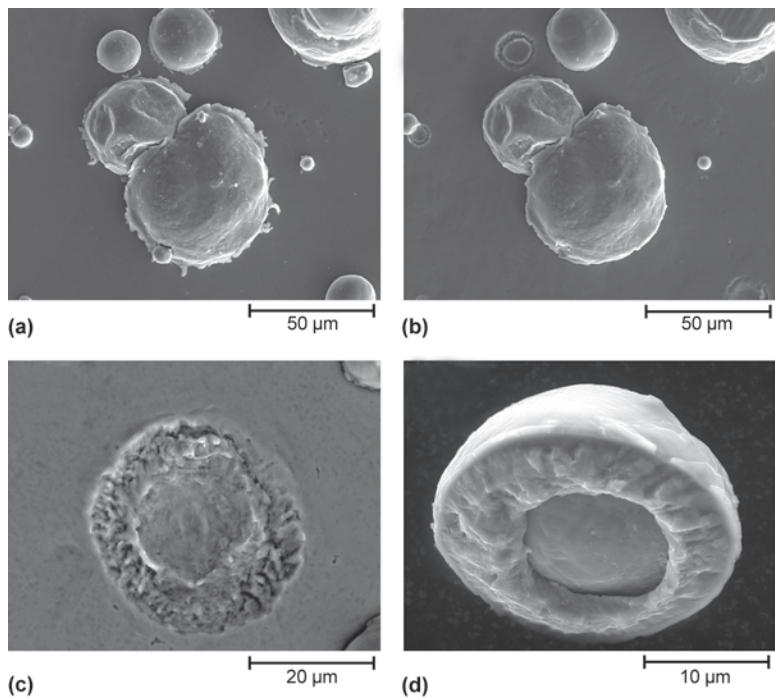


Fig. 2.7 (a) Scanning electron microscope (SEM) plane view of impact morphologies for cold-sprayed Ti-6Al-4V-particles on a titanium substrate. (b) SEM micrograph of the same area after cavitation testing as external load. (c) SEM micrograph of the fracture morphology at the substrate site after cavitation. (d) A Ti-6Al-4V particle that was removed from the titanium substrate by cavitation, showing the fraction of originally well-bonded interfaces

particle and substrate is stronger than the ultimate strength of the substrate material (Ref 2.45, 2.46).

Particular Cases of Materials with Less-Common Deformation Behavior. The purely ductile plastic behavior and the regular thermal softening assumed in the previous section do not apply to all materials. Some materials show a more pronounced elastic deformation and can store high amounts of energy elastically, such as shape memory alloys or bulk metallic glasses. Moreover, at the high strain rates of $10^9/s$, some engineering materials exhibit increasingly brittle behavior and tend to fracture upon impact. This is especially problematic for high-strength alloys containing intermetallic phases or composites. For these particular cases, it must be investigated in detail what microscopic processes for plastic deformation and heat production are available and can be activated under the given impact conditions. In principle, heat generation by plastic deformation apart from dislocation related processes could also occur by twinning or by shear banding (Ref 2.47). Under sufficiently high impact energies, strain softening and ASI may also take place in these more problematic materials. However, depending on the elementary slip and deformation processes of a material, there may be only a very narrow parameter window for successful coating buildup by the processes described in the previous section. For a more comprehensive understanding, different cases must be distinguished.

Materials with Particularly High Elastic Deformation Limits. For all types of materials, a significant amount of energy is stored elastically in particle and substrate during the impact. Thus, bonding in the ASI zones by cooling must take place within a certain limited time frame and should be sufficiently strong to withstand the elastic rebound energies (Ref 2.48, 2.49) of particle and substrate. At the time of onset of the rebound, the interface is usually still at high temperature, thus weaker than at low temperatures. If the rebound energy is too high and the forces exceed the ultimate tensile limit of the bonded zone, the freshly bonded areas may rip apart again, and the particle may bounce back as a result. On the one hand, this applies to all impact events that result in a minimum amount of bonded area. On the other hand, such rebounds become prominent specifically for materials with low interface strength. Any partial rebound by elastic recovery gives rise to a narrow gap in the nonbonded zones between particle and substrate (Ref 2.50, 2.51). As a rule of thumb, approximately 10 to 15% of the common interface area should be well bonded for the interface to withstand elastic bounce-back forces (Ref 2.23). These bounce-back effects are more important, sometimes even decisive, for cold spraying materials that store high amounts of elastic energy. Figure 2.8 depicts the example of superelastic NiTi particle impacts onto a NiTi substrate and respective rebounds. In the case of rebounds, the comparatively large amount of bonded zone was still in a highly viscous state when the elastic bounce-back forces arose, leading to pronounced ligaments before com-

plete liftoff. Similar effects are also observed for cold spraying of bulk metallic glasses (Ref 2.47, 2.52–2.55). These examples show that the formation of shear instabilities is a necessary but insufficient criterion for bonding. The particle will not adhere if the time required for the viscous interface to become rigid is much longer than the actual impact and deformation duration.

Also, for standard metals, the strength of the bonded zone will depend on heat dissipation. However, faster heat dissipation also somewhat counteracts the formation of ASI, thus requiring additional impact energy. Even if bonding is sufficiently strong and the particle remains bonded, the rebound may lead to a more or less pronounced spatial separation between particle and substrate in the area of the south pole. Therefore, a higher excess impact energy is desirable to achieve a larger extent of ASI down toward the south pole in any case. In summary, the competition between bonding and bounce back is critical and further limits the parameter window for successful deposition, in particular for materials with large rebound energies such as shape memory alloys or bulk metallic glasses.

Materials with Anomalous Thermal Softening Behavior. A number of engineering materials such as iron aluminides or nickel-base superalloys are carefully tuned to avoid thermal softening over wide application temperature regimes (Ref 2.56, 2.57). Their properties are mainly due to an inverse softening behavior of intermetallic precipitates that are embedded into a solid-solution metallic matrix, and to well-tuned compositional balances. Strength may increase with the temperature of the intermetallic phases; when this phenomenon occurs, it is usually due to changes in stacking fault or antisite energies that hinder dislocation gliding (Ref 2.58, 2.59).

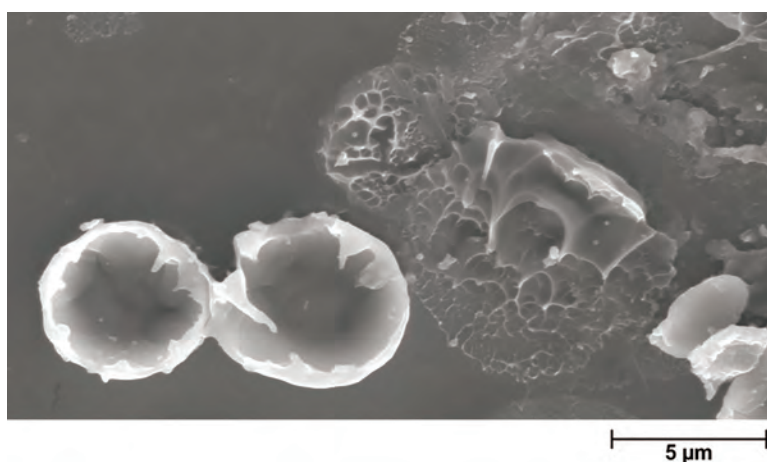


Fig. 2.8 SEM micrograph showing single-impact events of NiTi particles on a NiTi substrate (N_2 ; $p = 3.3$ MPa, or 480 psi; $T = 600$ °C, or 1110 °F). Remnants of particle material can be observed.

In addition, intermetallics often show higher strain-rate hardening and strain-rate sensitivity than pure metals with less complex crystallographic structures (Ref 2.60–2.62). An example is FeAl (Ref 2.63).

The strength of FeAl increases with temperature before softening at higher temperatures (Ref 2.60). The peak in strength is more pronounced and shifted to higher temperatures if higher strain rates are applied (Ref 2.64). For cold spraying, with high strain rates of up to $10^9/s$, peak temperatures of more than 800 °C (1470 °F) can be expected. An increase in strength with temperature counteracts the formation of ASI, because heat does not lead to softening and more, highly localized deformation. Under these conditions, no temperature spike occurs, and the deformation and heat are distributed over a larger volume. Therefore, impact conditions must aim for the highest possible temperatures to overcome the peak in strength and to achieve a regular softening behavior with further temperature increase by plastic deformation. This consideration affects not only the impacting particle but also the response of those already adhering to the substrate. Successful coating formation for this material has been possible by using maximum process gas temperatures, relatively short stand-off distance, slow traverse speed of the gun, and coarser particle sizes. Coating microstructures of cold-sprayed iron aluminide are shown in Fig. 2.9. Under optimized conditions, particle and substrate temperatures upon impact are sufficiently high, enabling coating formation.

Materials with Limited Plasticity under High Strain Rates. If the plasticity of a material at high strain rates lies below a certain limit, heat generation along the interface may fail to provide sufficient energy for bonding; that is, the deformation ends before the occurrence of ASI in Fig. 2.4. Cracks may occur in the direction of the highest shear stress, or particles may fracture completely.

Zinc-base two-phase alloys are examples of materials with unfavorable crystal structure and high strain-rate sensitivity. Figure 2.10 shows single impacts of a Zn-6.3wt%Mg powder (Ref 2.65). At a gas temperature of 350 °C (660 °F) and a pressure of 2 MPa (290 psi), some particles are successfully deposited (Fig. 2.10a), but others break (Fig. 2.10c). Increasing the pressure to 3 MPa (435 psi) yields a higher impact velocity and thus leads to higher strain rates. Whether as a consequence of higher strain-rate hardening and strain-rate sensitivity or of a smaller number of slip systems to activate, the material obviously reacts in a more brittle manner, and the particles shatter upon impact. Only small fragments remain bonded (Fig. 2.10 e, g). At a process gas pressure of 3 MPa (435 psi), increasing the process gas temperature to 400 °C (750 °F) leads to less fracture (Fig. 2.10d). A rise in temperature may increase plastic deformability through thermal softening. However, for this particular alloy, the maximum accessible gas temperature is limited by the melting point of the material and the risk of nozzle clogging. At a given impact temperature that, in principle, would allow for bonding, the deposition efficiency may pass through

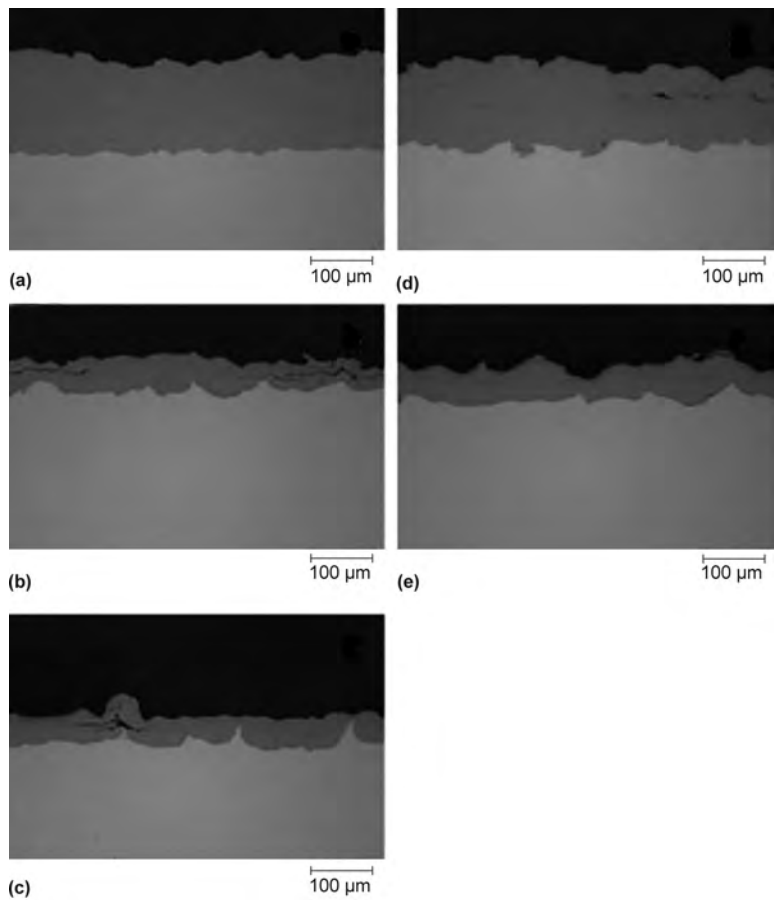


Fig. 2.9 SEM cross-sectional micrographs of cold-sprayed FeAl coatings on steel 316L substrate. Four layers obtained with fine powder at (a) short, (b) medium, and (c) long spray distances, and obtained with coarse powders at (d) short and (e) medium spray distances. Source: Ref 2.63

a maximum with increasing pressure. While too-low pressures and thus low impact velocities are not sufficient for bonding, too-high pressures lead to fracturing and thus lower deposition efficiency.

Ceramic Materials. In general, the brittle behavior of ceramic materials renders them unsuitable for cold spraying. However, in a few niche applications, embedding single ceramic particles in metallic surfaces by cold spraying has been attempted. In cold spraying, under very rare conditions, bonding of ceramic particulates has been observed (Ref 2.36, 2.37). Nevertheless, in the related process of aerosol spraying, deposition of fine ceramic particles by kinetic energy has been feasible (Ref 2.19–2.22, 2.66). In contrast to cold spraying, quite a number of various ceramic materials have been so far successfully deposited as coatings by aerosol spraying. Possible explanations for bonding by kinetic impact of ceramics

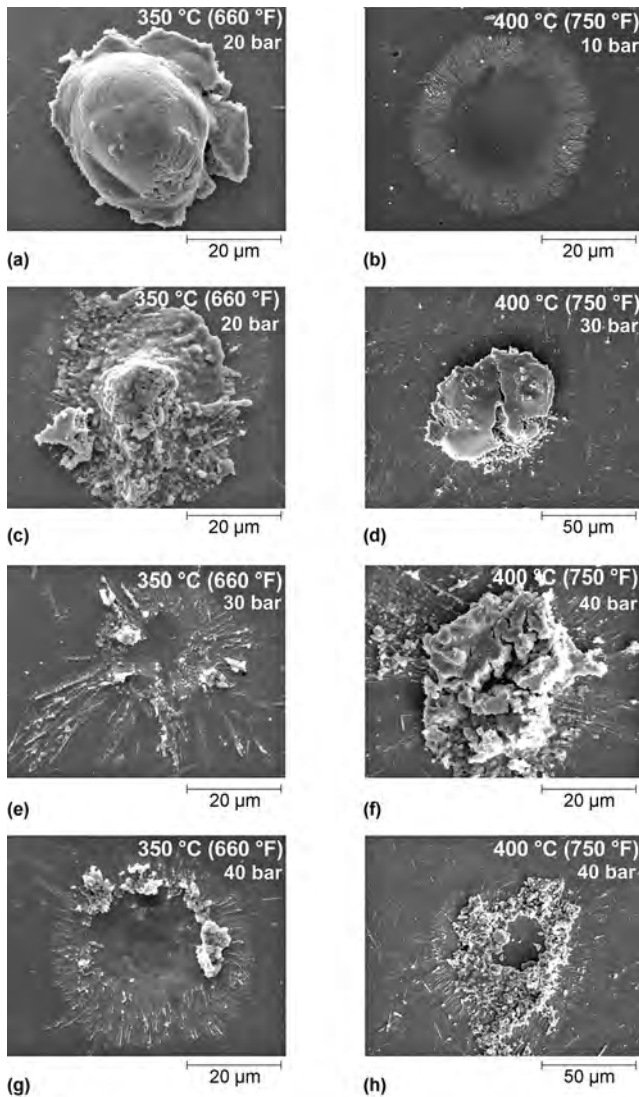


Fig. 2.10 SEM micrographs of typical single-impact events for Zn-6.3wt%Mg alloy particles under different process parameters, as indicated

are suggested, and the involved particular conditions are discussed in the following.

Bulk Ceramic Feedstock Particles. Brittle materials such as ceramics do not show plastic strain but fracture if a critical stress is exceeded. Thus, cold spraying of bulk ceramic powders results in particle fracture, and the substrate undergoes surface damage similar to that caused by grit blasting, that is, roughening by deformation and erosive wear. In case of ductile substrates, fragments of broken spray particles may be embedded in the

surface, either by interlocking as in grit blasting or by ASI occurring on the substrate side. Such embedded particle fragments cannot be described as a regular coating. Thus, cold spraying of brittle ceramic powder normally does not result in continuous coatings. In aerosol spraying, the situation is different. In this technique, bonding of submicron particles is associated with fracture of spray particles. Possible workarounds for ceramic layer formation in cold spraying are discussed subsequently.

Agglomerated Ceramic Feedstock Particles. Under compression, agglomerated ceramic particles may behave differently from single ceramic particles of the same size. Instead of total failure and fragmentation, agglomerates may experience only partial failure of single bonds between primary particulates. Such behavior can also have consequences for cold spraying. In the literature, a couple of cases report the formation of ceramic coatings on the basis of agglomerated nanoparticles (Ref 2.36, 2.67), which cannot be explained by any plastic mechanical deformation. Figure 2.11 shows an example of an anatase titanium dioxide layer cold sprayed onto steel. It seems that some material could also be deposited through secondary impacts. The adhering spray layer consists of numerous layers of primary nanosized particles.

An experimentally proven model for conversion of kinetic energy into heat for bonding in cold spraying of such materials is still lacking. However, based on recent molecular dynamics (MD) simulations (Ref 2.68) and experimental studies (Ref 2.67), a mechanism based on fracture and fusion may be proposed. This is, however, somewhat speculative and needs further confirmation. For the application to cold spraying, it must be considered that titanium dioxide powders that have so far been successfully deposited through secondary particle impacts consist of agglomerates of mostly nanosized primary particles.

Like ductile materials, brittle particles undergo high stresses during impact. However, plastic deformation, predominantly localized in the contact zone, cannot contribute to stress relaxation. Instead, the stress will lead to elastic compression in the direction of impact throughout the particle and concomitant tensile stresses in the circumferential direction. Consequently, if the ultimate tensile strength is exceeded, cracks will de-



Fig. 2.11 SEM cross-sectional micrograph of a cold-sprayed TiO₂ coating on a stainless steel substrate that consists of multiple layers of primary particles. The ceramic layer shows some cracks. Source: Ref 2.67

velop; that is, the kinetic energy is converted into broken bonds and new surface energy. Depending on the energy balance between kinetic energy of the particle and energy of the broken chemical bonds, different deformation morphologies are developed. Either few cracks are formed—and the whole secondary particle fractures into larger fragments—or multiple cracks develop that are either stopped before reaching the surface or shatter the secondary particle into small pieces. Furthermore, depending on the stored or released elastic energy, fragments may rebound or continue their path toward the substrate, with varying velocities. For fragments in the submicron range, the surface-to-volume ratio is unfavorably large for thermodynamic stability. For ultrafine copper powder, it has been observed that nanosized particles can spontaneously sinter to any other particle or surface under clean conditions, which is attributed to a reduction of surface area (Ref 2.69). Upon rebonding of formerly shattered fragments to any other surface, the chemical binding energy is released in the form of heat, allowing for even more diffusion and sintering. In addition, the freshly broken fragments have highly chemically active surfaces with unsaturated bonds, which may further facilitate rebonding. According to the current understanding, agglomerated particles may disintegrate into a cloud of their constituent nanosized primary particulates, which then sinter to the surface. The mechanism similarly applies to aerosol deposition of submicron particles (Ref 2.19, 2.70).

This model is supported by the recent MD simulations (Ref 2.68) that show crack formation and closure during impact of small particles at critical velocities. Furthermore, experimental studies in cold spraying of anatase titanium dioxide powder (Ref 2.67) point to the importance of powder design to facilitate deposition by quasi-plastic deformation under multiple fractures. Respective examples are given in Fig. 2.12. In static compressive stress-strain tests on single particles, different failure modes are observed:

- Stress accumulation and brittle, catastrophic failure, that is, bulk ceramic behavior (particle characteristic A, Fig. 2.12a)
- Quasi-plastic deformation behavior, where particles may form small microscopic cracks already at lower load levels, exhibiting significant strain at comparatively low stress levels (particle characteristic B, Fig. 2.12b).

Particles that show brittle deformation under compression (characteristic A) usually do not deposit (Fig. 2.12c), whereas under identical process conditions, particles that show quasi-plastic behavior (characteristic B) do deposit (Fig. 2.12d). Therefore, the deposition behavior may be predicted on the basis of quasi-static compression tests (Ref 2.67). Interestingly, mixed fracture modes between the two categories (A and B) could also be observed, but these did not contribute to layer formation.

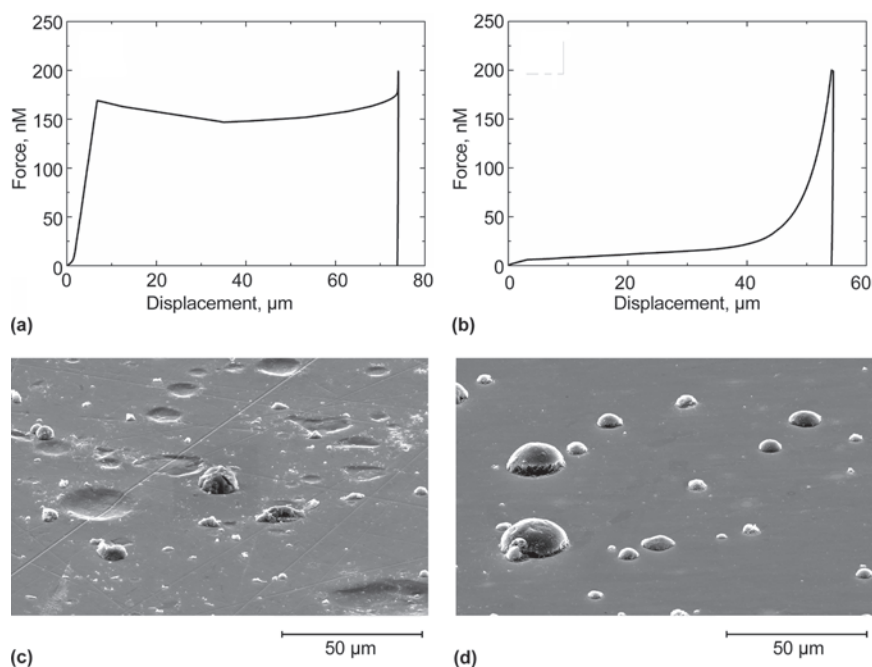


Fig. 2.12 Force-displacement diagrams under compression for single TiO_2 powder particles of different batches, showing (a) brittle and (b) quasi-plastic deformation and (c, d) respective single-impact events on polished stainless steel surfaces. Source: Ref 2.67

In conclusion, fraction and fusion on a submicron scale is proposed as the dominating critical mechanism during cold spray deposition of agglomerated feedstock powders of brittle ceramic materials. Macroscopically, this may appear as quasi-plastic behavior of these agglomerates, similar to the interpretation given in literature (Ref 2.19, 2.20).

Composite Materials. For a number of applications, composite materials are of high interest to meet challenging requirements and combine desired properties. Cold spraying has certain advantages because the materials remain below their melting temperature. Often these materials consist of different phases with large differences in mechanical strengths and melting temperatures, limiting common fabrication techniques. Both affect the deformation process upon impact and impose particular challenges for successful coating production. In principle, the powder feedstock may consist of a mixed powder blend or even be discharged from two separate powder feeders simultaneously, providing an opportunity to produce graded coatings. In another approach, two different materials or phases are fabricated by composing smaller primary particulates to an agglomerated and sintered feedstock. The two cases lead to substantially different impact behavior and are therefore discussed in separate sections.

Powder Blends. Ideally, conditions for bonding should be met by all the constituent materials in powder blends to allow for successful deposition. To a certain extent, impact temperature and velocities for the different powder materials within the blend can be fine-tuned by different size cuts. The different thermal properties and material densities must also be considered. While the heat conductivity and heat capacity govern heatup and cooldown of the particles, the density is important for the acceleration and impact velocity of particles. Figure 2.13 shows an example for cold spraying a titanium-molybdenum powder blend. Under optimum conditions, 41% Mo could be obtained in the coating, based on an initial volume content of 50% Mo in the powder feedstock.

If the mechanical properties of the constituents of the powder blend are too different and the windows of deposition cannot overlap, successful deposition may still be possible if one constituent has sufficient ductility to embed the others. This has been shown for powder blends of one ductile and one hard phase, for example, metal/ceramic powder blends. Although the hard-phase particles do not deform at all, they are embedded into the softer material that undergoes ASI and provides the heat required for bonding. As compared to impacts onto the same material, by a higher

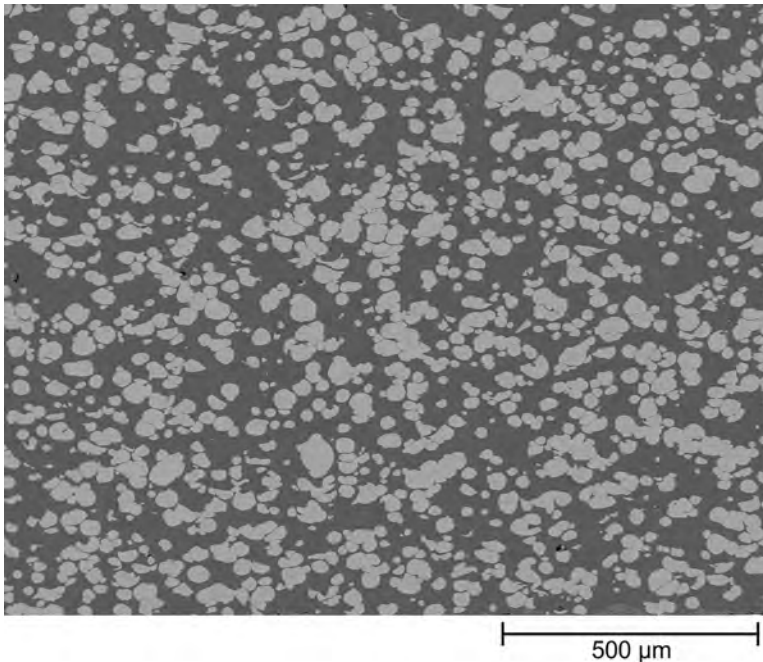


Fig. 2.13 SEM micrograph of a titanium-molybdenum composite cold sprayed with nitrogen at a process gas pressure of 4.2 MPa (610 psi) and a process gas temperature of 930 °C (1700 °F). The volume content of 50% Mo in the powder blend was reduced to 41% in the final coating at an overall deposition efficiency of 70%.

deceleration the softer material experiences more plastic strain depositing onto the composite containing hard-phase particles. Moreover, the soft material also converts the kinetic energy of the hard-phase particles into plastic deformation and heat. Obviously, this works only if the volume fraction of the hard phase is below a certain limit. If a hard-phase particle impacts directly on another hard-phase particle, bonding will usually not occur. Thus, the hard-phase fraction within the coating is generally significantly lower than in the feedstock powder blend. So far, at most, close to 50% volume fraction of hard phase in the coating has been obtained, and only if starting with a much higher fraction in the powder blend of approximately 80% or even more (Ref 2.71–2.76). As an example, Fig. 2.14 shows the individual deposition efficiencies of soft and hard constituents as well as compositions of powder feedstock and attained coatings for cold spraying powder blends of copper and tungsten.

In addition to volume fraction, geometrical boundaries related to the particle size distributions also must be taken into account. The best results are obtained if the particle sizes of hard and soft materials are in a comparable range. Often, the hard-phase particles are significantly smaller. This condition results in different fluid dynamics and unfavorable geometrical conditions. The smaller hard-phase particles can be bonded only at the interface between two big soft particles, which reduces the attainable volume fraction drastically. The examples in Fig. 2.15 show coatings based on cold spraying copper-tungsten powder blends with hard-phase contents of 50 vol%, using different-sized cuts. As compared to the blend sprayed with similar sizes of soft and hard particles, smaller hard-phase sizes result in drastically lower tungsten contents in the coating at lower deposition efficiencies. If, in contrast, the hard particles are bigger than the soft particles, the probability of a hard-phase particle impacting on another hard particle increases. Such events will not result in successful bonding, and, under extreme conditions, crack formation and fracture could occur. Thus, formation of a composite coating may fail for blends with large hard-phase particles.

For all cases of powder blends, the adhesion between hard and soft particles also must be taken into consideration. As discussed in the previous section for cold spraying onto different substrate types, such adhesion is influenced by the amount and location of ASI under the locally different deceleration of impacting particles. Thus, cold spraying of powder blends of materials with largely mismatching mechanical properties will remain challenging.

Composite Powders. Another option for deposition of composite materials is to start out with a composite powder, in which internal interfaces are already joined. Hard metal coatings have been successfully produced in this manner on the basis of porous agglomerated and sintered feedstock (Ref 2.77–2.82) or dense high-energy milled powders (Ref 2.83–2.86). Such materials can be treated as homogeneous regarding impact velocity

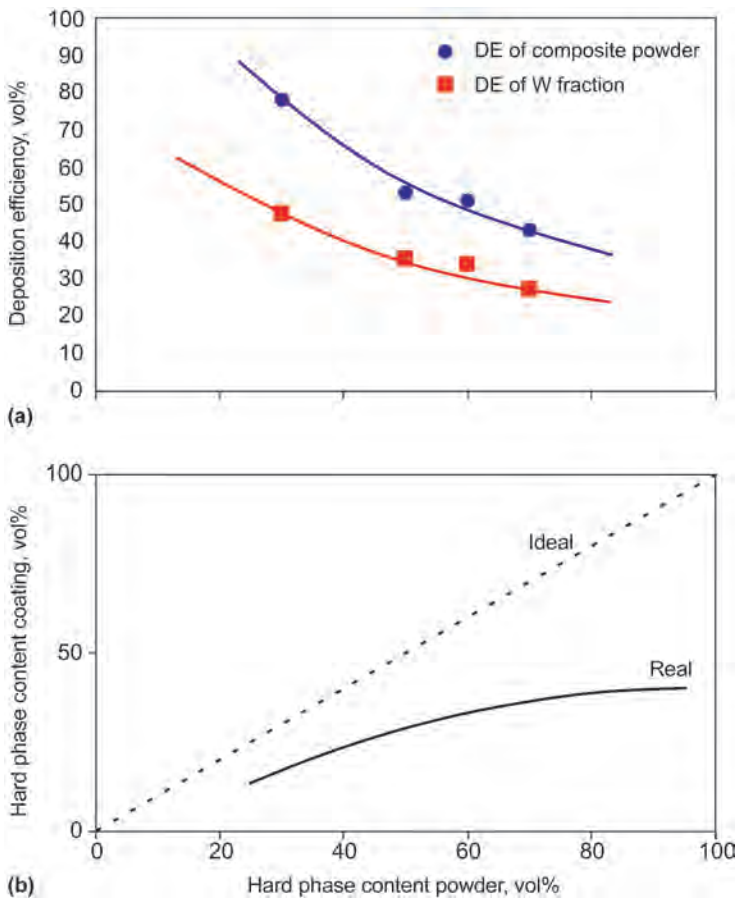


Fig. 2.14 (a) Individual deposition efficiencies (DE) and (b) hard-phase contents in the powders and the coatings for cold spraying copper-tungsten blends of similar particle-size cuts. Cold spraying was performed with nitrogen at a process gas pressure of 4 MPa (580 psi) and a process gas temperature of 900 °C (1650 °F).

and impact temperature. However, the deformation behavior upon impact is critically dependent on the phase distribution and microstructure. Only with sufficient deformability can coatings be obtained, so the ductile phase should be present in a significant volume fraction and as a continuous network.

Core/Shell Powders. Recently, special powders have been prepared for cold spraying by coating the hard phase with a softer shell material (Ref 2.87, 2.88). The intention is to facilitate deformation and bonding in the outer shell while “hiding” the hard-phase material inside in regions with less stress upon impact, avoiding fracture or badly bonded areas. However, geometrically, the hard-phase volume fraction is also limited. For

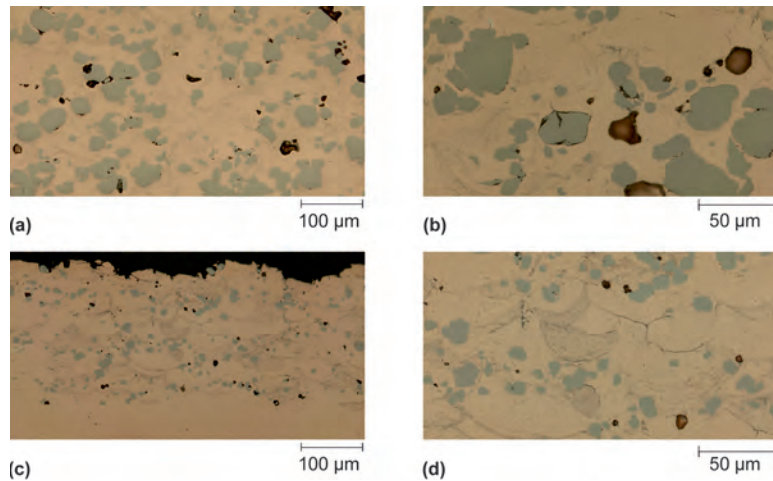


Fig. 2.15 Effect of geometrical conditions in cold spraying a powder blend of 50 vol% copper and 50 vol% tungsten particles (a, b) with coarse hard-phase particles in sizes of 22 to 45 μm and (c, d) fine hard particles in sizes of 5 to 15 μm . Cold spraying was performed with nitrogen at a process gas pressure of 4 MPa (580 psi) and a process gas temperature of 900 $^{\circ}\text{C}$ (1650 $^{\circ}\text{F}$). If hard-phase particles are much smaller than the ductile particles, here given in sizes of 16 to 38 μm , the deposition efficiency decreases from 50% to approximately 20%, because only a small amount of the hard phase is incorporated into the coating.

application, usually hard-phase dimensions of approximately 5 μm are desirable. For a volume fraction of 50%, the ductile shell would then only have a thickness of approximately 1.3 μm , which is rather thin for the required deformation process and usual strain values. Upon plastic deformation of the ductile shell, stress may accumulate at the interface to the brittle core. Even if the hard phase has a high strength and does not fracture, the accumulated stress may ultimately cause delamination between core and shell. These faults may later cause failure in the application of these composite coatings. Simulations are ongoing, with the aim of improving the impact behavior of core/shell powders by tailored powder design and adaption of process parameters (Ref 2.89). Apart from the scientific considerations, preparation of core/shell powder feedstock is more complicated, and thus, costs are rather high.

2.3 Bonding between Dissimilar Spray and Substrate Materials

The mechanisms of bonding between identical materials apply to all cases of repair of parts with the same material. They also apply to any thick coating after reaching sufficient thickness and depositing already

onto coating material. However, for particles impacting on a dissimilar material, conditions will vary significantly as a result of their differing mechanical and thermal properties. These determine the bond strength between substrate and coating. As described previously, such conditions also apply if a composite powder or a powder blend of different materials is cold sprayed. In that case, bonding between dissimilar materials will determine coating cohesion, that is, coating strength. In the case of different spray and substrate materials, the adhesion will be affected, as elucidated in the following.

The highest bond strengths can be achieved if particle and substrate materials are similar. For dissimilar coating and substrate material, lower strengths are generally expected (Ref 2.90). Experimental results have demonstrated that the bond strength of cold-sprayed coatings on hard substrates is lower than on soft substrates (Ref 2.28). Slight mismatches of properties may be accounted for if the critical conditions for ASI formation of both materials can be met simultaneously. Slight differences in properties for two given materials may be compensated for by fine-tuning particle impact temperature or substrate temperature. However, achieving sufficiently high bonding strength on substrates with larger mismatching mechanical properties can be quite challenging. In principle, an appropriate description has to deal with the deceleration of impacting particles and associated time scales. Following such an approach, the critical velocity for bonding may be replaced by a critical deceleration upon impact, accounting for the volume in which the kinetic energy of the particle is deposited. The two extreme ends of the scale are discussed in the following sections.

Soft Substrates. If the substrate is softer, the impacting particles may penetrate deeply. This consideration also applies to a substrate with certain microporosity. As shown in Fig. 2.16 for the impact of a copper ball onto an aluminum plate, the typical deformation zone may extend over a larger pathway (Ref 2.91). Consequently, the kinetic energy, deformation, and heat generation are distributed over longer time scales and a larger volume. Thus, the process is less adiabatic and the resulting temperature rise is less pronounced. Nevertheless, ASI may occur on the softer substrate (Fig. 2.16), manifested as traces of aluminum on the copper ball. Formation of ASI only on the substrate side could be a prerequisite for bonding, although it may not be a sufficient condition.

However, even if a substrate is too soft to provide the critical conditions for formation of ASI on the particle side, the flow of the substrate material around the penetrating particle may result in bonding as a result of mechanical interlocking. In any case, the first embedded particles will harden the substrate, thus causing sufficient particle deceleration and hence ASI on the subsequent impinging particles.

Hard Substrates. If the substrate is much harder than the impacting particle, good bond strength may be hard to achieve. While the particle can

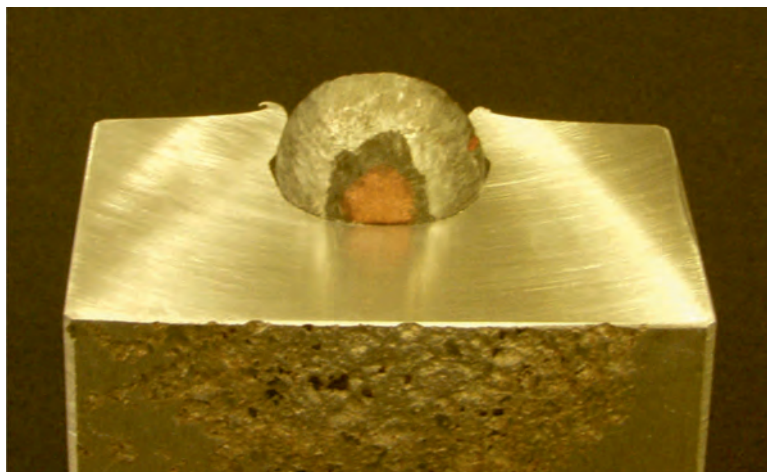


Fig. 2.16 Cross section of a 20 mm (0.8 in.) copper ball that impacted onto an aluminum substrate at a velocity of 800 m/s (2600 ft/s), showing the effects of particles penetrating deeply into a soft substrate during cold spraying

still deform plastically and provide ASI, the substrate may deform only elastically to a rather low extent. In that case, deceleration of the particle will be higher than with soft substrates, so that ASI will be easier to achieve. However, the jet that forms at the interface is not trapped between the deforming particle and deforming substrate but flows freely parallel to the substrate surface. Therefore, the hot areas of the particle and jet do not necessarily stay in close contact with the substrate and may fail to facilitate bonding (Fig. 2.17).

In addition, any eventually bonded area may rip apart again under the influence of the higher elastic bounce-back forces exerted by the substrate. In similar deformation pairs, the bonded area can be extended down toward the south pole region of the particle by increasing the impact velocity at a given temperature. Higher impact velocities are not advisable for rather brittle substrates, though, harder impacts may cause damage. In particular, for ceramic substrates, even regular spray parameters may not be applicable, because the high momentum of the impacting particles could give rise to cracks in the ceramic substrate. This is particularly problematic for high-density spray materials such as copper. As a work-around, e.g., for processing copper coatings onto alumina, an intermediate cold-sprayed aluminum coating is able to damp the impact of the subsequent copper particles (Ref 2.92–2.94). Figure 2.18 shows examples of cold-sprayed copper coatings on thermally sprayed alumina layers. As shown in Fig. 2.18(a) for using an interlayer, the impact of aluminum particles is less problematic regarding crack initiation because of the lower density of aluminum. In addition, an intermediate aluminum coating is less sensitive

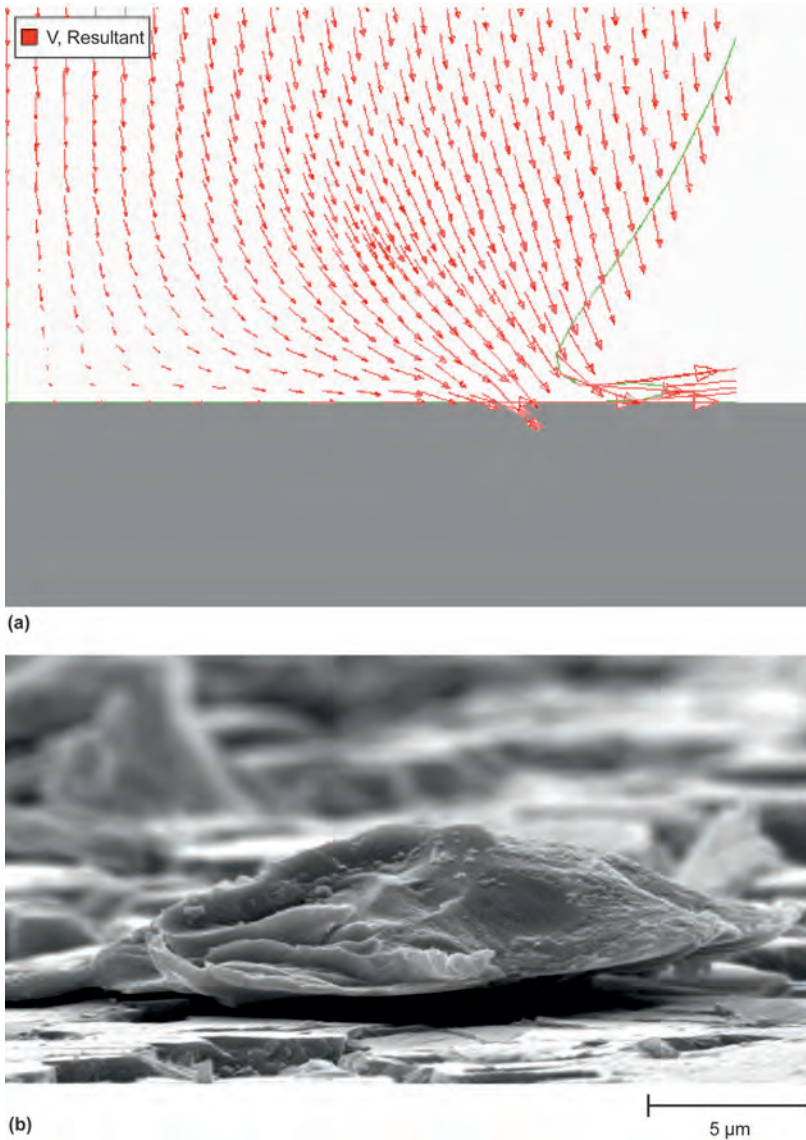


Fig. 2.17 (a) Two-dimensional simulation results of the impact of Cu onto a rigid substrate showing the velocity vectors for each volume cell for an impact velocity of 500 m/s (1650 ft/s). At the interface between particle and substrate, the flow direction is outward. (b) Single impact of a copper particle cold sprayed onto a suspension high-velocity oxyfuel-sprayed Al_2O_3 layer

to adsorbants on the surface of the ceramic. Comprehensive investigations on direct coating of ceramics with copper (Ref 2.95) show that preheating of the substrates can also facilitate coating formation (Fig. 2.18b), even under high process parameters (process gas pressure of 3 MPa, or 435 psi; process gas temperature of 600 °C, or 1110 °F). The absence of cracks

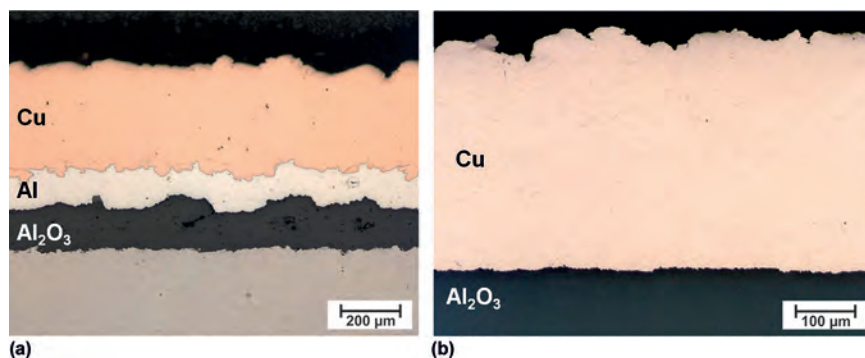


Fig. 2.18 Optical micrographs of cold-sprayed copper coatings on thermally sprayed Al_2O_3 coatings. (a) Copper on a cold-sprayed aluminum bond coat, processed onto a D-gun-sprayed Al_2O_3 coating using a nonheated substrate. (b) Copper directly cold sprayed onto a suspension high-velocity oxyfuel-sprayed Al_2O_3 coating, preheated to 350 °C (660 °F)

may be explained by a higher fracture toughness of the ceramic substrate at elevated temperature.

In summary, modified parameters may be needed in the case of mismatched particle/substrate mechanical properties. In such a case, optimization may be sought in terms of “critical deceleration” rather than critical velocity. Critical deceleration would correlate with the critical impact velocity for identical substrate and particle materials but would be reached at lower particle velocities for harder substrates.

2.4 Parameters for Improved Coating Quality

Whether critical conditions for successful bonding are met or not depends on several process and powder parameters. This section elucidates the influence and interdependence of different parameters with respect to reaching optimum conditions for coating formation. Impact velocity and impact temperature of a particle are the main critical process parameters that determine the impact behavior of the particle and its successful bonding. The impact temperature affects the deformability and strength of the particle, and the impact velocity affects the resulting strain rate.

At first glance, one may expect that the bonding process at a given temperature and for a sufficiently ductile material is directly related to the kinetic energy of a particle, that is, its velocity and mass (particle size or material density). However, this view does not reflect the complexity of the process, because the local temperature at the interface is strongly affected by the time and volume in which this kinetic energy is converted to heat. The deformation time is related to the impact velocity and tends to have an effect opposite to that of heat dissipation time. The deformation

volume is related to the mechanical properties of the material and the size of the impacting particle. Together, these influence the local deformation rates and thus determine the conditions for the formation of ASI and their possible extent along particle-particle or particle-substrate interfaces. Because the amount of bonded interfaces by ASI directly correlates with the attained coating properties, a more detailed discussion of the different parameters is required. Certainly all the different parameters are somewhat interdependent, but their influences are discussed separately with respect to the process variables.

Beyond the Critical Velocity—Window of Deposition. The concept of critical velocity is illustrated in Fig. 2.2. In reality, there is a range of particle velocities for every cold spraying condition, so deposition should be discussed in terms of an average particle velocity. The (technical) critical velocity required for bonding is defined at a deposition efficiency of 50% of the impacting particle mass (Ref 2.41). Even for a monosized powder, there is a velocity distribution that is due to nonuniform gas velocities over the nozzle cross section by friction at the nozzle walls. Moreover, as previously discussed, any group of particles constitutes a certain particle size distribution, and the individual particles actually have different size-specific or true critical velocities. Consequently, the technical critical velocity, as defined via deposition efficiency, in principle includes the weighted average of the distributions of the true critical velocities and of the respective size-dependent impact velocities resulting from the various processing conditions. Thus, this definition should only be used as a guide for average conditions, for example, to estimate costs for production of parts.

Equation 3.4 in Chapter 3, “Modeling and Simulation of Cold Spray,” in this book presents the critical velocity as a function of particle strength, particle density, particle impact temperature, melting temperature, and heat capacity. As previously stressed, the critical velocity must be exceeded to attain high amounts of bonded interfaces and thus good coating qualities. For example, for cold spraying of copper, Fig. 2.19 compares deposition efficiencies (DEs) and attainable mechanical strengths over a range of impact velocities.

Merely exceeding the technical critical velocity, even achieving a DE of almost 100%, does not guarantee high mechanical strength. For optimum bonding of the particles to the substrate or to already adhering particles, substantially higher impact velocity may be required to ensure extensive areas of ASI. Exceeding critical conditions for bonding to higher levels also results in a more pronounced flattening of the particles. Under such conditions, the bonding of each particle and, consequently, the mechanical properties of the coating are significantly improved. Any excess of velocity for a given temperature after reaching maximum DE will be converted to an increased fraction of well-bonded area, resulting in an improved tensile strength of the coating.

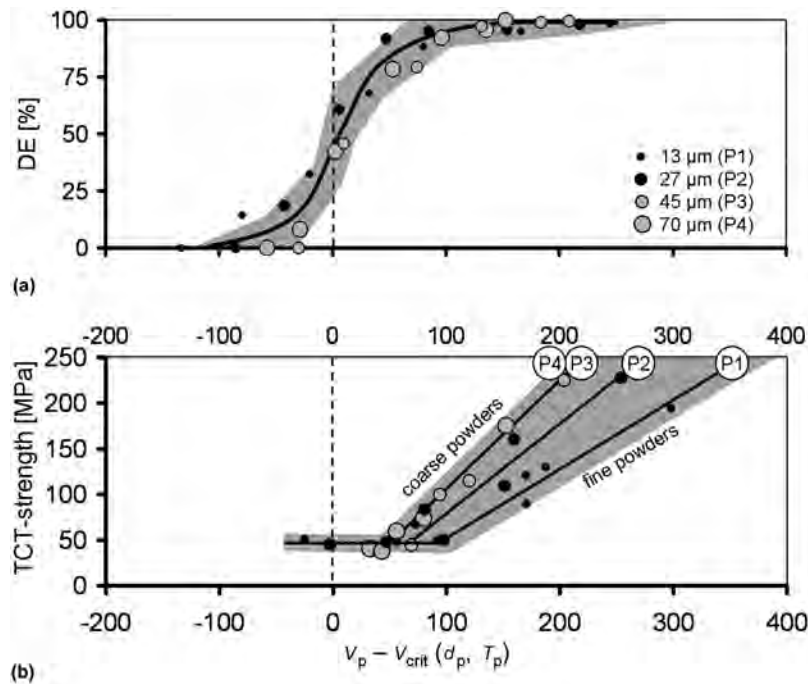


Fig. 2.19 Attainable (a) deposition efficiencies (DE) and (b) tubular coating tensile (TCT) strengths for cold spraying copper in different powder size cuts as a function of the particle velocity excess with respect to critical velocity. Source: Ref 2.34

However, at too high an impact velocity, erosion related to hydrodynamic processes can take place. The area between the critical and erosion velocities defines the window of deposition (WoD) (Ref 2.41). Figure 2.20 shows the WoD as a function of temperature for the case of cold spraying copper (Ref 2.34). The technical critical and erosion velocities are functions of temperature, because the temperature influences deformability and strength of a material. For pure metals and most other alloys, strength decreases with increasing temperature, and kinetic impact energy can therefore be replaced partially by thermal impact energy. Optimum mechanical properties of the coating are usually achieved if the impact conditions are in the upper range of the WoD. The influences of different powder and process parameters on the resulting impact velocity and impact temperature are described subsequently.

Influence of Powder Particle Size. The particle size determines impact velocity, impact temperature, critical velocity, and process stability and is therefore one of the most important parameters for fine-tuning coating formation and properties according to the mechanisms discussed previously (Ref 2.41). The schematic in Fig. 2.21 shows the critical velocities and impact velocities for a certain spray parameter set as functions of particle size. As illustrated in the figure, the particle impact velocity curve

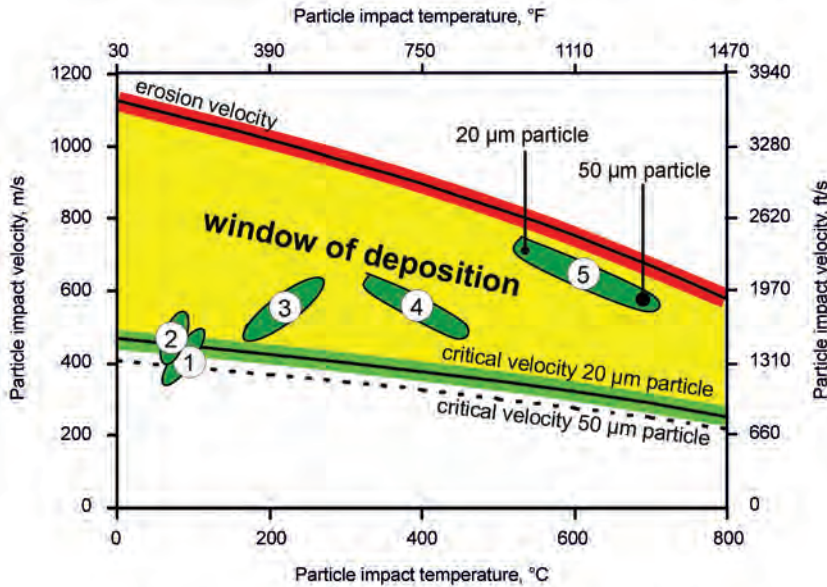


Fig. 2.20 Window of deposition for cold spraying copper as a function of particle temperature and velocity. The impact conditions for copper refer to process parameters by spraying with nitrogen as a process gas under (1, 2) $p_{\text{gas}} = 3 \text{ MPa}$ (435 psi) and $T_{\text{gas}} = 300 \text{ °C}$ (570 °F), using trumpet- and bell-shaped nozzle geometries, (3) $p_{\text{gas}} = 3 \text{ MPa}$ and $T_{\text{gas}} = 600 \text{ °C}$ (1110 °F), (4) $p_{\text{gas}} = 3 \text{ MPa}$ and $T_{\text{gas}} = 600 \text{ °C}$, and (5) $p_{\text{gas}} = 4 \text{ MPa}$ (580 psi) and $T_{\text{gas}} = 900 \text{ °C}$ (1650 °F). The higher impact temperatures in (4) and (5) were achieved by injecting the spray powder further upstream from the nozzle throat (–135 mm, or –5.3 in., instead of –25 mm, or –1 in.). The range of impact conditions covers the size distribution of the given spray feedstock. More details are given in Ref 2.34.

intersects that of the critical velocity twice, showing that too-small and too-large particles will not contribute to coating formation. The different size dependencies are explained as follows. Figure 2.22 shows the calculated gas as well as particle temperatures and velocities over the path through prechamber, nozzle, and free jet for the cold spraying of pure nickel powder. In addition, respective impact conditions within the WoD are displayed. This subject is discussed further in Chapter 3, “Modeling and Simulation of Cold Spray,” in this book.

Smaller particles have smaller moments of inertia. Therefore, acceleration in the gas stream is fast and these particles reach higher velocities than the larger ones (compare Fig. 2.22c and d). However, the bow shock in front of the substrate, which slows down the particles to a certain extent, also must be considered. The bow shock develops as a half-moon-shaped zone of stagnant gas pressure and is due to the slowdown of the gas to zero velocity right on the substrate surface. For smaller particles with their lower moments of inertia, the slow-down effect is more pronounced than for larger ones. Below a critical moment of inertia, this may lead to deflection to the sides with the gas stream, so these smallest parti-

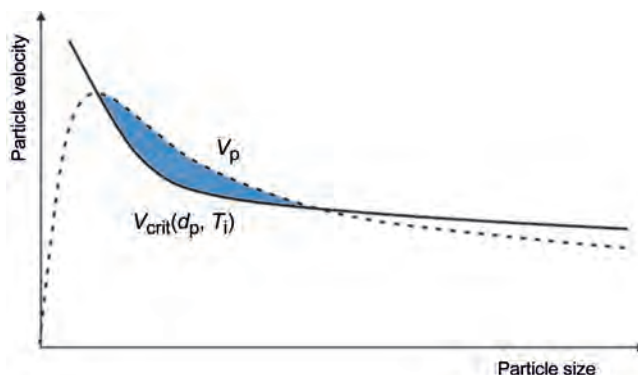


Fig. 2.21 Particle velocity and critical velocity for given process parameters as a function of particle size (schematic). Successful deposition is possible only if the particle impact velocity exceeds the critical velocity. Thus, the powder size distribution should be in the range between the two intersections of the curve.

cles do not deposit. This critical moment of inertia depends not only on the size of the particle but also on its mass and thus on the density of the material. For example, the lower critical size for copper is approximately $5\ \mu\text{m}$.

Smaller particles also have smaller thermal inertia and therefore reach the temperature of the propellant gas very quickly. They heat up quickly while traveling in the hot gas stream before the throat of the nozzle, but they also cool down quickly in the expanding gas stream. Bigger particles heat up more slowly to the core but can store more heat. Thus, it makes sense to choose a longer preheating time, so that bigger particles can reach temperatures close to the gas temperature (compare Fig. 2.22a and b). Because of the higher thermal momentum, the bigger particles lose little thermal energy in the expanding gas stream. Because they travel at high velocity, the time for cooling is limited. Consequently, with sufficient preheating, bigger particles typically impact at higher temperatures than smaller ones. Achieving this result may require a point of particle injection higher upstream of the nozzle throat for preheating or other means of preheating. This point is discussed in the requirements for cold spray equipment.

Smaller particles have a higher critical velocity for bonding. This higher value is due to heat dissipation, which is discussed briefly here and in more detail in Chapter 3, “Modeling and Simulation of Cold Spray,” in this book.

Regarding the deformation process upon impact itself, everything scales linearly with particle size; that is, a particle half the size has half the deformation zone thickness (x) but also takes half the time (t) for deformation from first contact to zero velocity. Thermal heat dissipation, however, is relatively faster for smaller particles. In detail, for a given temperature,

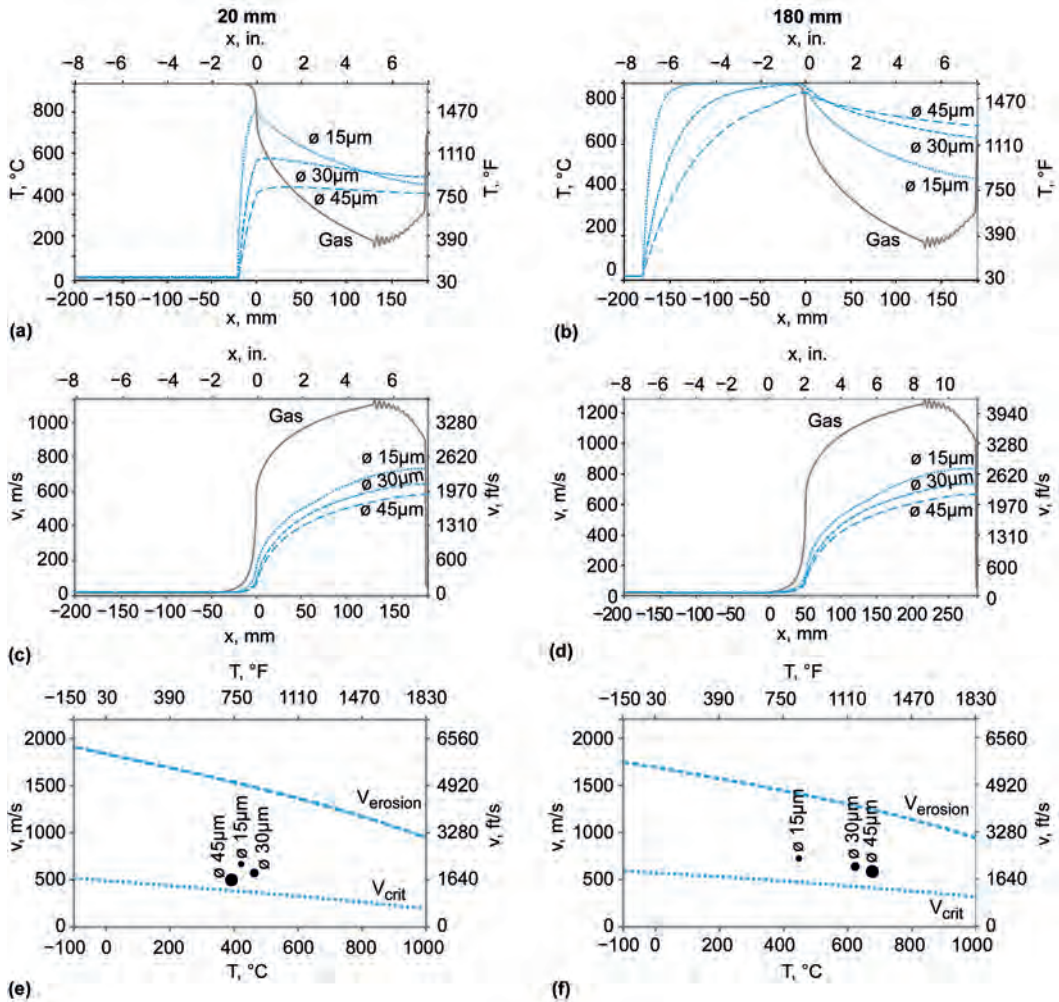


Fig. 2.22 Influence of different powder injection points before the nozzle throat (20 mm, or 0.8 in., in a, c, and e versus 180 mm, or 7 in., in b, d, and f) on (a, b) particle heating, (c, d) acceleration, and (e, f) impact parameters within the window of deposition. The calculations were performed for cold spraying commercially pure nickel (Ni-99.7) at a process gas temperature of 900 °C (1650 °F) and a process gas pressure of 4 MPa (580 psi). Courtesy of Kinetic Spray Solutions, Buchholz, Germany

heat travel distance is proportional to square root of time. Thus, x/t is constant and does not depend on particle size. Cutting the diameter of the particle in half reduces the heat dissipation time to one-quarter of the time for the original particle. Conversely, the deformation zone of a double-sized particle is twice as wide and the time for the deformation process is twice as long, so the time needed to transport the heat from the deformation zone is four times as long, and this zone stays at a higher temperature for a longer time. In other words, the shearing process for the smaller particles is less adiabatic because the heat is spread over a larger volume

in proportion to particle size. This factor is especially important for materials with high heat conductivity, such as copper and aluminum alloys (Ref 2.41).

Interestingly, the deformation and conversion to heat does not depend on kinetic impact energy but only on velocity; that is, neither particle size nor material density are important for the maximum temperature in the interface, but only velocity. A higher velocity decreases the time for heat dissipation and therefore increases adiabaticity. Similarly, strain-rate hardening effects are more critical for smaller particles, because a more pronounced strain-rate hardening will result in larger deformation zones, that is, decreased adiabaticity, which is more problematic for smaller particles.

The foregoing discussion demonstrates that the interplay between particle velocity and critical velocity on the needed excess velocity for bonding is quite complex with respect to powder size selection and requires comprehensive calculations and modeling for systematic optimization.

Powder particle size distribution is also important for the stability of the cold spray process. As discussed previously, smaller particles are accelerated more rapidly than larger ones. If the powder feed rate is in a viable range for actual production of parts, the smaller particles may hit larger particles, generally resulting in a velocity vector component perpendicular to the nozzle axis. Consequently, some smaller particles may hit the nozzle and deposit inside, finally leading to nozzle clogging. Thus, a more narrow size distribution is always advisable and will lead to more homogeneous acceleration and deposition. In addition, smaller particles show poorer flowability than larger ones. Thus, with smaller particles, powder feeding may be not continuous or even not possible at all, limiting the process reliability.

Impact velocities can be increased by gas pressure and temperature, and critical velocities can be decreased by higher particle temperatures attained in hotter gas jets or by more efficient powder preheating. Thus, particle sizes and process conditions should be well tuned for optimum process efficiency and coating performance, as further discussed in the following sections.

Influence of Powder Injection on Particle Temperature. The particle impact temperature can be adjusted via the process gas temperature or by a systematic choice of particle sizes and powder preheating. As noted previously, the point of powder injection determines the time that particles are exposed to the gas jet and respective heating or cooling. Larger particles have more “thermal momentum,” that is, they do not cool down as fast in the expanding gas stream if they are sufficiently preheated as small particles, simply because they can store more heat. In cases of upstream powder injection, sufficient preheating of particles can be achieved by using elongated prechambers, in which the particles are in contact with the hot gas for a longer time before passing through the throat of the nozzle,

as discussed in Chapter 3, “Modeling and Simulation of Cold Spray,” in this book and in Ref 2.34 and 2.95, or by separate heating in the powder feed line (Ref 2.74, 2.84, 2.97–2.99). Figure 2.22(a) and (b) shows examples of calculated particle temperatures for two different prechamber lengths during cold spraying of nickel. Smaller particles will always adopt the gas temperature rather quickly, and because of the fast cooldown upon expansion of the gas, their impact temperature cannot be improved by longer preheating. In contrast, the impact temperature of larger particles increases substantially with initially attained temperatures before the nozzle throat. For larger particles, such preheating is particularly beneficial because higher temperature helps to compensate for the lack of energy due to smaller impact velocities as compared to smaller particles (compare Fig. 2.22c and d). In cases of downstream powder injection, particles are mainly cooled by the expanding gas stream. Higher particle temperatures can then be realized only by external powder preheating. In summary, sufficient powder preheating allows adjustment of the powder impact conditions with respect to the temperature dependence of the critical velocity, as shown in Fig. 2.22(e) and (f).

Influence of Process Gas Temperature and Pressure. At the nozzle throat, the process gas travels with the velocity of sound, which is dependent on the type of gas and the gas temperature. Any increase in gas temperature results in higher gas velocities in the smallest cross section and thus in the expanding regime of the nozzle. In consequence, particle velocities are increased. A higher gas pressure increases the drag force for accelerating the particles, so that (all else being equal) particle velocities increase with process gas pressure. Nevertheless, a higher gas pressure also increases bow shock effects, which could decelerate particles in front of the substrate; this effect may be particularly prominent for smaller particles and for spray materials with low density, such as aluminum. If the particles have enough time to pick up sufficient heat from the hot gas before the nozzle throat, their temperatures will also be increased by spraying with higher gas temperatures. In consequence, impact conditions are improved by both higher velocities and higher temperatures.

The calculated impact conditions for particles of different sizes in the WoD given in Fig. 2.22(e) and (f) for the example of cold spraying nickel also demonstrate the cooling in the expanding regime of the nozzle. Particles of all sizes reach the process gas temperature before the nozzle throat, but then by cooling in the expanding regime, cool down to quite different temperatures (Fig. 2.22c, d). An increased pressure and thus higher heat capacity of the process gas could be beneficial for heating up larger particles before the nozzle throat. Downstream from the nozzle throat, a higher gas pressure enhances cooling in the expanding gas jet, which must be considered for small particles of low-density materials. In summary, process gas temperature and pressure must be finely tuned with respect to the spray material of choice. Under ideal conditions, calculation

of impact conditions will also provide a basis for the selection of particle sizes to exceed the critical condition for optimum bonding.

The calculations for cold spraying nickel at a process gas temperature of 900 °C (1650 °F) and a process gas pressure of 4 MPa (580 psi) demonstrate that the powder impact conditions in the WoD are well above critical conditions for bonding (Fig. 2.22e, f). Cold spray experiments proved that dense nickel coatings can be produced at process gas temperatures between 800 and 1000 °C (1470 and 1830 °F) ($p_{\text{gas}} = 4 \text{ MPa}$) (Ref 2.100). The respective coating cross sections for both conditions in Fig. 2.23 do not show any porosity. Nevertheless, such absence of porosity provides no information on real coating quality. As an example, Fig. 2.24 compares attained coating hardness and coating strength for different cold spray conditions. By increasing the process gas temperature from 800 to 1000 °C, the ultimate coating strength can nearly be doubled from approximately 270 to approximately 500 MPa (40 to 70 ksi) by enhanced

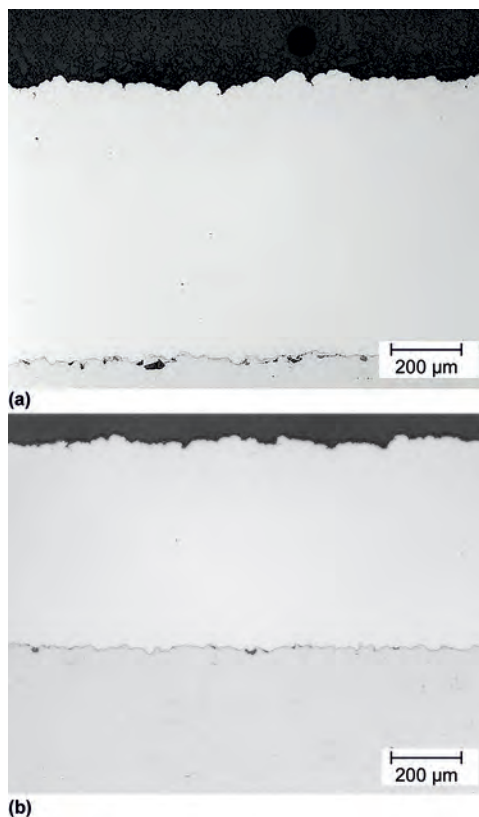


Fig. 2.23 Microstructures of commercially pure nickel (Ni-99.7) coatings, cold sprayed with nitrogen as process gas at a process gas pressure of 4 MPa (580 psi) and process gas temperatures of (a) 800 °C (1470 °F) and (b) 1000 °C (1830 °F). Both coatings are dense, showing no internal porosity.

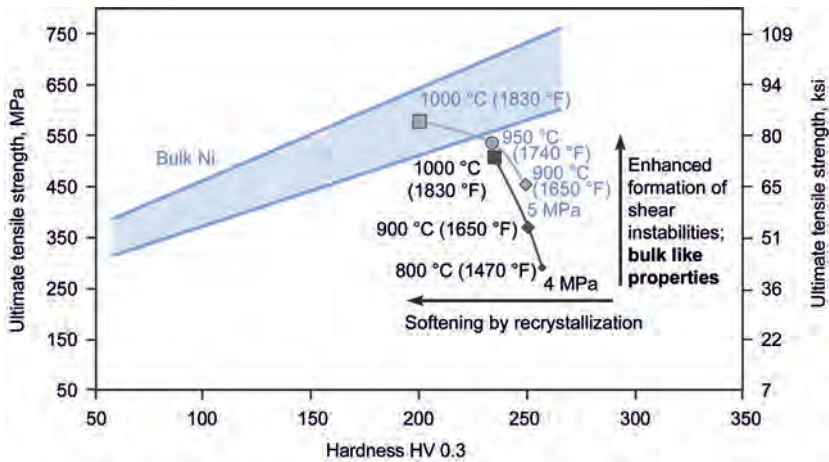


Fig. 2.24 Correlation between coating strength and coating hardness for different process conditions in cold spraying commercially pure nickel with nitrogen as process gas. The data range for differently work-hardened bulk material is shown for comparison. By using higher spray parameter sets, the coating strength can be significantly improved, achieving the range of deformed bulk nickel. The associated reduction in coating hardness for higher spray parameter sets is probably due to thermal recrystallization.

formation of ASI. By an increase of the process gas pressure from 4 to 5 MPa (580 to 725 psi) at high gas temperatures, strengths comparable to that of work-hardened bulk nickel can be obtained.

The associated slight decrease of coating hardness for cold spraying at higher process gas temperatures can be attributed to softening by thermal recrystallization of the highly strain-hardened coatings. On the one hand, the higher gas and particle impact temperatures result in higher substrate temperatures. On the other hand, a higher degree of deformation results in lower recrystallization temperatures. The example also demonstrates that coating hardness fails to provide information on coating quality. The resistance against deformation under compression only reflects the degree of work hardening or, for less-well-sprayed coatings, the amount of porosity. Information on well-bonded particle-particle interfaces can be obtained only by mechanical tensile tests (Ref 2.101).

Influence of Nozzle Design. The expansion ratio of the nozzle determines the gas velocity and temperature at the nozzle exit. The length and geometry of the nozzle determines the acceleration profile of spray particles, as discussed in Chapter 3, “Modeling and Simulation of Cold Spray,” in this book. Thus, under ideal conditions, specific nozzle designs should account for individual spray material densities and particular powder-size distributions to guarantee maximum acceleration of spray particles. In reality, the differences are less pronounced, and a certain nozzle design can be applied to a range of powder specifications. Geometries computed according to the method of characteristics (Ref 2.34, 2.102) provide homo-

geneous laminar flow and acceleration of the process gas and spray particles. In addition, with a nearly parallel gas stream at the nozzle exit, intermixing with the ambient atmosphere and the development of shock diamonds can be reduced, resulting in less turbulent flow and thus higher velocities.

Moreover, the absolute diameter of the nozzle is important. At the inner nozzle wall, the gas velocity is zero as a result of friction. The larger the nozzle diameter, the smaller is the influence of this friction layer. In other words, the smaller the nozzle diameter, the larger is the volume fraction of the gas that will experience friction effects. Thus, the average gas velocity decreases with decreasing nozzle cross section. This results in different particle velocities. Figure 2.25 compares experimentally obtained particle velocities in cold spraying using different geometries. The spray conditions with respect to gas pressure and temperature were adjusted for respective generations of spray systems. Calculated impact conditions for cold spraying titanium with different nozzle types are given in Fig. 2.26. Employing a wider nozzle can result in 60 m/s (200 ft/s) higher particle velocities (Ref 2.103). Reduced particle impact temperatures by alterna-

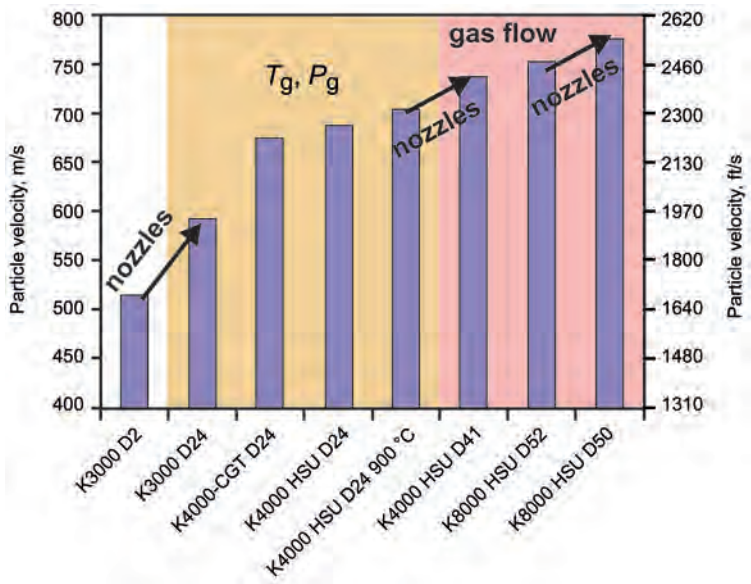


Fig. 2.25 Measured average particle velocities of an Al_2O_3 powder ($-90 + 45 \mu\text{m}$) for different spray systems and nozzles. Gas pressure and temperature: 3 MPa /500 °C (435 psi/930 °F) for K3000; 4 MPa /800 °C (580 psi/1470 °F) for K4000 and K8000. The velocity for K4000 with nozzle D24 at 900 °C (1650 °F) is also given for comparison. Nozzle differences concern throat diameters (D), expansion ratios (E), and lengths of diverging section (L), with type 2, trumpet shape ($D = 2.7 \text{ mm}$, or 0.1 in.; $E = 8.8$; $L = 75 \text{ mm}$, or 3 in.); 24, bell shape ($D = 2.7 \text{ mm}$; $E = 5.6$; $L = 130 \text{ mm}$, or 5 in.); 41, bell shape ($D = 2.7 \text{ mm}$; $E = 8.9$; $L = 230 \text{ mm}$, or 9 in.); 52, bell shape ($D = 3.3 \text{ mm}$, or 0.13 in.; $E = 7.6$; $L = 230 \text{ mm}$); 50, bell shape ($D = 3.8 \text{ mm}$, or 0.15 in.; $E = 7.6$; $L = 230 \text{ mm}$)

tive nozzle design are mainly due to larger expansion ratios and longer nozzle lengths. Further details are discussed in Chapter 3, “Modeling and Simulation of Cold Spray,” in this book.

Influence of Kinematic Parameters of the Gun/Substrate Manipulation System. Bonding quality in cold spraying depends not only on primary spray conditions but also on substrate temperatures (Ref 2.29, 2.63, 2.94, 2.104–2.107). Locally achieved substrate temperatures depend on spray conditions and on the kinematic parameters during coating processing (Ref 2.108). The temperature of the substrate will decrease with higher gun traverse speed and higher stand-off distance between gun and substrate. Conversely, lower traverse speed and lower stand-off distance will lead to higher temperatures of the already deposited layers, thus causing thermal softening on substrate sites and potentially allowing the formation of ASI and thus better bonded interfaces than on cooler substrates. There is, however, a trade-off, because at higher temperatures, most materials are prone to react more strongly with the surrounding atmosphere. Thus, the coating may ultimately have higher impurity contents.

In summary, the effective substrate temperature, as adjusted by direct heating or kinematics during spraying, plays an additional, important role for coating quality. Because effective substrate temperatures may differ

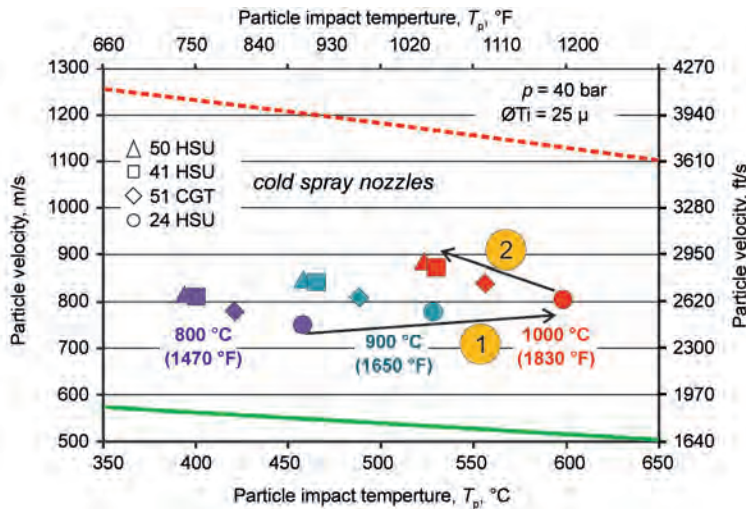


Fig. 2.26 Calculated velocities of titanium particles with a diameter of 25 μ m for cold spraying with different gas temperatures (1) and different nozzle geometries (2) in comparison to the critical velocity. Nozzles differ in throat diameters (D), expansion ratios (E), and lengths of diverging section (L), with type 24 ($D = 2.7$ mm, or 0.1 in.; $E = 5.6$; $L = 130$ mm, or 5 in.); 51 ($D = 3.3$ mm, or 0.13 in.; $E = 6.4$; $L = 180$ mm, or 7 in.); 41 ($D = 2.7$ mm; $E = 8.9$; $L = 230$ mm, or 9 in.); 50 ($D = 3.8$ mm, or 0.15 in.; $E = 7.6$; $L = 230$ mm). Wider nozzle throats, larger expansion ratios, and longer nozzle lengths account for higher particle velocities. Low particle impact temperatures are mainly due to larger expansion ratios and longer nozzle lengths.

for the individual spray passes or spray layers in building up a full coating (Ref 2.55, 2.109), coating quality may eventually vary for the layers deposited in different passes.

In addition to thermal factors, the impact angle influences the deformation upon impact and thus coating quality (Ref 2.35, 2.110). For the formation of ASI, the velocity vector perpendicular to the surface is relevant. Thus, the coating quality scales with the sine of the impact angle, meaning that perpendicular impacts (90 ± 10) would be favorable. In practice, staying within the range of optimum spray angles could become difficult for cold spraying onto complex parts or dealing with repair work. Complex parts demand sophisticated robotics that guarantee close-to-perpendicular impact angles and constant local traverse speeds. With respect to repair, machining of worn parts must be performed in such a way that spray angles do not deviate much from perpendicular impacts (Ref 2.103).

2.5 Requirements for Cold Spray Equipment

Cold spray equipment has been continuously developed to achieve optimum impact conditions for a large variety of materials, that is, to increase the range of pressures and temperatures for higher powder impact velocities and temperatures. Metals that show low strength or low melting temperature can be successfully deposited by moderate conditions, using less-expensive low pressure/low-temperature equipment. More powerful equipment providing higher pressures and higher temperatures becomes necessary for processing high-strength materials. Higher pressures and nozzles with larger throat diameter allow for higher impact velocities. Higher nominal power allows for higher process gas temperature. Higher process gas temperatures yield two positive effects: the velocity of sound, which is reached in the smallest cross section of the nozzle, increases and thus, so does the achievable particle velocity; and higher particle impact temperatures enhancing thermal softening, which decrease the critical velocity. Together, these effects result in a higher excess above critical conditions or, more precisely, in a higher coating quality parameter, η , defined as the ratio between impact velocity and critical velocity (see Chapter 3, “Modeling and Simulation of Cold Spray,” in this book). Thus, better coating qualities can be obtained by spraying with higher process gas temperatures. Different manufacturers provide different cold spray facilities, each with its own particular advantages for certain materials and applications. The range of available cold spray systems is the topic of Chapter 4, “Cold Spray Equipment,” in this book. Here, only the main points from the scientific point of view are addressed, that is, opportunities to adjust and fine-tune the required particle temperature and velocity for successful bonding upon impact.

Adjusting Particle Impact Temperature. The particle impact temperature can be adjusted via the process gas temperature or by a systematic

choice of particle sizes and preheating. As noted earlier, larger particles have more “thermal momentum;” that is, they do not cool down as fast as small particles in the expanding gas stream if they are sufficiently preheated, simply because they can store more heat (see the section “Influence of Powder Injection on Particle Temperature” in this chapter for further details). This effect can be effectively utilized only if the powder injection velocity is not too high, that is, if injection tubes are wide enough and the gas flow through the powder feeder is not too high.

By using both higher process gas temperatures and powder preheating in connection with larger particle sizes, better impact conditions within the WoD can be achieved, yielding improved coating properties. However, higher temperatures may also facilitate reactions with the ambient atmosphere or nitrogen, so impurity levels should be checked carefully. Moreover, higher temperatures increase the risks of nozzle clogging.

Nozzle clogging has so far been the predominant problem for cold spraying of aluminum- and nickel-base alloys. Therefore, process parameters have until recently been limited to values that lead only to unsatisfactory coating qualities. For cold spraying of nickel, a breakthrough was achieved by using water-cooled nozzles, for example, enabling a rise of the process gas temperatures from 700 to 1000 °C (1290 to 1830 °F) without the risk of nozzle clogging (Ref 2.100). Under such conditions with, respectively, high particle impact temperatures and velocities, nickel coatings could be processed as dense and corrosion-resistant coatings.

Apart from water cooling, also the choice of nozzle material can be decisive for avoiding nozzle clogging. For aluminum, nozzles made of polybenzimidazole or silicon carbide offer advantages to operating at higher process gas temperatures (see Chapter 4, “Cold Spray Equipment,” in this book). Nevertheless, nozzle clogging is still one major limiting factor in enhancing process gas temperatures in cold spraying, and more work is underway to find possible solutions.

Adjusting Particle Impact Velocity. Alternatively to the use of high process gas temperatures, improved impact conditions may also be achieved by increasing particle velocities using higher gas pressures, expensive helium instead of nitrogen, or specially designed nozzles.

Higher velocities may be reached by further increasing process gas pressures. This increase imposes certain technical challenges at high temperatures for the gun material and may be less energy efficient than the other measures. However, impact conditions using nitrogen have been significantly improved by increasing the pressure to 6 MPa (870 psi) for certain materials (e.g., titanium) (Ref 2.111), and further increases may be feasible. Apart from technical challenges, too-high process gas pressures may be economically unfavorable because of the high gas consumption that scales with pressure.

The velocity of sound scales with the density of a gas. Therefore, helium reaches substantially higher velocities if passing through a de Laval

nozzle than nitrogen does. However, helium is also a substantially more expensive and limited resource, so its use will be reasonable only for particular cases or when a helium recycling system has been installed (Ref 2.112).

Apart from process gas temperature, nozzle design is critical and is the most economical way to optimize an existing setup. Fluid dynamic calculations demonstrate that boundary layer phenomena within the nozzle lead to a significant loss in energy for narrower nozzles and make the process less efficient. As discussed previously, wider nozzles minimize the influence of this boundary layer and increase mean particle velocity (compare Fig. 2.25 and 2.26). The practice of using wider nozzles has further advantages by allowing for higher powder feed rates, without reducing particle velocities by too-high mass loads in comparison to gas mass flow. By using two powder feeders and a nozzle with a throat diameter of 3.8 mm (0.15 in.), 15 kg (33 lb) of copper could be sprayed per hour without exceeding a powder mass load of approximately 10% (Ref 2.113).

Concerning equipment, further research is in progress that allows for cold spraying high-strength alloys or for offering special solutions. Further details are provided in Chapter 4, “Cold Spray Equipment,” in this book.

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CHAPTER 3

Modeling and Simulation of Cold Spray

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A CENTRAL CONCEPT IN COLD SPRAYING of metallic materials is that deposition takes place if the particle velocity upon impact, v_p , becomes greater than a critical velocity, v_{cr} (Ref 3.1–3.4). A further conjecture is that the quality of cold-sprayed deposits depends on the ratio of v_p to v_{cr} ; for example, the tensile strength of the cold-sprayed coating increases linearly with increasing $\eta = v_p/v_{cr}$ (Ref 3.5). Therefore, to ensure successful and optimized cold spraying, the influence of various process and material parameters on both v_p and v_{cr} should be well understood. Application of modeling and simulation in cold spray research is a robust and feasible way to reach this goal.

The critical velocity can be conceived as a powder characteristic that depends mainly on material properties. On the other hand, the particle velocity and temperature, v_p and T_p , can be regarded as impact conditions that depend mainly on the process parameters, such as gas temperature, gas pressure, and nozzle dimensions. There is also an influence of the particle temperature on the critical velocity, which effectively makes the powder characteristics vary when the process parameters are changed. As shown in Table 3.1, some parameters influence both v_p and v_{cr} , while others influence either v_p or v_{cr} . Moreover, many of these correlations, such as that concerning the particle size, do not follow a monotonic trend (Ref

Table 3.1 Effect of key materials and process parameters on v_p and v_{cr}

Parameter	Effect on v_p	Effect on T_p	Effect on v_{cr}
Particle			
Melting temperature	...	...	↑
Specific heat	...	↑↓	↑↓
Hardness	...	...	↑
Density	↑↓	↑↓	↑↓
Size	↑↓	↑↓	↑↓
Gas			
Temperature	↑	↑	↓(a)
Pressure	↑↓	...	...
Nozzle			
Length	↑	↑↓	↑↓

(a) In special cases, for example, Ni3Al, where the material strength increases with increasing temperature up to 800 °C (1470 °F), an increase in particle temperature may result in an increase in the critical velocity.

3.5). These complex dependencies pose a challenging optimization problem. Modeling and simulation of cold spray is particularly aimed at this problem and is intended to provide a means to understand and explicitly express these dependencies.

The modeling and simulation activities in the field of cold spray can be divided into two main parts:

- *Solid mechanics*: mainly to study particle deformation and bonding during impact
- *Fluid dynamics*: mainly to work out particle velocity and particle temperature

There are additional modeling activities that are relevant to cold spray research but are aimed at problems different from the aforementioned objectives. Examples include modeling of substrate heating and buildup of residual stresses in cold spraying (Ref 3.6). This chapter focuses on the previously mentioned two main parts of modeling work in cold spray research.

3.1 Modeling and Simulation of Particle Impact

Bonding and deposition in cold spraying are understood to be closely connected to the thermomechanical phenomena pertaining to high-velocity impact of particles. Direct experimental study of these phenomena is nevertheless difficult, if not impossible, because of the associated small time and length scales—nanosecond and micrometer, respectively. The dynamic and stochastic nature of particle impact during cold spraying also makes it almost impossible to perform any in situ experimental observations. For this reason, modeling and numerical analysis of particle impact have been used to complement experimental studies in cold spray research.

Aims and Questions

The main objective in modeling of particle impact is to investigate the deformation process, and related phenomena during impact, which lead to particle bonding and deposition. A general question concerns the mechanism of bonding at the microstructural level: Under what conditions, and to what extent, will metallurgical bonding occur between a substrate and an impinging particle? This question is pursued mainly to allow prediction of conditions that lead to successful cold spray deposition for different combinations of material and process parameters. More specific questions in the study of particle impact concern the following topics:

- Overall deformation of particles as a result of initial and secondary impacts; morphological aspects of particle bonding and deposition
- Localization of deformation and shear instability; development of mechanical and temperature field variables at the interface of particle and substrate; bonding mechanisms
- Estimation of critical velocity for bonding (and/or erosion) for a given set of material parameters, particle size, and particle impact temperature
- Mechanical state of the deposit, for example, in relation to residual stresses; phase transformation and microstructural changes

These questions are normally pursued within the framework of a parameter study, for example, to investigate the effect of various material properties and process parameters on the deposition efficiency and on the final properties of cold-sprayed deposits (Ref 3.5, 3.7, 3.8).

Apart from the main factors listed in Table 3.1, numerical investigations can be used to study the effect of other influential factors in cold spraying. Some of these factors include:

- Properties, temperature, and surface condition of the substrate, especially when these are different from those of the impinging particles
- Morphology, ductility/brittleness, strength-temperature dependencies, structural inhomogeneity (e.g., in the case of composites or agglomerates), and surface condition of the particles
- Particle size distribution and volume or mass fraction (in case of powder mixtures) of the feedstock powder
- Spraying angle and its effect on the deposition efficiency and coating quality

Underlying Physical Phenomena

There are several physical phenomena that can play a role during the impact and bonding process. In fact, it is normally not the process of particle bonding that is modeled; it is rather the relevant physical processes

pertaining to particle bonding that are described or illustrated through mathematical modeling or numerical simulation. These physical phenomena and the corresponding models are discussed subsequently.

Deformation and Materials Models. The process of deformation plays the key role in accommodation of particles in a cold-sprayed deposit. Therefore, almost all models of particle impact and bonding start with the analysis of plastic deformation of particles during impact and bonding. This is often pursued through continuum-level models of deformation, which have been widely used in cold spray research. The constitutive plastic properties of the involved materials are the main input to these models. For the case of metallic materials, the deformation is normally considered to be viscoplastic, that is, strain-rate dependent, and hence described as a relationship between the flow stress on one side and the plastic strain, strain rate, and temperature on the other side. The temperature dependence of the flow stress in these material models is based on the consideration of thermally activated dislocation mechanics, which is generally manifested as thermal softening, not considering microstructural changes. A well-known and widely used example of models that describe viscoplastic response of materials at high strain rate is the Johnson-Cook plasticity model (Ref 3.9):

$$\sigma = (A + B\varepsilon^n)(1 + C \ln \dot{\varepsilon}^*)(1 - T^{*m}) \quad (\text{Eq 3.1})$$

where σ is the flow stress; ε is the equivalent plastic strain; $\dot{\varepsilon}^*$ is the equivalent plastic strain rate normalized with respect to a reference strain rate; $T^* = (T - T_{\text{ref}})/(T_m - T_{\text{ref}})$, in which T_{ref} is the temperature above which thermal softening is considered to occur, and T_m is the melting temperature; and A , B , n , and m are material constants. Alternative models that describe viscoplastic response of materials include the Steinberg-Cochran-Guinan-Lund model (Ref 3.10, 3.11) and the Zerilli-Armstrong model (Ref 3.12). The selection of appropriate material model is made with respect to availability of the material parameters and also with the aim of obtaining the most realistic description of the deformation behavior over a large range of strain, strain rate, and temperature. For example, the Johnson-Cook model may be used appropriately to describe high strain-rate deformation of copper, while the Zerilli-Armstrong model may be more appropriate for the case of Ti-6Al-4V, which exhibits a nonlinear relationship between flow stress and logarithm of strain rate (Ref 3.13). There are also a number of other material models that have been used for the simulation of particle impact in cold spraying (Ref 3.14). The selection of an appropriate viscoplastic model continues to remain a challenge for particle impact modeling, particularly in view of the fact that strain rate in cold spraying can be as high as 10^9 s^{-1} (Ref 3.15); experimentally evaluated material data hardly exist for this range of strain rate. There is also a need for reliable plastic constitutive properties of materials in the low-strain-

rate regime, which are not widely available for microparticles. So far, properties of microparticles have been taken, as a first approximation, to be the same as those of bulk material. This has proved to be a useful assumption for practical purposes. Nevertheless, there are cases in which discrepancies between the particle and the bulk data are significant, as well as cases in which material is produced only in the powder form and the bulk data do not exist in the first place. There are methods underway to tackle the latter problem, where particle compression experiments are combined with numerical simulation to determine plastic constitutive properties of microparticles in the low-strain-rate regime (Ref 3.16).

The elastic response of the materials, too, plays a role in the deformation behavior of particles during high-velocity impact, although to a lesser extent than the viscoplastic response. Elasticity becomes all the more important when modeling of particle impact incorporates particle rebounding. Elastic behavior can be described either by linear elasticity or by an equation of state (EOS), that is, the relationship between pressure and volume at a given temperature. The latter is more appropriate for the cases of relatively high impact velocities. Examples of EOS for solid materials include the linear Mie-Grüneisen equation of state (Ref 3.17):

$$p - p_H = \rho \Gamma (E_m - E_H) \quad (\text{Eq 3.2})$$

where p_H and E_H are the Hugoniot pressure and specific energy, respectively, and Γ is the Grüneisen ratio. In the modeling of particle impact, EOS is normally used together with elastic shear modulus.

Energy Dissipation and Heat Transfer. The kinetic energy of an impinging particle is, to a large extent, consumed as the required work for plastic deformation, which dissipates eventually as heat. A smaller fraction of this energy, considered to be roughly 10% or less, is stored within the material as nonthermal internal energy, as a result either of long-range residual (elastic) stresses or of structural defects such as dislocations or twin boundaries.

In modeling of high-strain-rate deformation, the heat generation is often assumed to be adiabatic because of the very short time scales involved. In cold spray, on the other hand, the particles are in the micrometer-sized range so that the length scale is small, too. The assumption of adiabaticity can be assessed with respect to the value of the dimensionless parameter $\beta = x^2/\alpha t$, in which x is a characteristic system dimension, α is thermal diffusivity, and t is the process time (Ref 3.18). A value of β equal to or greater than unity is usually regarded as justifying the assumption of adiabatic heating. Considering typical values of $10^{-6} \text{ m}^2/\text{s}$ for α and 10^{-8} s for t , the condition of adiabaticity is satisfied when the width of the plastically deformed zone is larger than 10^{-7} m . This is conceived to be the case for the impact of large particles, namely larger than 1 mm (0.04 in.) in diameter (Ref 3.5). For smaller particles, there is deviation from adiabatic heat-

ing. In such cases, conductive heat transfer should be considered, particularly when studying the effect of particle size on the deformation behavior and bonding of particles in cold spraying (Ref 3.19).

Adiabatic shear instability is generally associated with high-strain-rate plastic deformation. It is normally a cause for failure of metallic components subjected to dynamic loading, which is manifested as formation of adiabatic shear bands (Ref 3.20). The idea of shear band formation can be explained in view of the plastic response of a typical work-hardening material (Fig. 3.1) (Ref 3.21).

As mentioned, normally a large fraction (approximately 90%) of the plastic work dissipates into heat. Under adiabatic heating conditions, the generated heat remains in the deformed region. This normally happens when the deformation takes place over a very short period of time, so there is negligible heat transfer to conduct the generated heat away from the deformed region. As a result, there would be thermal softening with the progress of deformation, counteracting work hardening. The interplay between thermal softening and work hardening leads eventually to a maximum flow stress at a characteristic shear strain, $\gamma_{\max}$, beyond which point there will be strain softening. Under the condition of strain softening, the material becomes inherently unstable with respect to plastic deformation. This means that the material becomes susceptible to localization, which may occur at any stage during further deformation. In bulk materials, localization normally starts at the most prominent nonuniformity. This is

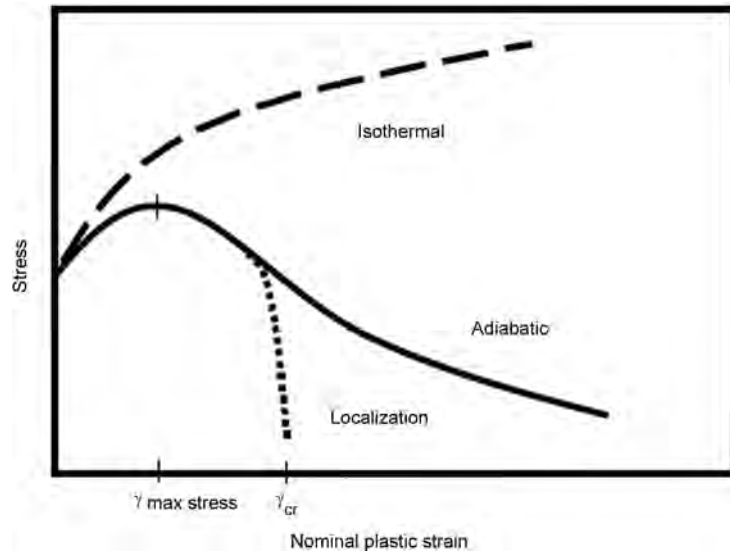


Fig. 3.1 Stress-strain variation for a typical work-hardening material during a torsion experiment. Localization may occur in adiabatic heating in the strain-softening region, that is, after the flow stress reaches a maximum. Source: Ref 3.21

signified by a nominal critical shear strain, γ_{cr} , at which point the straining and heating at the shear band intensify, while the neighboring regions stop deforming further (Ref 3.21). The real strain at the shear band is always larger than the nominal value. As is shown later in this chapter, a similar condition arises at the interface between an impinging particle and the substrate in cold spraying.

Microstructural Phenomena. The microstructure of the material may undergo changes during the impact. These changes can influence not only the deformation and the bonding behavior, for example, by reducing the flow stress, but also the final property of the deposit. For instance, there is evidence of dynamic recrystallization (Ref 3.22) and strain-induced phase transformation (Ref 3.23–3.25) in cold spraying. In this case, softening of material, in addition to that resulting from thermally activated dislocation dynamics, would be expected to occur. Nevertheless, the exact effect of these changes on the deformation and bonding behavior is yet to be studied quantitatively and incorporated into the modeling of particle impact.

Another aspect of presumably relevant microstructural changes is the generation of geometrically necessary dislocations (GNDs) that are due to strain gradients (Ref 3.26). These GNDs give rise to hardening of the material, in addition to that resulting from work hardening, and may thus be considered to influence the deformation and bonding behavior. The existing models of particle impact in cold spray have so far not included strain gradient effects, which could presumably be relevant for the study of particle size effect in cold spray.

A further microstructural phenomenon is fracture and fragmentation, which could be particularly relevant for the analysis of bonding mechanism of intrinsically brittle materials. As is discussed later in this chapter, modeling of particle impact for brittle materials has been used as a basis to explain aerosol deposition (Ref 3.27), which can be considered as a close variation of cold spray. Cold spray deposition of ceramics is nevertheless a challenging topic yet to be explored.

Modeling and Simulation Methods

The majority of modeling techniques used for the analysis of particle impact in cold spraying have been based on continuum mechanics and, in particular, have involved mesh-based methods of numerical simulation. The focus has been on finite-element simulation of particle impact in two and three dimensions, using Lagrangian, Eulerian, or combined formulations. In contrast, few analyses have involved mesh-free methods, such as smoothed-particle hydrodynamics or molecular dynamics simulation. Application of these methods in cold spray research is summarized as follows.

Finite-Element Method. The finite-element method (FEM) has been the most widely used method in the simulation of particle impact in cold spraying. Using this method, the geometry of the deforming particle as

well as strain, stress, and temperature fields can be calculated and displayed for given impact velocities, impact angles, particle and substrate geometries, and material parameters. The work of Dykhuizen et al. (Ref 3.28) is one of the earliest yet most elaborate examples of application of FEM in the study of particle impact in cold spraying. They used an Eulerian-based FEM software package, called CTH, which was developed at Sandia National Laboratories for modeling of large-deformation dynamic problems (Ref 3.29). Dykhuizen et al. used an axisymmetric model and assumed adiabatic conditions.

Following this work, Assadi et al. used the commercial software package Abaqus for Lagrangian-based FEM simulation of particle impact (Ref 3.15). They also used axisymmetric models of particle impact and assumed adiabatic conditions. They focused on the evolution of field variables at the particle-substrate interface and, in particular, explored the conditions for adiabatic shear instability. This work was further continued by Schmidt et al. (Ref 3.19), who included heat transfer to study the effect of particle size on the critical velocity. They also proposed a framework for the calculation of window of deposition in cold spraying.

A number of other studies have used similar methods based on FEM, using commercial software packages such as Abaqus and LS-DYNA, to investigate bonding and deposition in cold spraying for various material properties and impact scenarios (Ref 3.30–3.40). Among the most notable of these works is that of Yu et al. (Ref 3.35), who used an Eulerian model in Abaqus to simulate the impact of homogeneous particles. The Eulerian formulation does not have the problems associated with the Lagrangian formulation, namely, excessive mesh distortion and unrealistic development of the deformation morphology. As is shown later, it is equally possible to diagnose the conditions for adiabatic shear instability in the Eulerian models, although the existing literature on the subject appears to suggest otherwise. A drawback in the Eulerian algorithm in Abaqus has been the lack of axisymmetric option, so that a quasi-two-dimensional (2-D) model (equivalent to a plain-strain model) within a three-dimensional (3-D) domain has been used to make the simulations computationally feasible.

Mesh-Free Methods. Smoothed-particle hydrodynamics (SPH) has been used for the simulation of particle impact in cold spraying by some researchers (Ref 3.34, 3.36, 3.41, 3.42). In principle, this method is a Lagrangian method in the sense that the nodes move with the material, but it does not have the mesh-related problems, such as mesh distortion in the Lagrangian FEM. It was developed originally to simulate fluid flow but has been successfully applied to viscoplastic deformation of solids. A reservation with SPH is that it may lack sufficient spatial resolution for intricate analysis of the interfacial phenomena in particle impact.

An alternative method to simulate particle impact is molecular dynamics (MD). The domain size in MD is in the nanometer range, and hence, simulation of particle impact using MD is inevitably limited to nanopar-

ticles. There are a few examples of the simulation of particle impact using MD (Ref 3.27, 3.43). These examples pertain to aerosol deposition, which is a close variation of cold spraying but works with submicron particles and is performed in a partially evacuated chamber (Ref 3.44).

Analytical and Semiempirical Models. The interaction of an impinging particle and the substrate has also been treated through analytical models, for example, by Wu et al. (Ref 3.45). They considered the particle-substrate interaction with respect to analytically estimated adhesion and rebound energies and postulated that bonding would occur if the former is greater than the latter. There have also been analytical treatments of the problem by the inventors of the cold spray process (Ref 3.46). They proposed a method for the estimation of the overall strain (flattening ratio) of the particle, the contact time, the deformation pattern, and the temperature distribution at the particle-substrate interface. Further analytical treatments concern estimation of the critical velocity through semiempirical equations. Examples include equations by Schmidt et al. (Ref 3.19), which are based on an energy balance between the initial kinetic energy of the particle and the internal energy rise, and by Hussain et al. (Ref 3.47), which take account of mechanical interlocking of the particles and the substrate.

Most of these treatments aim at providing a predictive relationship between the critical velocity for bonding and the respective material properties, based on simplifying assumptions and application of adjustable parameters. Some of the main results of these analyses are discussed in the following sections.

Main Outcome

Particle Deformation and Interfacial Phenomena. Many important features of simulated particle impact in cold spraying were shown for the first time by Dykhuizen et al. (Ref 3.28). Their simulations showed the development of particle shape and the corresponding field variables, such as temperature, during impact of copper particles (Fig. 3.2).

A central question about bonding mechanisms has long been whether or not there is partial melting at the interface of the particle and substrate, and whether or not this could be responsible for bonding. Dykhuizen et al. reported no indication of melting in their simulations; the maximum temperature was 1200 K (160 K below the melting point) for a copper particle impinging a stainless steel substrate at an impact velocity of 700 m/s (2300 ft/s). Nevertheless, they showed indications of the so-called jet formation, which is also a key feature in explosive welding, at impact velocities higher than 400 m/s (1310 ft/s). Because of the technical characteristics of their software (the Eulerian-based CTH code), bonding was always assumed to occur as soon as the interacting parts came into contact. The bonding mechanism was therefore explained only qualitatively, in view of

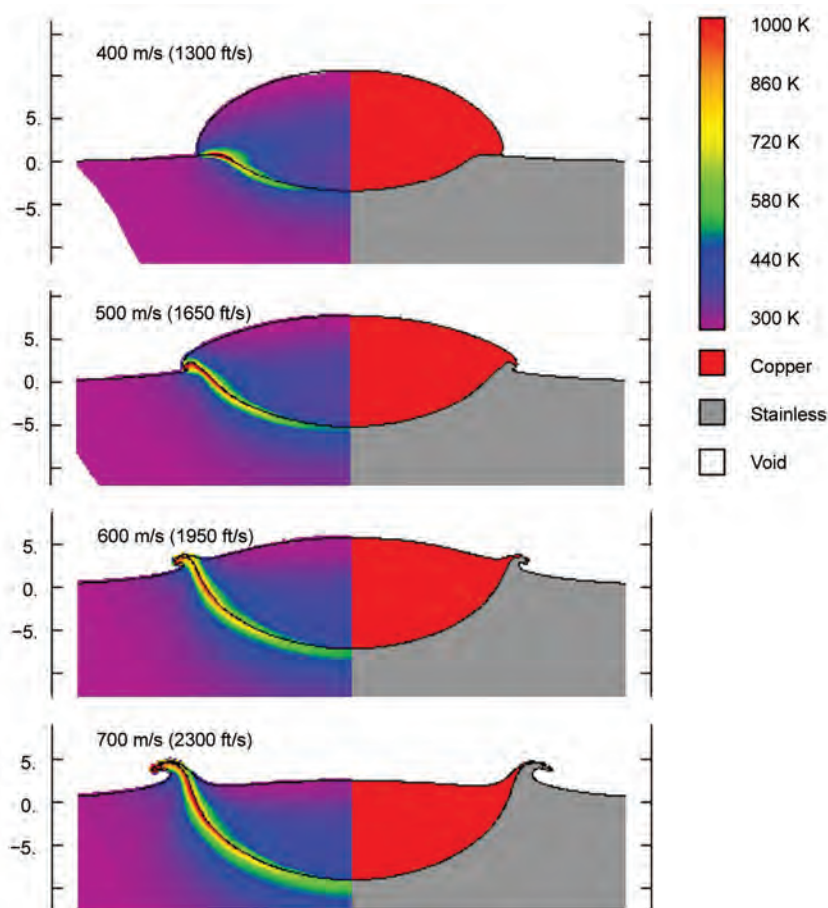


Fig. 3.2 Splat shapes calculated by Dykhuizen et al. Left side shows temperature; right side shows material type. Source: Ref 3.28

the general features of the simulation results, namely jet formation, temperature rise, and high-pressure buildup at the interacting surfaces.

Following this work, Assadi et al. (Ref 3.15) used the Lagrangian formulation in Abaqus/Explicit to simulate the impact of copper particles on a copper substrate. This subsequent work did not model the entire process of bonding either; the interacting surfaces would either separate or tie together based simply on the selection of the corresponding option by the user. Nonetheless, the work focused on a quantitative analysis of the field variables near the interacting surfaces and thus on the thermomechanical conditions that could be linked to the bonding mechanism. A main outcome of this work was that, at or beyond certain impact velocities, adiabatic shear instability (ASI) would occur at the particle-substrate interface (Fig. 3.3).

The transition from strain hardening to strain softening and ASI has been found to occur over a narrow and well-defined range of impact ve-

locity (Fig. 3.4). In view of this fact, ASI has been taken as a possible prerequisite for particle bonding. It also relates to jet formation, as in explosive welding. Based on this conjecture, the effect of different material parameters on the critical velocity could be investigated theoretically and predicted quantitatively, as is further discussed in the section “Prediction of Critical Velocity” that follows.

The occurrence of ASI during particle impact was demonstrated further by others using Lagrangian-based FEM (Ref 3.3, 3.31, 3.48). Some of these subsequent studies indicated the possibility of partial melting at the interface, for example, in the case of impact of copper particles on an aluminum substrate (Ref 3.49). Nevertheless, interface melting has not been established as a common feature in cold spraying, nor has it been unarguably shown to be a necessary condition for bonding.

The occurrence and prominence of ASI as shown by numerical simulation is influenced by a number of factors in addition to the particle impact velocity. These include both computational and physical factors, for ex-

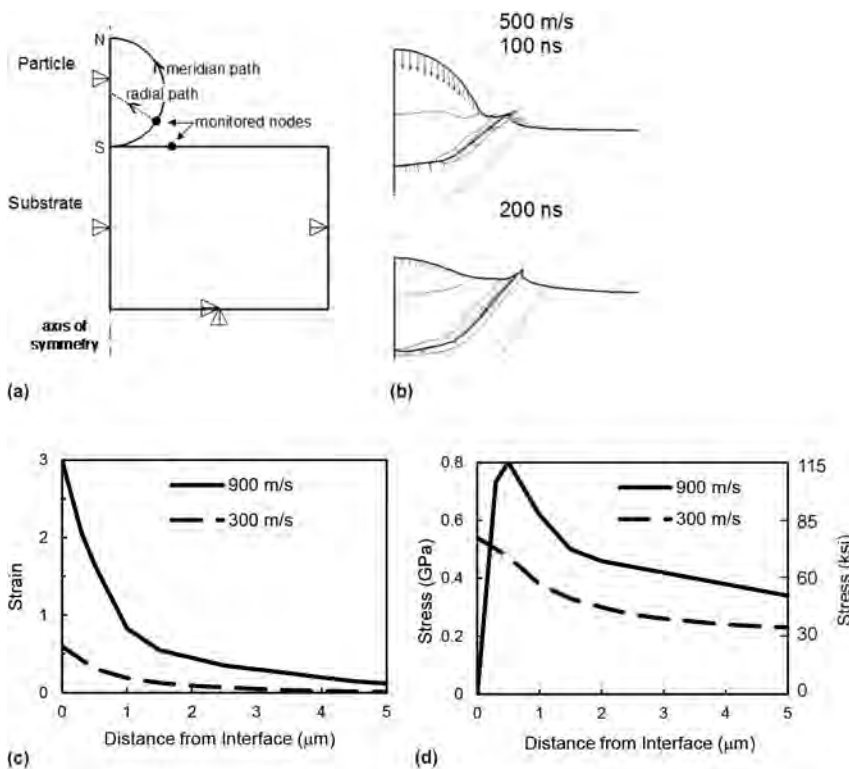


Fig. 3.3 Lagrangian-based finite-element method simulation of particle impact, showing (a) the initial configuration and boundary conditions, (b) simulated splat shapes for a copper particle impinging a copper substrate, (c) plastic strain profile, and (d) flow stress profile along the radial path. Both strain and stress increase monotonically by approaching the interface for 300 m/s (1000 ft/s), whereas for 900 m/s (3000 ft/s) the shear stress exhibits a drastic decrease at the interface, indicating adiabatic shear instability. Source: Ref 3.15

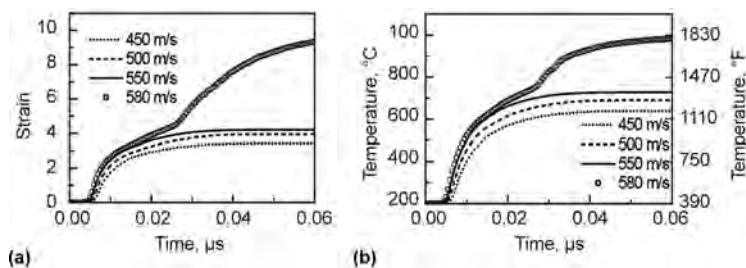


Fig. 3.4 Temporal development of (a) plastic strain and (b) temperature at a point on the surface of an impinging particle for various impact velocities. There is a change in trend of variation of these variables with time as the initial particle velocity is increased from 550 to 580 m/s (1800 to 1900 ft/s), indicating adiabatic shear instability. Source: Ref 3.15

ample, the mesh size and the heat-transfer conditions, respectively. Generally, shear instability is more prominent for smaller mesh sizes. On the other hand, shear instability is hindered or shifted to higher impact velocities if heat transfer is included. The latter effect can be used as a basis to examine the role of particle size in cold spraying. As shown in Fig. 3.5, larger particles show a more prominent rise in the maximum temperature, indicating ASI, whereas for the smallest particle there is no indication of ASI. This effect can be explained as follows. As mentioned previously in the section “Energy Dissipation and Heat Transfer,” adiabaticity may be expressed with regard to the dimensionless parameter $\beta = x^2/\alpha t$, in which x is a characteristic length. Assuming that x scales with particle diameter, the impact of larger particles will be more adiabatic than the smaller ones. As a result, larger particles would be more susceptible to exhibit ASI than smaller ones.

The threshold of ASI is considered to mark the minimum condition for particle bonding. Beyond this condition, for example, with the increase of particle impact, the extent of ASI and the fraction of bonded area increase. Increased bonded area in turn results in increased bond strengths, which is generally favorable. As shown in Fig. 3.6, simulations demonstrate how the extent of ASI at the particle-substrate interface increases with increasing impact velocity. In consistence with experimental observations, ASI is shown to start initially at the rim of the contact area. By increasing the impact velocity, the ASI area extends toward the south pole of the particle (Ref 3.50). Nevertheless, the fraction of bonded area reaches a saturation limit; that is, the south pole never experiences ASI in a perpendicular particle impact.

Manifestation of ASI in the Eulerian-based FEM is considered to be less straightforward than that in Lagrangian FEM. As shown in Fig. 3.3, in the Lagrangian formulation the transition to shear instability is signified by a sharp jump in the history of maximum plastic strain, which occurs over a relatively narrow range of impact velocity. This is not the case in

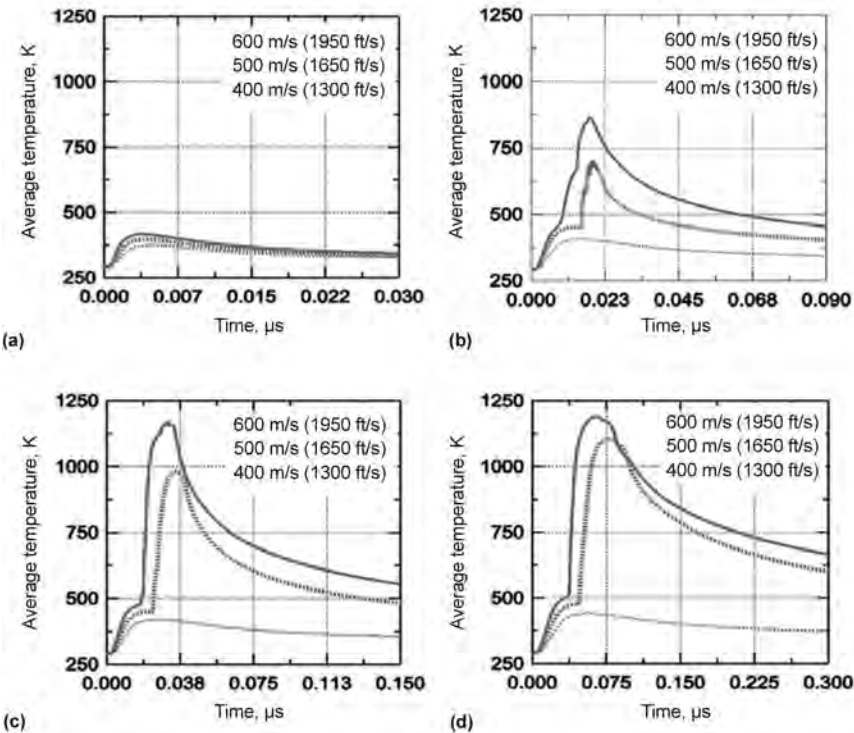


Fig. 3.5 Temporal evolution of the maximum temperature at the contact surface of copper particles of different size and for different impact velocities. (a) 5 μm . (b) 15 μm . (c) 25 μm . (d) 50 μm . Source: Ref 3.19

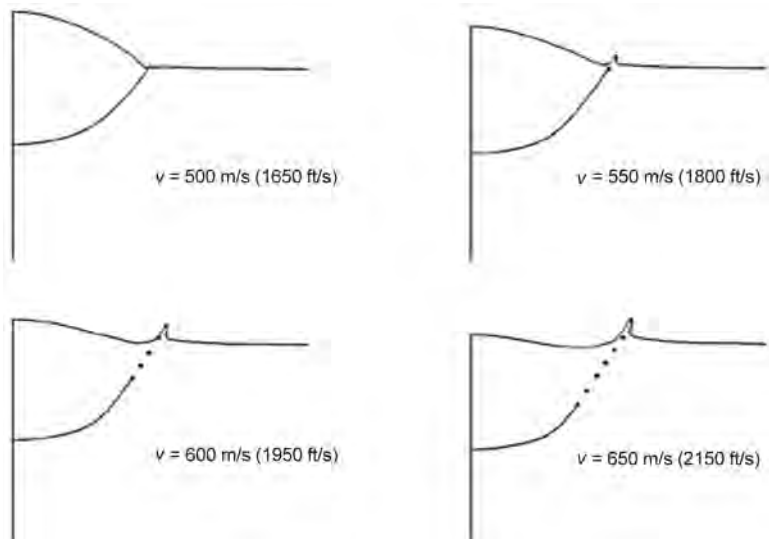


Fig. 3.6 Calculated contours of a copper particle impacting onto a copper substrate at four different velocities. The dotted lines at the particle-substrate interfaces indicate the areas that undergo adiabatic shear instability. Source: Ref 3.50

the Eulerian formulation, as shown by Wang et al. (Ref 3.40). On the other hand, strain softening, which is the prerequisite for ASI, can be clearly identified as a decline in the equivalent stress profile at the circumferential contact region (Fig. 3.7).

Apart from impact conditions (v_p and T_p) and particle size, there are a number of other factors that may influence deformation and bonding of particles in cold spraying. The existence of a surface oxide layer, particularly for aluminum alloy powders, is an example of this. Yin et al. (Ref 3.37) used an Eulerian-based FEM to model impact of particles covered with an oxide layer. The main idea was to investigate distribution of oxide as a result of particle impact. They showed that while a part of the oxide layer is removed from the interface during impact, there are always some oxide residues that remain in the central region (Fig. 3.8). These results demonstrate further the characteristic feature of no bonding at the south-pole region.

The concept of a surface oxide layer can be employed as a basis not only to study the distribution of oxides but also to simulate the process of particle bonding (Ref 3.51). This simulation has been achieved by using a pressure-dependent yield model for the oxide in the Eulerian approach. In this model, bonding occurs when the oxide layer breaks apart, allowing contact between the particle and substrate materials. Likewise, separation and rebounding occurs through dilation of the oxide layer that remains as a continuous layer between the particle and substrate (Fig. 3.9).

Comprehensive modeling of particle bonding, as discussed previously, is particularly useful for the analysis of more complex impact scenarios, for example, in the case of cold spraying of agglomerates or composites

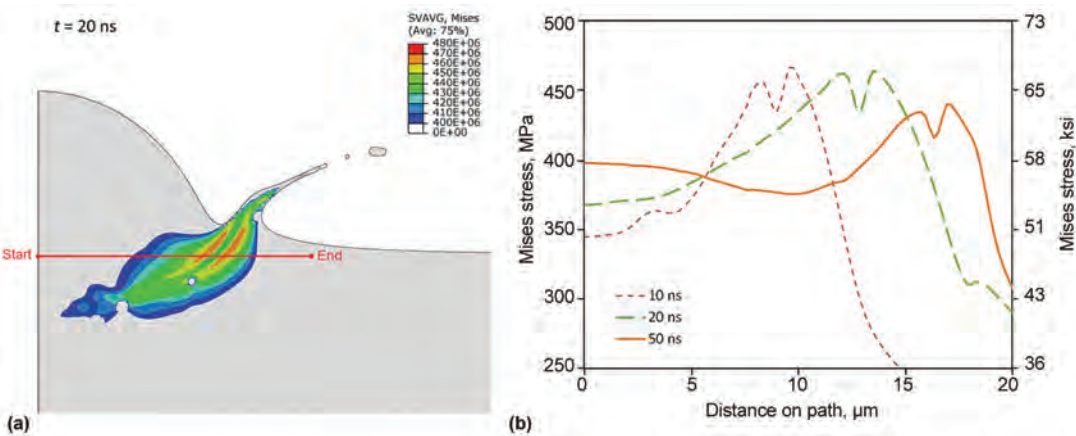


Fig. 3.7 Manifestation of strain softening as a local drop on the stress profile in the simulation of particle impact using a quasi-two-dimensional model and the Eulerian formulation in ABAQUS/Explicit. The path of the stress profiles (b) is shown on the snapshot (a). The calculations assume adiabatic conditions for the impact of a copper particle impinging a copper substrate at 500 m/s (1650 ft/s). Source: Ref 3.51

(Fig. 3.10). In such cases, the problem is not confined to the bonding between particle and substrate; it also involves bonding between particles within impinging agglomerates. As shown in Fig. 3.10, there is no indication of bonding for the composite agglomerate, whereas for the homogeneous agglomerate there is some deposition. It is of interest that only lower particles within the homogeneous agglomerate bond to the substrate, and there is no bonding between the particles within the agglomerate, which experience less deceleration and may thus not develop ASI, as

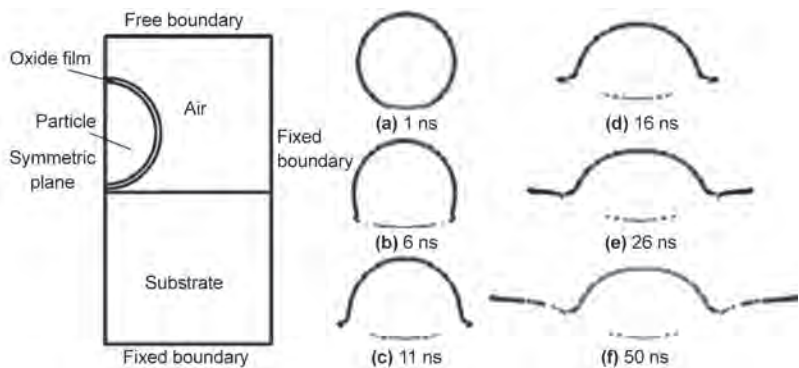


Fig. 3.8 Initial configuration (left) and the simulation results (a–f) showing the impact morphology and the evolution of the oxide film on an Al 6061-T6 particle during impact onto a substrate of the same material at a velocity of 700 m/s (2300 ft/s). Source: Ref 3.37

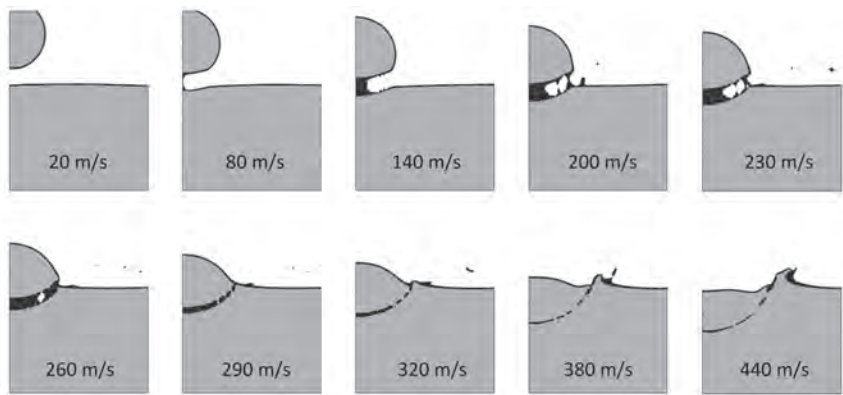


Fig. 3.9 Concurrent simulation of bonding and rebounding using an adiabatic quasi-two-dimensional model in ABAQUS/Explicit using the Eulerian algorithm. The oxide layer is described by a pressure-dependent yield model, allowing dilation at negligible tensile strength. For this example of a copper particle on a copper substrate, the computational parameters are adjusted in such a way that rebounding occurs only when the impact velocity is below 260 m/s (850 ft/s). Note that this value corresponds to the critical velocity of a purely adiabatic case, as in the impact test with 20 mm bullets (Fig. 3.12).

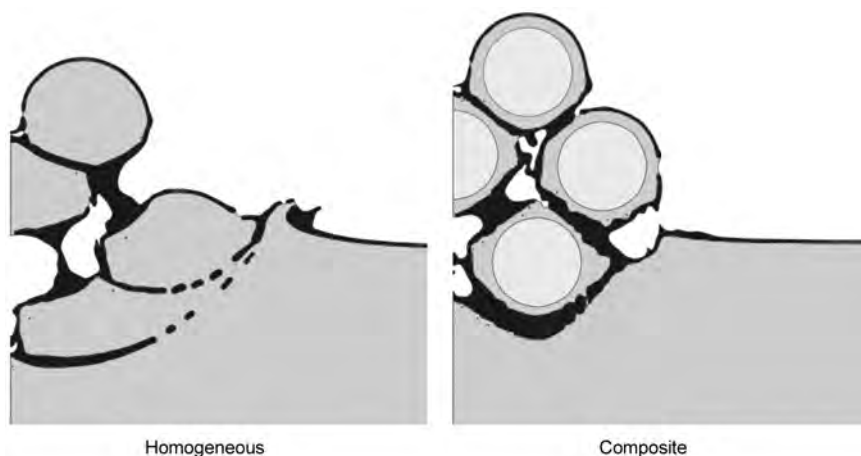


Fig. 3.10 Concurrent simulation of bonding and rebounding for agglomerates of homogeneous and composite copper particles impinging a copper substrate at 320 m/s (1050 ft/s). The homogeneous agglomerate bonds partially to the substrate, while all particles of the composite agglomerate rebound from the surface.

discussed in Chapter 2, *Process Science of Cold Spray*, in this book. No bonding is achieved for the case of composite agglomerate.

There is also much interest in the study of bonding between dissimilar materials, for which concurrent simulation of particle bonding and rebounding, as illustrated previously, is considered to be helpful. This method of simulation would allow study of complex interaction of multiple bodies without the need to track the individual interacting surfaces in the search for ASI.

Prediction of Critical Velocity. Theoretical estimation of critical velocity requires, first of all, postulation of a criterion for bonding. In explosive welding, for instance, formation of a jet at the interface is considered as a criterion for successful bonding. Jet formation is also a common feature in cold spraying. In modeling of particle impact, however, there is no simple way that the threshold of jet formation could be pinpointed quantitatively. On the other hand, there is a sharp change in the trend of all field variables at ASI. Thus, ASI can be taken as a criterion for bonding in a first approximation.

Based on this criterion, the critical velocity has been defined as the minimum velocity required to induce ASI (Ref 3.15). The value of the critical velocity can thus be calculated based on the simulation of particle impact. It should be noted, however, that the calculated value is influenced by several computational parameters, such as the mesh size and the selected calculation algorithms. These parameters should be adjusted with respect to experimental values. In this respect, impact simulations should be viewed as a means for parameter study. In this way, the effect of vari-

ous material properties on the critical velocity of copper was worked out as a linear relationship:

$$v_{cr} = 667 - 14\rho + 0.08T_m + 0.1\sigma_u - 0.4T_i \quad (\text{Eq 3.3})$$

where ρ is the density in g/cm^3 , T_m is the melting temperature in $^\circ\text{C}$, σ_u is the ultimate strength in MPa, and T_i is the initial particle temperature in $^\circ\text{C}$. This formula is worked out for small changes in properties with respect to those of copper as reference material.

A more general formula for critical velocity, covering a wider range of material parameters, was subsequently proposed by Schmidt et al. (Ref 3.19):

$$v_{cr} = k_1 \sqrt{c_p(T_m - T_p) + 16 \frac{\sigma}{\rho_p} \left(\frac{T_m - T_p}{T_m - 293} \right)} \quad (\text{Eq 3.4})$$

where k_1 is a dimensionless fitting parameter, which is in the range of 0.5 to 0.6 for metallic materials. Equation 3.4 is, in fact, a fitting function, developed based on an energy balance between the kinetic energy on one side and the sum of thermal and mechanical potential energies on the other side. This formula is contrived to fit both simulation and experimental data and is based on the assumption that the ultimate strength of the particle decreases linearly with increasing temperature. The latter assumption is not always true; for the case of nickel-base superalloys and some inter-metallic compounds, for example, the flow stress may remain constant or even increase with increasing temperature up to a few hundred degrees.

Figure 3.11 shows the results of calculation of critical velocity based on Eq 3.4 for a number of materials. A main property of both Eq 3.3 and 3.4 is that the critical velocity decreases with increasing particle temperature, reaching zero at the melting point. Neither equation considers the effect of substrate material properties and substrate temperature.

The effect of particle size can be incorporated into the aforementioned relation by taking k_1 as a function of particle diameter, d_p . By fitting the existing experimental data for copper particles, one obtains (Ref 3.19):

$$k_1 = 0.64 (d_p / d_p^{\text{ref}})^{-0.18} \quad (\text{Eq 3.5a})$$

and

$$v_{cr} = v_{cr}^{\text{ref}} (d_p / d_p^{\text{ref}})^{-0.18} \sqrt{1 - T_p / T_m} \quad (\text{Eq 3.5b})$$

where d_p^{ref} is a reference particle size, and v_{cr}^{ref} is a reference critical velocity, which are for copper powder approximately $20 \mu\text{m}$ and 500 m/s (1640 ft/s), respectively (Fig. 3.12). The particle size effect for other materials is yet to be quantified. As mentioned previously, smaller particles are generally expected to have larger critical velocities. The influence of

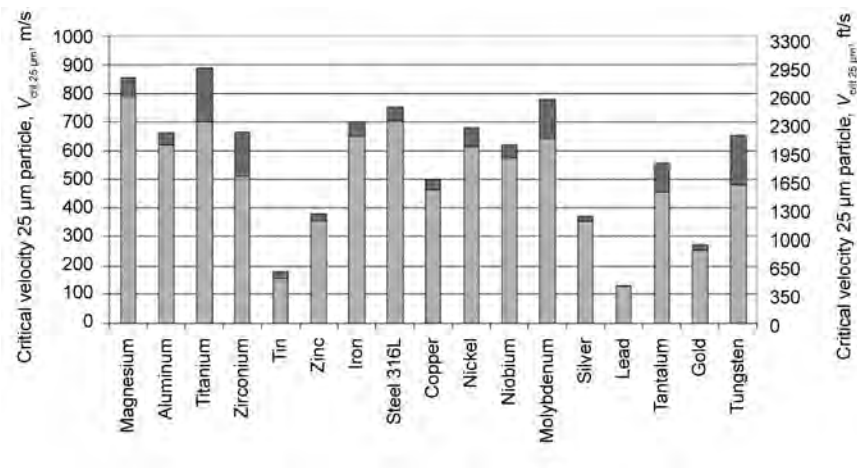


Fig. 3.11 Critical impact velocity for a 25 µm particle calculated for different materials with Eq 3.4. Source: Ref 3.19

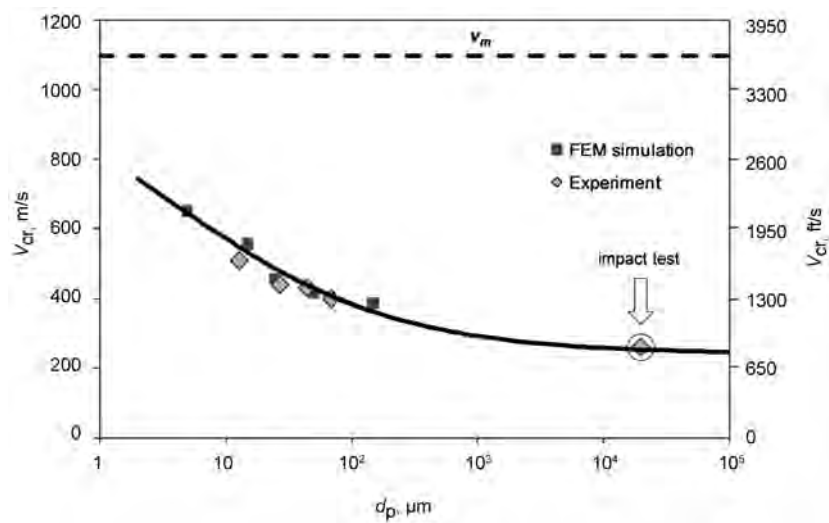


Fig. 3.12 Variation of the critical impact velocity with particle size for copper. The solid lines correspond to the analytical model in Ref 3.5, while the dotted lines show the upper limit of the critical velocity, corresponding to zero adiabaticity. The particle temperature upon impact is assumed to be 300 K. The impact test corresponds to experiments with 20 mm bullets.

particle size on the critical velocity has been analyzed and quantified with respect to heat-transfer considerations (Ref 3.5, 3.19). This dependency has also been conceived to relate to the oxygen content of particles, which would understandably be a size-dependent factor as well (Ref 3.52). Other factors playing a role in the size dependence of critical velocity are strain

gradient and strain-rate hardening effects, both of which would conceivably result in an increase of critical velocity with decreasing particle size.

Brittle Materials. Much of the research in cold spraying has focused on metallic materials, that is, materials with an intrinsic capacity to deform plastically. In recent years, however, attention has been paid to cold spraying of ceramic materials, which, unlike metallic materials, lack the capacity to deform plastically at room temperature. To date, there have been hardly any numerical studies of particle impact and bonding in cold spraying of ceramics. The only available simulations of particle impact for ceramic materials concern the aerosol deposition (AD) process, which may be regarded as a close variation of cold spray. For example, Ogawa (Ref 3.43, 3.53, 3.54) employed molecular dynamics (MD) to explore the influence of various parameters, such as particle velocity and crystallographic orientations, on the impact behavior of nanoparticles in AD (Fig. 3.13).

A subsequent MD study (Ref 3.27) further considered the effect of particle size on the impact behavior. The results showed that the deformation and bonding of intrinsically brittle nanoparticles depend on both the particle size and the particle impact velocity. Smaller particles were shown to be more resistant to fragmentation, that is, to require larger impact velocity to fracture, whereas larger particles would fracture more easily. This phenomenon was due to the role of surface energy in relation to the creation of new surfaces. Figure 3.14 shows the results of simulation together with that of an analytical model of fracture. The gray area in Fig. 3.14 designates combinations of particle size and particle impact velocity leading to deposition.

Further work is needed in this area, particularly to extend the length scale of the simulation to values relevant to cold spraying. Alternative modeling techniques may be needed to bridge the length scales. A major

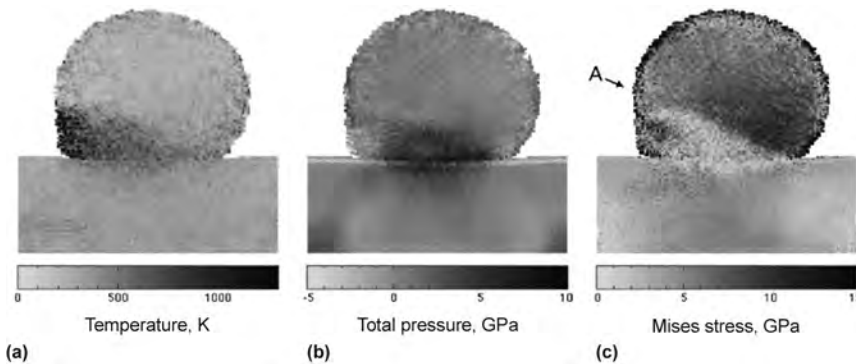


Fig. 3.13 Results of molecular dynamics simulation of impact of a zirconia nanoparticle at 1000 m/s (3300 ft/s) on a zirconia substrate, showing distribution of (a) temperature, (b) pressure, and (c) Mises stress. Arrow A denotes the slip plane in the particle. Source: Ref 3.43

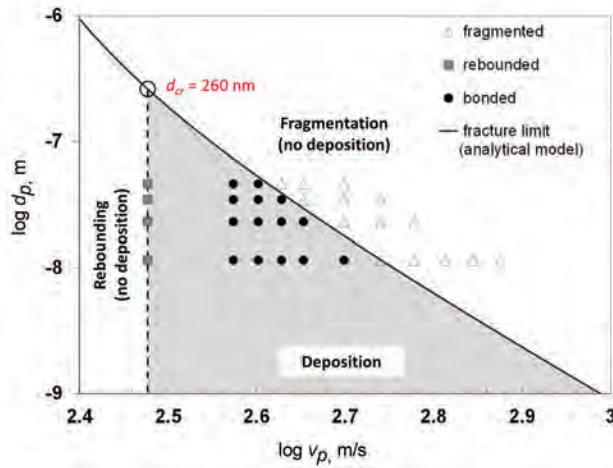


Fig. 3.14 Overview of the results of molecular dynamics simulations, in comparison with an analytical model of fracture, showing the window of deposition (gray area) for intrinsically brittle nanoparticles. Source: Ref 3.27

challenge is to understand the deformation mechanisms of ceramics, which are yet to be fully explored, and then to implement them in a numerical model.

3.2 Modeling and Simulation of In-Flight History of Particles

Particle impact can result in erosion, bonding, or rebound, depending on the impact conditions, that is, depending on the values of the particle velocity and temperature, v_p and T_p , upon particle impact. It is possible to compute the temporal evolution of v_p and T_p —the in-flight history—from models of flow of gas and particles in the prechamber, nozzle, and free jet. This section discusses briefly how this computation is usually achieved. There is also a discussion of the main outcome of such computations in cold spray research and development.

Aims and Questions

The objective in modeling of in-flight history of particles in cold spraying is to work out the impact conditions, for example, to predict whether cold spray deposition will take place under a given set of process parameters. A more particular aim is to help further development of cold spraying technology with respect to equipment and nozzle design. Together with studies based on solid mechanics and materials science, modeling of in-flight history is ultimately aimed at improvement of the cold spray facilities, employment of new spray materials, and selection of optimal pro-

cess parameters. Specific questions in this regard concern the following topics:

- Estimation of v_p and T_p for a given set of material properties, such as density and specific heat capacity, and process parameters, such as gas type, gas pressure, gas temperature, and nozzle dimensions
- Optimization of the nozzle dimensions and the equipment specifications, such as heating power, powder feed rate, and length of the prechamber

Principal Concepts and Methods

Modeling of in-flight history of particles is largely based on computational fluid dynamics, including the heat transfer between gas and particle. It normally starts with the evaluation of the state of process gas at any given point within a convergent-divergent (de Laval) nozzle and in the free stream. As soon as the gas velocity and gas temperature are known, particle acceleration and heat transfer between gas and particle can be calculated. This can be done in one or two dimensions, as described subsequently.

As a first approach, an isentropic one-dimensional (1-D) model can be used to calculate the temporal evolution of gas and particle velocity and temperature through the nozzle. The 1-D calculations describe the flow along the axis of a nozzle, not considering heat and friction losses. In the case of isentropic ideal gas flow in one dimension, the changes of state of the gas can be expressed as functions of the local Mach number, Ma , and the isentropic coefficient, κ , as follows (Ref 3.2):

$$\frac{p}{p_0} = f_p(Ma, \kappa); \quad \frac{\rho}{\rho_0} = f_\rho(Ma, \kappa); \quad \frac{T}{T_0} = f_T(Ma, \kappa) \quad (\text{Eq 3.6})$$

where κ is the isentropic coefficient, which is a constant 1.67 for monatomic gases such as helium and a function of temperature for diatomic gases such as nitrogen, but its value is approximately 1.4, close to the environmental temperature. The local Mach number is:

$$Ma = v / \sqrt{\kappa RT}$$

where v is the local gas velocity, and T is the local gas temperature. The aforementioned gas dynamic functions are widely used for isentropic flow through a convergent-divergent nozzle; they can be found, for example, in Ref 3.55. The Mach number, hence the gas velocity, and the isentropic coefficient relate to the cross section, A , along the nozzle:

$$\frac{A^*}{A} = M \left[\frac{2}{\kappa + 1} + \frac{\kappa - 1}{\kappa + 1} M^2 \right]^{\frac{\kappa + 1}{2(\kappa - 1)}} \quad (\text{Eq 3.7})$$

where A^* is the cross section at the throat of the nozzle. Particle acceleration in the nozzle results from the drag force on the particle. Thus, particle velocity for a spherical particle can be calculated from a force balance given as (Ref 3.56):

$$v_p \frac{dv_p}{dz} = \frac{3}{4} C_d \frac{\rho(v - v_p) |v - v_p|}{\rho_p d_p} \quad (\text{Eq 3.8})$$

where ρ and ρ_p are the density of gas and particle, respectively; C_d is the drag coefficient; and z is the axial distance from the nozzle throat. The drag coefficient is usually a function of the particle Reynolds number, $Re_p = \rho |v - v_p| d_p / \mu$, or a constant in a certain Reynolds number range. At relative velocities between gas and particle approaching or exceeding the local sound velocity, the drag coefficient becomes a function of the particle Mach number as well, $Ma_p = |v - v_p| / \sqrt{\kappa RT}$. In the case $Ma_p > 1$, a shock forms in front of the particle, which may have a considerable influence on the particle acceleration (Ref 3.2).

The aforementioned differential equation is solved numerically, while using the gas dynamic equations (Eq 3.6, 3.7), and considering the geometrical relationship between the local cross section of the nozzle, A , along the axis z for the given nozzle. In this equation, the gravitational force is neglected, because the residence time of the particles in the flow is very short. In these 1-D isentropic computations, only single particles are considered; thus, the gas is not impeded by the presence of one particle.

The heating or cooling of the particle can be evaluated through the following differential equation (Ref 3.56):

$$v_p \frac{dT_p}{dz} = \frac{6h(T' - T_p)}{\rho_p c_p d_p} \quad (\text{Eq 3.9})$$

where c_p is the specific heat of the particle material. Here, the gas temperature is written as T' , because at high relative velocities the gas temperature in the vicinity of the particle can be very different from the free-stream gas temperature. Further, for heat-transfer calculations, it is normally assumed that the particle has internally a uniform temperature at any time, so that a lumped element model can be used (Ref 3.2). This assumption is valid for small metallic particles with relatively high thermal conductivity, where the following condition for the Biot number is met:

$$Bi = \frac{hd_p}{k_p} < 0.1 \quad (\text{Eq 3.10})$$

in which h is the gas heat-transfer coefficient, and k_p the thermal conductivity of the particle. The heat-transfer coefficient is obtained from a Nus-

selt number, Nu , given as a function of the Reynolds and Prandtl, Pr , numbers:

$$Nu = h d_p / k = 2 + 0.6 Re_p^{0.5} Pr^{0.333} \quad (\text{Eq 3.11})$$

where k is the thermal conductivity of the gas. As with the drag coefficient, this Nusselt number is valid only if the relative velocity between gas and particle is small, but as soon as it approaches or exceeds the sound velocity, the Nusselt number also becomes a function of the Ma_p . The particle temperature calculations are performed numerically in parallel with the calculation of particle velocity, for example, using the finite-difference method.

The 1-D calculations describe the flow only along the axis of a nozzle and do not consider heat and friction losses of the gas. To obtain a more realistic description of gas-particle flow, computational fluid dynamics (CFD) in 2-D (axisymmetric) or 3-D can be employed. This is normally performed using commercial CFD codes such as ANSYS Fluent. A CFD model of cold spray normally includes the nozzle, the substrate, and a part of the atmosphere around the exit of the nozzle. This is to take into account the intermixture of the ambient air with the free jet and the resulting influence on the velocity and temperature of the gas and particles. The domain is discretized into a large number (up to a few hundred thousand) of finite-volume cells, for which the flow and temperature fields are worked out. Turbulence and frictional losses are taken into account. The Navier-Stokes equations, energy equations, and further scalar equations, for example, for two-phase flow, are solved for each cell. Because the flow is turbulent, appropriate turbulence models should be carefully selected.

Even in the more elaborate 2-D computations with computer codes, the particle concentration in the flow is normally so small (approximately less than 0.01 vol%) that particle-particle interaction can be neglected. Nevertheless, there have been treatments of the problem, for example, for cold spraying of metal-ceramic mixtures (Ref 3.57), that consider particle-particle interaction in the stream. Further, as soon as the particle mass flow rate is a substantial fraction of the total gas mass flow rate, the gas-particle interaction must be considered because, due to the presence of this “cloud” of particles, the gas temperature and velocity fields change considerably.

A 2-D CFD simulation gives detailed information about the gas temperature and velocity fields, particle trajectories, temperatures, and velocities throughout the nozzle and the free jet. This is nevertheless obtained at the price of extensive computer resources and computational time, as compared to those required for 1-D isentropic simulations.

Main Outcome

Particle Velocity and Temperature. Figure 3.15 shows an example of the results obtained from 2-D simulation of gas and particle flow in cold

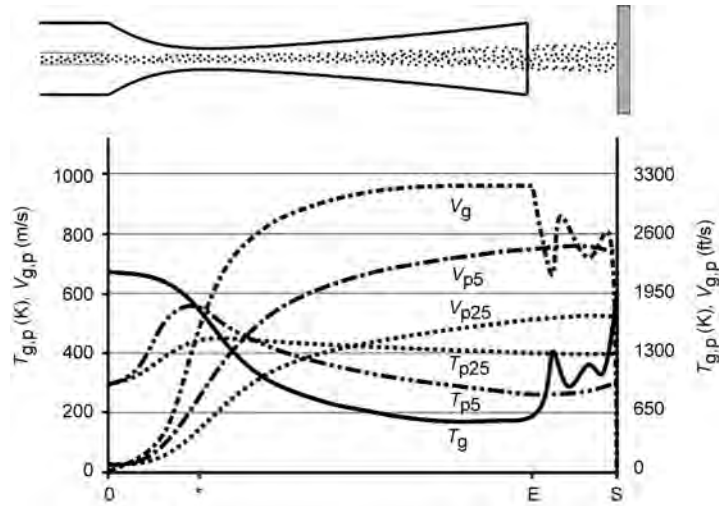


Fig. 3.15 Temperature and velocity development along the nozzle axis for nitrogen as the process gas (g) and two different copper particle sizes (5 and 25 μm), $T_0 = 593 \text{ K}$, $p_0 = 25 \text{ bar}$. The nozzle has an expansion ratio of 9. Source: Ref 3.2

spraying, using Fluent (Ref 3.2). The results show that most of the gas acceleration takes place in the area of the nozzle throat and in the first part of the divergent section of the nozzle. In this example, the process gas reaches 90% of its exit velocity in the first third of the divergent section. Along the convergent section, the gas temperature decreases to approximately 80% of the initial stagnation temperature (in Kelvin). Further decrease of the gas temperature in the diverging section depends on the expansion ratio and varies from 80% to approximately 25% of the initial gas inlet temperature. The irregular changes of the gas velocity and temperature in the free jet are the result of shocks, because of overexpansion in this particular example.

Similar results are obtained from 1-D isentropic calculations, as shown in Fig. 3.16. Both 1-D and 2-D simulations capture main features of supersonic flow in convergent-divergent nozzles. For instance, 1-D calculations similarly show that gas acceleration takes place primarily in the area of the nozzle throat and in the first part of the divergent section of the nozzle. They also show that the gas temperature drops to approximately 80% of the initial temperature in the convergent section.

A key feature in fluid flow calculations is that the process gas reaches sound velocity in the throat of the nozzle. Within the framework of isentropic calculations, the gas velocity does not depend on pressure. Nevertheless, increasing gas pressure results in increased particle velocities. This is due to increased gas densities and hence increased drag forces exerted on the particles. Moreover, velocity of sound depends on the gas

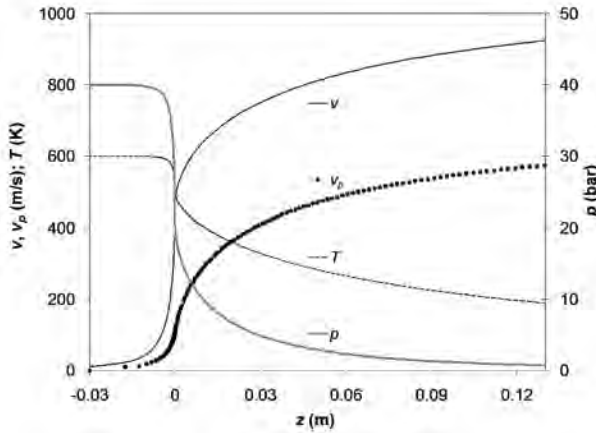


Fig. 3.16 Parametric plot of v , v_p , T , and p versus z , the axial distance from the nozzle throat, calculated using the isentropic flow model, for spraying $20\text{ }\mu\text{m}$ copper particles with nitrogen at 4 MPa (580 psi) and 600 K. The expansion ratio is 5.6, and the length of the divergent section is 130 mm (5 in.). The free jet is not included in this example. Source: Ref 3.5

temperature. Thus, raising the temperature increases the gas velocity and hence the particle velocity. An increased gas temperature has the additional advantage of increasing the particle temperature, which generally results in the decrease of critical velocity and hence better bonding conditions.

From a technological point of view, the particle velocity and temperature at the exit of the nozzle, or those upon impact on the substrate, are more relevant than the profiles shown previously. Therefore, most studies concern the effect of process parameters on these final values. Figure 3.17 shows examples for particle velocities and temperatures at nozzle exit for different gas pressures (Ref 3.58). At a fixed process gas pressure of 3 MPa (435 psi) as one of the examples, increasing the gas inlet temperature from 300 to 900 °C (570 to 1650 °F) will raise the particle impact velocity from 490 to approximately 620 m/s (1600 to 2035 ft/s) and the particle temperature from 70 to 330 °C (160 to 625 °F). The calculations also show the significant effect of pressure on the particle impact velocity. According to these calculations, the particle temperature is only slightly affected by the gas pressure.

The results of a simple 1-D isentropic calculation have been fitted into explicit correlation functions (Ref 3.51). Based on these functions, the particle velocity at the nozzle exit is obtained as an explicit function of process parameters, particle characteristics, and nozzle dimensions. For a nozzle with expansion ratio of 5.6, for instance, the particle velocity at the nozzle exit is given by:

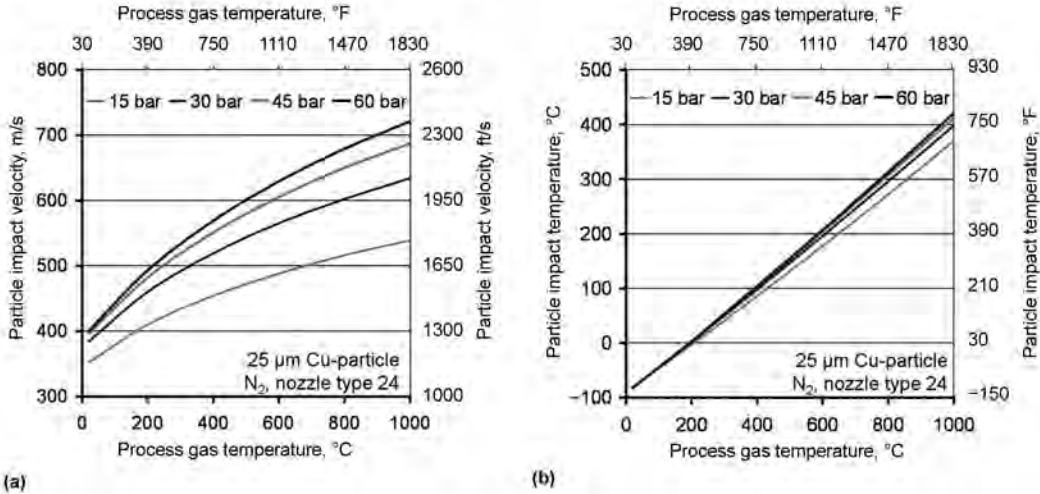


Fig. 3.17 Effect of process gas temperature and pressure on (a) impact velocity and (b) impact temperatures for copper particles (25 μm diameter) and nitrogen as process gas, calculated using a one-dimensional isentropic model for a method of characteristics nozzle. Source: Ref 3.59

$$v_p \approx \left(\frac{c_2}{\sqrt{RT_0}} + \sqrt{\frac{\rho_p d_p}{C_d L_d p_0}} \right)^{-1} \quad (\text{Eq 3.12})$$

where c_2 is 0.42 for nitrogen and 0.45 for helium, respectively. Note that Eq 3.12 fits the results of a simple 1-D model, as applied to a nozzle with a linear profile, assuming constant C_d . As mentioned previously, flow is in reality influenced by friction at the nozzle interior, and C_d is not constant. Also, the nozzle often has a nonlinear profile. This equation is also not applicable to downstream (e.g., low-pressure) cold spray systems, where powder is injected into the diverging section of the nozzle. For other expansion ratios, the same form of equation can be used, but the value of c_2 should be recalculated based on the correlation functions given in Ref 3.5.

In conventional cold spraying, a bow shock forms in front of the substrate. As a result, the velocity of particles upon impact on the substrate can be significantly lower than that given by Eq 3.12. Considering the bow-shock effect, the following expression can be used for the impact velocity:

$$v_{\text{p}} \approx v_p \left(1 + \frac{\rho_0 \delta}{\rho_p d_p} \right)^{-1} \quad (\text{Eq 3.13})$$

where δ is a fitting parameter, roughly in the range of 0.0005 to 0.001 m. The relation considers that the effect of bow shock is larger for smaller particles and vanishes for very large particles. This is shown in Fig. 3.18.

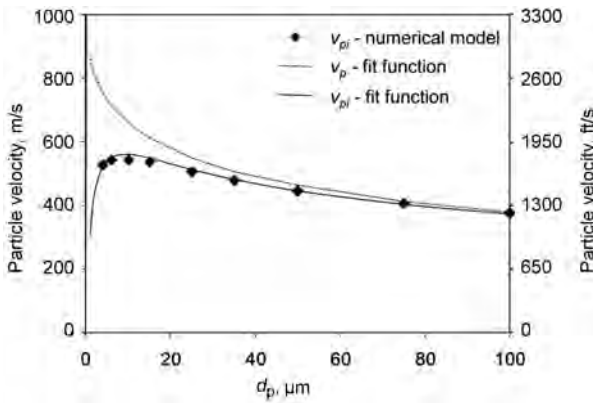


Fig. 3.18 Variation of the particle impact velocity for copper particles of different sizes (data points numerically calculated) compared to values obtained from the fit functions Eq 3.11 and 3.12. The calculation parameters are given in Ref 3.5.

Finding a similar correlation function for particle impact temperature is comparatively less straightforward. In addition to the parameters considered for the calculation of particle impact velocity, the impact temperature is expected to be influenced by factors such as the length of the prechamber and the stand-off distance. Therefore, simple correlation functions have been used as a first approximation for the estimation of particle impact temperature for a fixed particle size (Ref 3.5). These functions have been further developed to include the effect of particle size and have been implemented in the existing software programs for cold spraying (Kinetic Spray Solutions GmbH, Buchholz, Germany).

Nozzle Design. The nozzle is a key component in cold spray technology. Computational fluid dynamics can also be used to design nozzle geometries for optimum particle acceleration. Employing the so-called method of characteristics (MOC) has resulted in the design of bell-shaped nozzle contours, similar to that of rocket engines, with optimum performance (Ref 3.58, 3.59). Figure 3.19 shows the flow contours as computed for an optimum MOC nozzle compared to that for a trumpet-shaped nozzle, used in the early days of cold spraying. According to these computations, the velocity distribution at the exit of the MOC nozzle is significantly more homogeneous than that of the trumpet-shaped nozzle. Moreover, the parallel gas stream of the bell-shaped nozzle reduces intermixing with the surrounding atmosphere in the free jet. The more homogeneous velocity distribution and the higher gas velocities in the free jet contribute to more efficient particle acceleration. For the cold spraying of copper, the use of a bell-shaped MOC nozzle results in approximately 100 m/s (330 ft/s) higher particle velocities than attainable by cold spraying with a trumpet-shaped nozzle (Fig. 3.20). Higher impact velocities lead to better deposition efficiency and coating properties. It should be noted, however, that there is no universally optimum nozzle layout. Nozzle de-

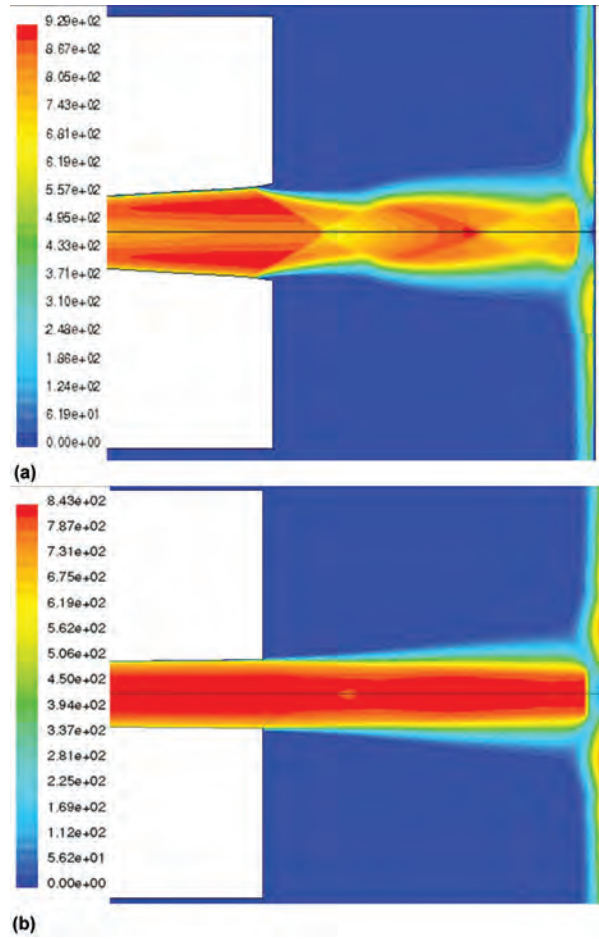


Fig. 3.19 Velocity contours of free gas jets at exits of (a) a trumpet-shaped nozzle and (b) a bell-shaped optimized nozzle design, as computed by FLUENT for nitrogen as the process gas at a gas inlet pressure of 3 MPa (435 psi) and a gas temperature of 320 °C (610 °F). Source: Ref 3.59

signs should be optimized with respect to the specific spray materials and the specific type of process gas, for example, helium or nitrogen. For instance, for cold spraying of copper and other feedstock powders of similar density with nitrogen as the process gas, the bell-shaped nozzle designed by MOC has a length of 130 mm (5.1 in.) of the diverging section and an expansion ratio of 5.8.

Apart from the nozzle length and profile, a key nozzle characteristic is the smallest cross section, that is, at the throat of the nozzle. This dimension is normally selected with respect to the maximum mass flow rate of the process gas, which can be calculated from:

$$m_t = A^* p_0 \sqrt{\frac{k}{RT_0}} \left(\frac{k+1}{2} \right)^{-\frac{k+1}{2(k-1)}} \quad (\text{Eq 3.14})$$

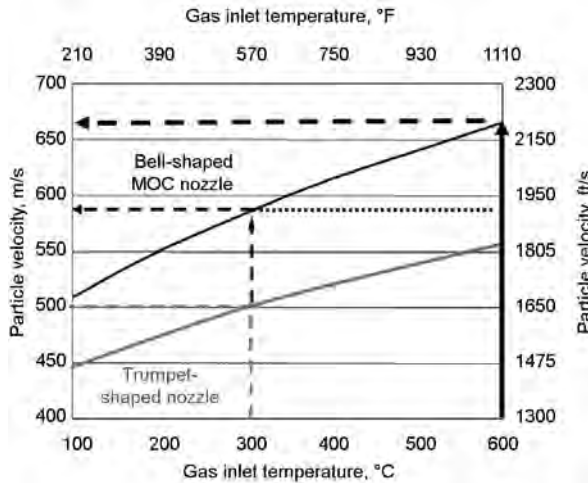


Fig. 3.20 Velocities of 20 μm copper particles accelerated by nitrogen as the process gas at a pressure of 3 MPa (435 psi), as computed by FLUENT. For gas temperatures of 300 to 600 $^{\circ}\text{C}$ (570 to 1110 $^{\circ}\text{F}$), the use of a bell-shaped method of characteristics (MOC) nozzle results in approximately 100 m/s (330 ft/s) higher impact velocities than what is attainable using a trumpet-shaped nozzle. Source: Ref 3.58

The maximum mass flow rate is determined in view of the heating capacity of the cold spray equipment. That is, to reach a certain gas temperature for the given equipment, the mass flow rate may have to be kept below a certain level. This can be achieved by selecting the right combination of gas pressure and nozzle throat diameter. For example, to keep gas consumption of nitrogen at 3 MPa (435 psi) below 100 m^3/h , the smallest cross section should not exceed 2.7 mm (0.1 in.).

For more accurate fluid dynamics calculations, the influence of boundary layer at the nozzle walls must be considered. As shown in Fig. 3.21(a), fluid dynamics calculations demonstrate that gas velocities at the nozzle exit are substantially reduced over a boundary layer thickness of approximately 1.0 to 1.5 mm (0.04 to 0.06 in.). Thus, larger nozzle diameters would result in overall higher gas and therefore particle velocities. As an example, Fig. 3.21(b) shows measured particle velocities in the free jet for different nozzle diameters and lengths. The comparison demonstrates that larger diameters of the smallest cross section, for identical expansion ratios, result in higher particle velocities. Increasing nozzle throat diameter from 1.7 to 2.7 mm (0.07 to 0.1 in.) at the same expansion ratio results in approximately 50 m/s (165 ft/s) higher particle velocities. Increasing the expansion ratio to 7.6 and the length of diverging section to 230 mm (9 in.) results only in approximately 10 m/s (33 ft/s) higher particle velocities. With a further enhanced width of 3.8 mm (0.15 in.), particle velocity increases by an additional 50 m/s (165 ft/s). Therefore, more powerful cold spray systems that could handle higher gas flow rates, associated

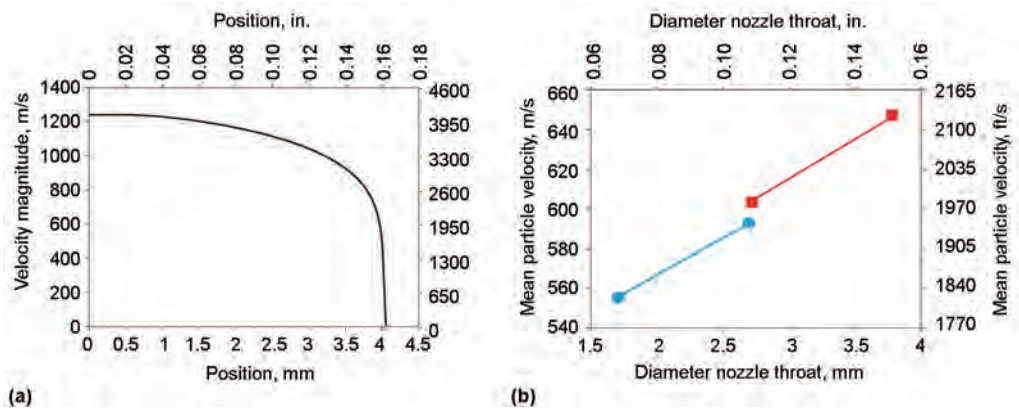


Fig. 3.21 (a) Gas velocity versus the radial distance from the axis of the nozzle at the exit, computed by FLUENT for a method of characteristics nozzle. Throat diameter: 2.7 mm (0.1 in.), $A/A^* = 5.6$, length of diverging section 130 mm (5 in.), with nitrogen as the process gas at $p_0 = 4$ MPa (580 psi) and $T_0 = 800$ °C (1470 °F). (b) Measured particle velocities for nozzles with different throat diameters and divergent section lengths of 130 and 230 mm (5 and 9 in.), respectively (A/A^* of 5.6 and 7.6). The velocities were determined at 60 mm (2.4 in.) downstream in the nozzle exit while cold spraying Al_2O_3 powder of 45 to 90 μm particle size at $p_0 = 3$ MPa (435 psi) and $T_0 = 500$ °C (930 °F).

with larger nozzle throats, could benefit from higher nozzle efficiencies. The examples also show that nozzle length has a minor influence on particle velocity. Because of the influence from boundary layers, too-long divergent nozzle sections may even lead to reduced particle velocities.

The aforementioned considerations in nozzle design concern the right compromise between high particle velocity and attainable mass flow rate of the process gas. Another consideration in nozzle design is the location of the powder injection, that is, the distance between the injection point and the nozzle throat. The residence time of the particles in the convergent section is relatively long, because of the relatively small particle velocities in that section. This longer residence time results in significant heating of particles before the nozzle throat. However, the residence time in the convergent section may not be sufficiently long for relatively large particles to reach the gas temperature before they enter the throat. Therefore, the upstream section may have to be extended beyond the convergent section by the use of a prechamber (Ref 3.60, 3.61). The development of particle temperature and the influence of the prechamber are shown in Fig. 3.22.

For the injection point 20 mm (0.8 in.) upstream, the smaller (5 μm) particle nearly reaches the gas temperature before entering the throat. Nevertheless, it cools down to temperatures of approximately 190 °C (375 °F) in the divergent section of the nozzle. The larger (50 μm) particle, in contrast, is heated to a maximum temperature of approximately 380 °C (715 °F). This is because of the larger thermal inertia of the larger particle. For the same reason, cooling in the divergent section is also less effective

for the larger particle, so that it leaves the nozzle with a temperature of approximately 330 °C (625 °F). For the injection point 135 mm (5.3 in.) upstream, the larger particle reaches the gas temperature as well, so that it leaves the nozzle with a temperature of approximately 600 °C (1110 °F). Corresponding impact temperatures of different particle sizes, injected 135 and 20 mm upstream of the smallest cross section, are illustrated in Fig. 3.23. The figure shows that higher particle temperatures can be achieved with larger particles if a prechamber is used. Therefore, using an elongated prechamber can be beneficial for cold spraying of relatively coarse powders.

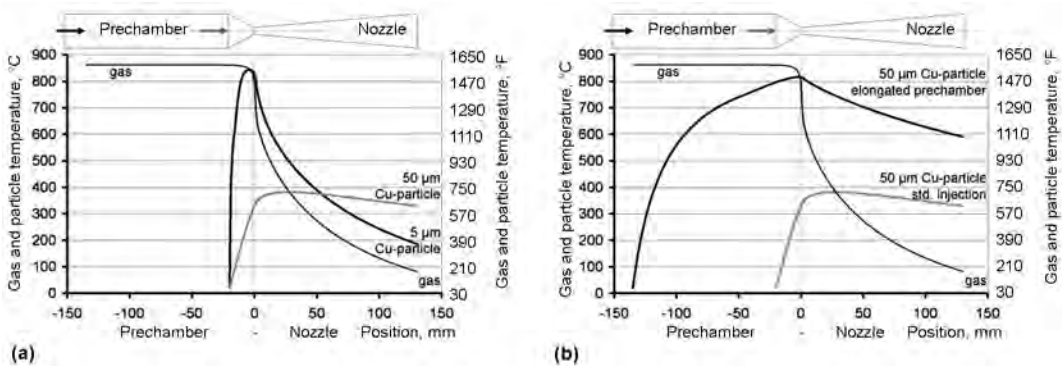


Fig. 3.22 Calculated particle temperature for copper particles of different sizes for particle injection at (a) 20 mm (0.8 in.) and (b) 135 mm (5.3 in.) upstream of the nozzle throat. The calculations are based on the one-dimensional isentropic model for a method of characteristics nozzle with nitrogen as the process gas at $T_0 = 900$ °C (1650 °F) and $p_0 = 4$ MPa (580 psi). Source: Ref 3.59

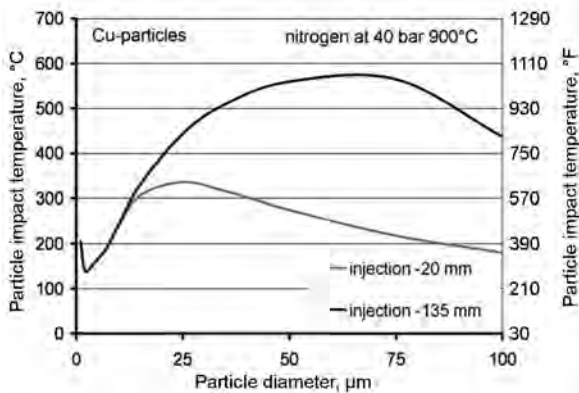


Fig. 3.23 Calculated copper particle impact temperatures as a function of particle size, calculated using the one-dimensional isentropic model for two different injection points, with the same conditions as in Fig. 3.20. Source: Ref 3.59

3.3 Integrated Modeling

A major outcome of the impact simulations is that they provide a basis for the estimation of critical velocity as a function of various material and process parameters. The fluid dynamics simulations, on the other hand, provide a basis for the calculation of impact conditions as a function of these parameters. Therefore, to optimize cold spray deposition for a given material, the results of both types of modeling (particle impact and fluid flow) should be integrated and considered simultaneously.

The concept of integrated modeling is illustrated by Fig. 3.24, showing variations of particle velocity and critical velocity with particle size. This integration is achieved by superimposing the results of fluid dynamics and solid mechanics analyses, examples of which are also shown separately in Fig. 3.12 and 3.18. The figure shows that for a given material and specific set of parameters, there will be an optimum size range in which the particle velocity is significantly higher than the critical velocity. At either side of this range, there would be either no deposition or only imperfect bonding. The figure demonstrates that there is an optimum range of particle size for any given set of process conditions, and vice versa. It also shows the effect of system specifications, namely, the length of the prechamber, on deposition characteristics.

In fact, Fig. 3.24 shows a parameter window that indicates the feasibility of cold spray deposition for a specific powder material under certain process conditions. A more convenient window of deposition can be illustrated in a diagram where particle velocity is plotted against particle temperature, as shown in Fig. 3.25 for the cold spraying of titanium. The data points shown in the figure correspond to impact conditions as calculated (using fluid dynamics modeling) for different particle sizes and dif-

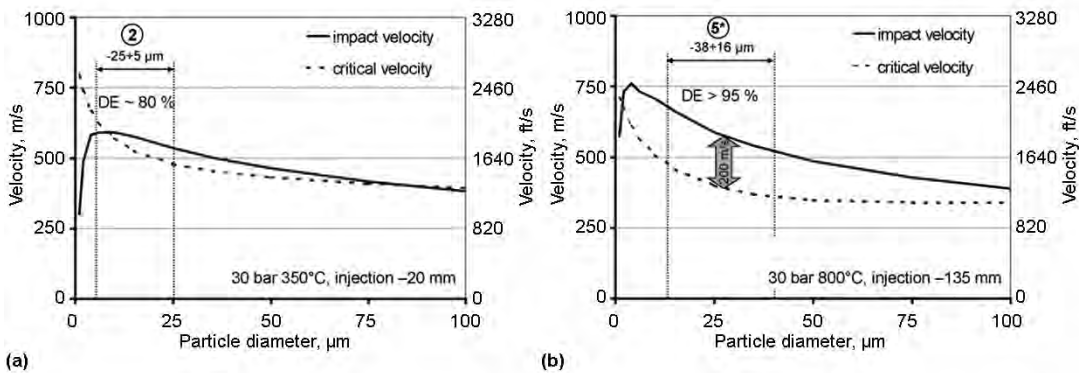


Fig. 3.24 Impact and critical velocities as a function of particle diameter calculated for two different process conditions in cold spraying of copper. Note that typical particle size ranges and deposition efficiencies are different for the two cases. DE, deposition efficiency. Source: Ref 3.59

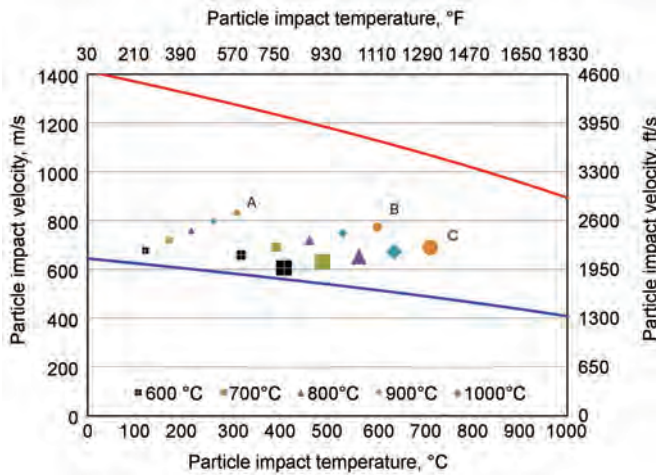


Fig. 3.25 Window of deposition illustrated on the plane of particle velocity and particle temperature for titanium powder sprayed with nitrogen and nozzle type D24 at 4 MPa (580 psi). The data points show impact conditions corresponding to particles of different sizes: (A) 10, (B) 25, and (C) 45 μm . The lower (blue) line shows the critical velocity, and the upper (red) line shows the erosion velocity. Source: Ref 3.62

ferent gas temperatures. The lines correspond to calculated critical velocities for bonding (blue) and erosion (red), for a particle size of 25 μm . The critical velocity for bonding is calculated based on Eq 3.4. The erosion velocity is calculated based on a similar equation but with different fitting parameters. The figure shows that all cases of spraying fall within the window of deposition. It also shows that the deposition conditions improve by increasing the initial gas temperature; both the temperature and the velocity of particles increase, resulting in a larger distance from the lower bound of the deposition window. The increase in particle velocity results from increased gas velocity, which increases—together with the velocity of sound—with increasing gas temperature. The effect of particle size on the quality of deposition is less straightforward in this example. Larger particles exhibit lower velocities on the one hand but higher temperatures on the other hand. In contrast, smaller particles lose heat—and cool down more effectively—in the divergent section of the nozzle, where the gas expands almost adiabatically. Considering that the critical velocity decreases with increasing temperature, the effect of particle size on the distance from the lower bound of the window of deposition, and hence on the deposition quality, is not immediately clear from the figure.

To quantify the distance from the lower bound of the window of deposition, one may consider the ratio of particle velocity to the critical velocity, that is, $\eta = v_p / v_c$. Interestingly, cold spray deposition characteristics ap-

pear to be a unique function of this ratio. As an example, Fig. 3.26 shows the normalized strength of cold-sprayed titanium coatings as a function of η . As shown in the figure, there is a linear relationship between the strength of the coating and η , regardless of the spraying conditions or particle size. The existence of such a relationship has also been demonstrated for copper (Ref 3.5).

The main point about the velocity ratio, η , is that, on the one hand, it combines the results of fluid dynamics computations with those from solid mechanics considerations, and, on the other hand, it relates uniquely to the final properties of the coating. Thus, the initial materials and process parameters can be correlated to the final properties. The concept of integrated modeling through the application of velocity ratio is summarized in Fig. 3.27.

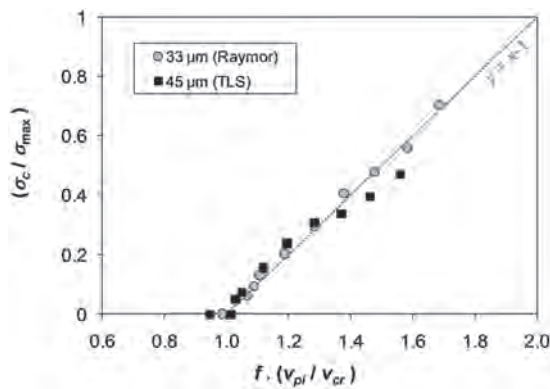


Fig. 3.26 Measured values of the normalized cohesive strength of cold-sprayed titanium coatings as plotted against the adjusted velocity ratio using a correction factor of $f = 1.08$. Source: Ref 3.5

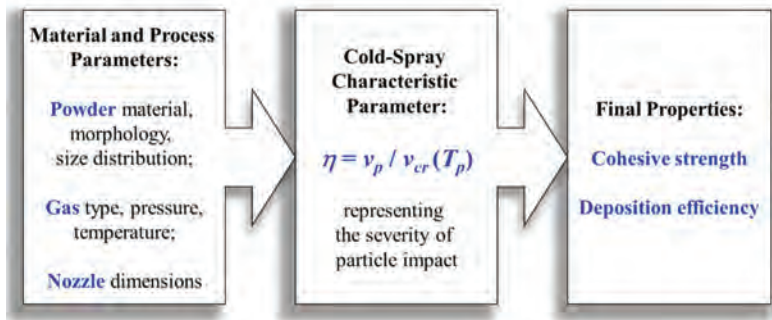


Fig. 3.27 Concept of integrated modeling, illustrated through definition of the cold spray characteristic parameter, η

Based on the aforementioned approach, the window of deposition may be illustrated alternatively on a plane of primary process parameters, namely, gas pressure, gas temperature, and particle size. This is done by plotting the respective η -contours on the given plane. Considering the desired value of η , one may select the right combination of primary cold spray parameters. Figure 3.28 shows an example of such parameter-selection maps as calculated for copper.

From the p_0 - T_0 map (Fig. 3.28a), it can be inferred that coating quality improves within certain limits by enhancing process gas temperature and pressure. Whereas increasing temperature appears to be always beneficial, increasing pressure beyond 4 MPa (580 psi) has only minor influence on the coating quality. The d_p - T_0 map (Fig. 3.28b) can be used to select the optimum range of particle size. For instance, aiming for $\eta = 1.5$, a range of particle size from 15 to 30 μm would appear to be favorable. It should be noted, however, that these maps do not consider limitations such as melting and nozzle clogging that could arise from selecting too-small particle sizes or too-high temperatures. Note that, in practice, gas temperature hardly goes beyond 1000 $^{\circ}\text{C}$ (1830 $^{\circ}\text{F}$) in cold spraying.

In summary, integrated modeling allows selection of optimum process parameters for cold spraying of a given material with respect to the desired coating properties. This optimization can be performed with regard to the process costs, which are also related to the process parameters. The concepts of deposition window and parameter-selection map can be used as robust tools to explore the potentials of cold spraying for various applications. In comparison with conventional thermal spraying techniques, for which parameter-selection maps are rare and relatively difficult to contrive, cold spraying may be regarded as a unique spraying process that can be thoroughly modeled and optimized based on the results of modeling.

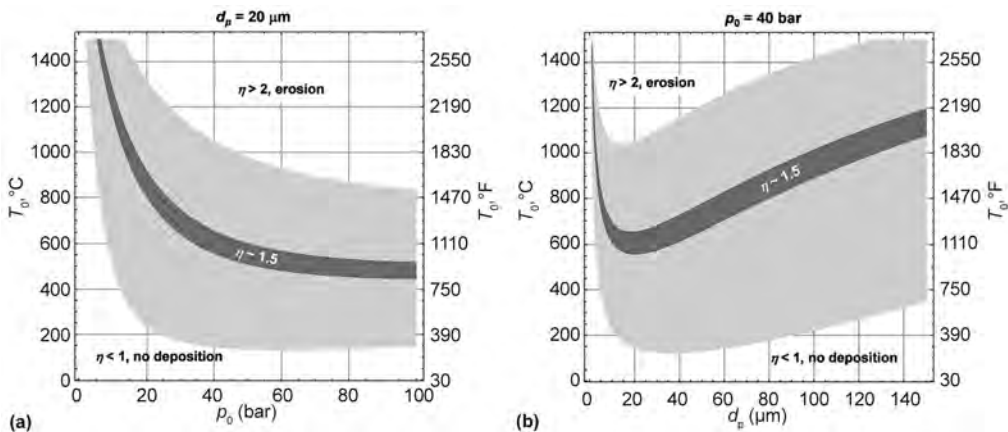


Fig. 3.28 Parameter-selection map for copper on the (a) p_0 - T_0 and (b) d_p - T_0 planes. Source: Ref 3.5

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CHAPTER 4

Cold Spray Equipment

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IN THE EARLY DAYS, all cold spray research and development (R&D) work was carried out with systems built in-house at various institutions, including ASB Industries (Barberton, OH), Sandia National Laboratories (Albuquerque, NM), and Helmut Schmidt University (HSU) (Hamburg, Germany). The commercial development of cold gas systems for industrial use began in approximately 2000. For development and commercialization of cold spray equipment, Cold Gas Technology (CGT) GmbH was established in Germany in 2000.

Following its founding, a considerable number of scientific investigations were carried out by a consortium that included CGT, HSU, Linde GmbH, and HC Starck. The successful cooperation between HSU and CGT was the basis of this complex development work.

The results of R&D studies by HSU scientists were used at CGT to create a detailed engineering design taking into consideration the requirements of industrial end users of the technology.

This chapter provides an overview of the state of the art in high-pressure cold spray equipment, including both spray systems and gas supply systems.

4.1 Spray Systems

CGT KINETIKS 3000 System. In 2002, the first two prototype testing facilities were delivered by CGT to HSU and Linde. Here, the achievable spray parameters were 2 MPa (290 psi) and 400 °C (750 °F). The coil heater required the use of a hot gas hose to lead the gas to the gun (Fig.

4.1). Here, energy was lost and the process temperature was limited by the hose. Furthermore, the flexibility of the cold spray gun was restricted by the stiffness of the hose. Soon, it appeared that the lifespan of the corrugated hose was limited, because it was often destroyed by bending and torsion.

Extensive studies were carried out at HSU and Linde, and, based on the results of these studies, the first commercial cold spray system, CGT KINETIKS 3000, was designed, built, and sold worldwide. This system, with a capability of 550 °C (1020 °F) at 3 MPa (435 psi) maximum, could be used to produce coatings of many materials for both research and industrial activities.

The CGT KINETIKS 3000 system introduced, for the first time, mass-flow-controlled gas flow rate, pressure or flow control of process gas, feedback-controlled gun temperature, the possibility of operating with nitrogen-helium gas mixtures, touch panel parameter input, data logging, and many other advanced features, which translated into the production of reliable coatings with reproducible properties.

CGT KINETIKS 4000 System. Permanent demands for higher process parameters were the reason for the fast development of new equipment with better performance. Solutions were vigorously sought to fulfill the requirements of the industry.

The KINETIKS 4000 line (Fig. 4.2) was designed. For this purpose, not only a new heating concept but also a powder feeder with a considerably higher operating pressure had to be developed. A heating filament that made it possible to forgo the hot gas hose was now integrated into the cold



Fig. 4.1 KINETIKS 3000 system



Fig. 4.2 KINETIKS 4000-47 (30 kW preheater) system

spray gun. The gas was now heated directly in the gun. Because of this, the flexibility when handling the gun improved substantively.

A new powder feeder was designed and manufactured by CGT. It was the first high-pressure powder feeder (4 MPa, or 580 psi) worldwide. This new design enabled easy disassembly and remounting without any tools. Emptying the powder feeder and cleaning all powder-contacting components can be done quickly and easily.

In 2006, approximately fifty KINETIKS 4000 systems were sold worldwide. The technical standard called for spray parameters of up to 4 MPa process pressure and 800 °C (1470 °F) process gas temperature; these were also the maximum achievable, because of the stress on the heating elements and the materials used for the gun and preheater.

CGT KINETIKS 8000 System. The goal in developing the next generation of equipment was to increase the process temperature up to 1000 °C (1830 °F). Helmut Schmidt University developed a prototype to meet this requirement. The KINETIKS 8000 (Fig. 4.3) was presented to the market in 2007, but the process temperature of 1000 °C could not be achieved for long spraying times; at that temperature, the lifetime of the heating elements was only a few hours.

Plasma Giken PCS 1000 System. In 2009, Plasma Giken presented the PCS 1000 cold spray system (Fig. 4.4). With process parameters of 5 MPa (725 psi) and 1000 °C, this equipment seems to be the next generation of cold gas systems. However, the gun dimensions of more than 1.2 m (4 ft) in length and a weight of almost 50 kg (110 lb) necessitate that the robot handling gun is capable of high load-bearing capacity. Over four units have been installed worldwide and are used primarily for scientific work.

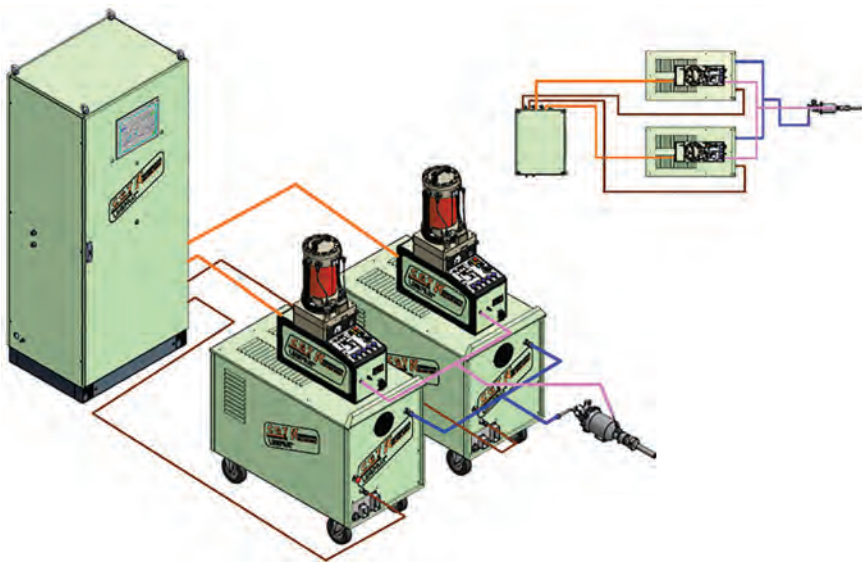


Fig. 4.3 KINETIKS 8000 system



Fig. 4.4 Plasma Giken PCS 1000 system. Courtesy of Plasma Giken

Impact Innovations ISS 5/8 and 5/11. Impact Innovations GmbH (Rattenkirchen, Germany) was founded in 2011 and began to design and develop a new cold spray system with higher process parameters and a variety of accessories. The current technical standard includes two different cold spray systems: the Impact 5/8, designed for a process temperature of 800 °C (1470 °F) and a process pressure of 5 MPa (720 psi), and the high-end Impact 5/11 (Fig. 4.5), designed for a process temperature of

1100 °C (2010 °F) and a process pressure of 5 MPa. It is also possible to manufacture and supply a custom-made system with a performance focused on the customer's application (e.g., 6 MPa, or 870 psi, and 1000 °C). Impact's modular design allows the production of custom-made systems with two, three, or more powder-feed units.

New accessories have been developed as well, including the following:

- An inner coating device has been developed. Now it is possible to coat the insides of pipes, down to a diameter of 80 mm (3 in.). The inside diameter spray head and adapter are shown in Fig. 4.6 and 4.7.
- A new heater design without a preheater and without a hot gas tube makes robotic handling of the gun much more flexible and avoids damage (of the hot gas tube).



Fig. 4.5 Impact Innovations ISS 5/11. Courtesy of Impact Innovations GmbH



Fig. 4.6 Inside diameter spray head. Courtesy of Impact Innovations GmbH

- A new ceramic spray nozzle is distinguished by very good high-temperature tolerance and a long lifetime. An additional air- or water-cooling system (Fig. 4.8) extends its lifespan. Further cooling of the nozzle prevents it from plugging.
- Fine powders and materials with a tendency to clog up the nozzle can be sprayed with a newly designed axial powder injection system. This device offers the option to adjust the powder injection point and thereby the distance between nozzle throat and powder tube.



Fig. 4.7 Inside diameter spray adapter. Courtesy of Impact Innovations GmbH

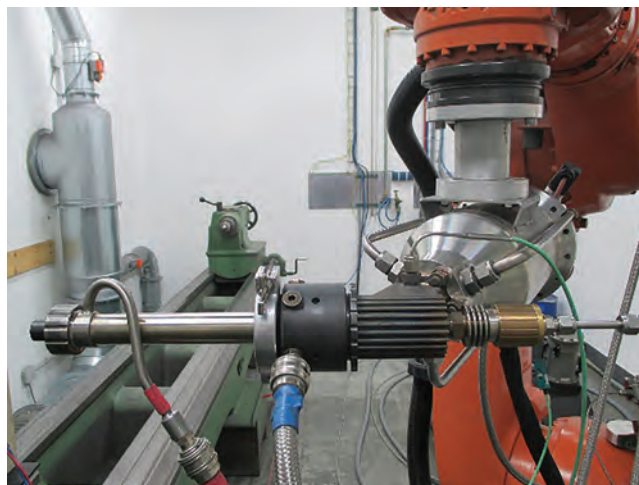


Fig. 4.8 Axial powder-feed adapter with water cooling. Courtesy of Impact Innovations GmbH

Portable High-Pressure (ASB 2000-2) System. Global R&D in cold spray technology had shown that a portable system with a handheld gun is required in some applications, such as in situ coating repair, spraying specific regions of a component without masking, spot repair of pinholes, and scratch repair. These requirements led to the development and commercialization of the ASB 2000-2 system.

Figure 4.9 shows the ASB 2000-2 system, which consists of a handheld gun, filament heater, control console, powder hopper, and connecting hoses and cables. This system can operate at 400 °C (750 °F) maximum gas (nitrogen or helium) temperature at 2 MPa (290 psi) maximum pressure. A touch panel on the console is used to input and control the process parameters. A handheld gun with a filament heater and a gun body, mounted directly onto the heater, is used for manual spray. A screw powder hopper is used to deliver a metered amount of powder for spraying.

This spray system, along with a diesel power generator and a bank of gas supply, can be mounted onto a pickup truck (Fig. 4.10) and transported for field operation.

Coatings of many materials, including metals (aluminum, copper, titanium, zinc, etc.), alloys (Ni-20Cr, 316SS, etc.), and composites, can be produced with this system, using nitrogen as the process gas. This system can also be used to produce coatings of high-strength materials, such as tantalum- and nickel-base superalloys, by switching the process gas from nitrogen to helium. Microstructural and mechanical investigations of



Fig. 4.9 Portable high-pressure cold spray system. Courtesy of ASB Industries, Inc.



Fig. 4.10 ASB 2000-2 system on a truck. Courtesy of ASB Industries, Inc.

sprayed coatings have shown that good, strong, dense coatings with clean interfaces and strong bonding to various substrates can be produced.

4.2 Gas Supply Systems

In general, helium and/or nitrogen gases are used in high-pressure cold spray processing. Figure 4.11 shows a typical installation to supply both helium and nitrogen for cold spray processing. Here, helium is supplied from high-pressure tube trailers, and nitrogen is drawn from a liquid nitrogen tank, pressurized by a cryogenic pump and gasified in a high-pressure vaporizer.

Helium is normally supplied as a bulk gas via either portable tube trailers that are swapped out or stationary high-pressure gas storage tubes refilled from tube trailers. The low molecular weight of helium provides a higher-velocity gas jet, in turn resulting in increased deposition efficiency and superior coating characteristics. However, because it is significantly more expensive (as much as 50 times more) than nitrogen due to its source and production process, its use for cold spray operation is not normally practical. A couple of recycling systems have been experimented with in two different installations to recover, purify, and reuse helium gas on site. However, such recycling systems are cumbersome to install and difficult to operate in open-atmospheric cold spray processing, unlike closed-environment systems such as for crystal growth. Hence, evolution of cold spray technology has concentrated on nitrogen-base systems, mimicking the higher velocity of the helium jet by increasing the pressure and temperature of the nitrogen jet.



Fig. 4.11 Gas supply systems for cold spray processing. Helium from the tube trailer on the left; nitrogen from the liquid nitrogen pump system on the right. Courtesy of ASB Industries, Inc.

Over 100 cold spray systems are operated around the globe with nitrogen as the process gas, and different gas supply systems have been adopted at different places. The following section deals with the aspects of high-pressure nitrogen supply systems for cold spray operations.

There are various industrial gas nitrogen supply modes, including packaged gas cylinders, bulk gaseous tubes, liquid cryogenic tanks ranging from smaller-style dewars to large tanks up to 76,000 L (20,000 gal) or more, and on-site generators. The cold spray process requires a relatively high pressure of 55 to 60 barg (800 to 870 psig) and a flow of 120 to 150 normal cubic meters per hour (4500 to 5700 standard cubic feet per hour), where a normal cubic meter per hour (Nm^3/h) is typically defined at conditions of 0 °C, 1.014 bara, dry. A standard cubic foot per hour (scfh) is typically defined at standard conditions of 70 °F, 14.7 psia, dry, and the units bara (psia) and barg (psig) represent absolute and gage pressure, respectively. Because of these requirements, the selection of the most effective supply mode is important for the operation and economics of the process.

The standard packaged gas cylinder, often referred to as a A-size unit, contains approximately 8 Nm^3 (300 scf) at 165 barg (2400 psig) and is often available in 12 or 16 packs of cylinders bundled together. This size would normally be too small and costly to be delivered and changed out during the ongoing operation of the process.

The bulk gas supply of nitrogen, via portable tube trailers that are swapped out or stationary high-pressure gas storage tubes refilled from tube trailers, is not a very common mode of supply and would normally not be economical because of the volume requirements of the process.

On-site nitrogen-generation systems are an economical supply mode for processes that are fairly continuous and with consistent flow rates and lower pressures. There are several common types of on-site generation systems available: noncryogenic air-separation methods, such as membrane and pressure swing adsorption, and cryogenic air separation via distillation. The choice of a particular system is a function of various factors, such as purity, flow rate/pattern, pressure, and power costs. The high purity and pressure requirements for cold spray would usually make the on-site systems uneconomical, especially because of the power and equipment costs for the gaseous compression of the nitrogen to the pressures required.

A liquid-nitrogen-base system using a cryogenic liquid pump is normally the best supply mode for this process. Figure 4.12 shows a schematic of the cryogenic-pump-based system, and Fig. 4.13 presents a typical operating installation. With this type of system, liquid nitrogen is offloaded from a delivery truck into a cryogenic storage tank. Industrial-grade liquid nitrogen is normally specified at 99.998% pure with 10 ppmv maximum oxygen.

A liquid nitrogen pumping system (Fig. 4.14) comprises several basic components: the cryogenic liquid storage tank with its associated controls, a cryogenic liquid pump to pressurize the liquid to high pressure, an ambient air vaporizer to convert the liquid to gaseous nitrogen, high-pressure gaseous storage tubes, and a pressure-control manifold to regulate the delivery pressure to the process houseline.

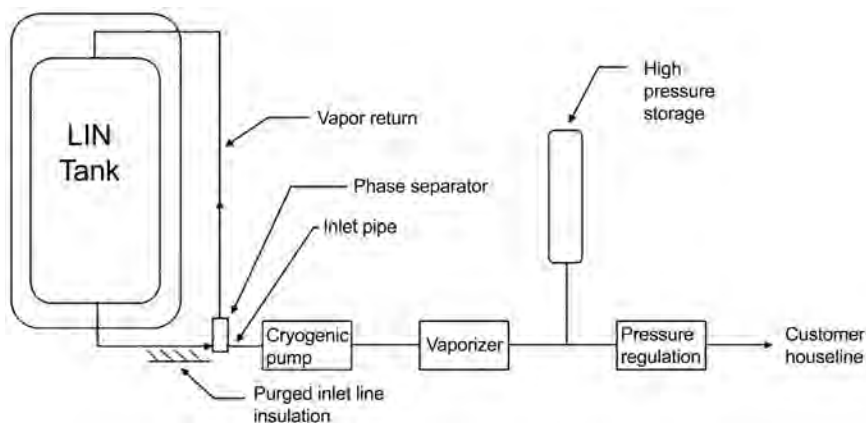


Fig. 4.12 Schematic showing the liquid nitrogen (LIN) pump system. Courtesy of Air Products and Chemicals, Inc.

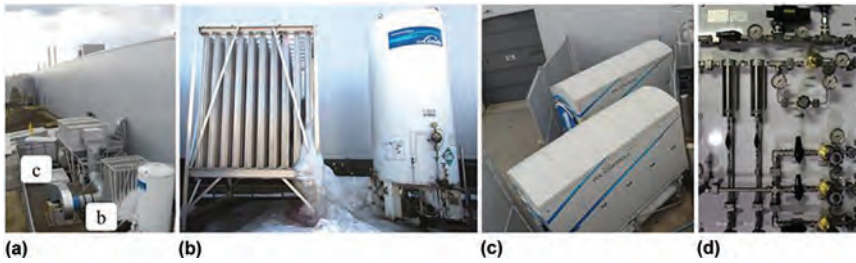


Fig. 4.13 (a) Overview. (b) Liquid nitrogen storage tank and evaporator (Linde). (c) High-pressure compressors (J.A. Becker & Söhne) with storage tanks located below. (d) Pressure regulation panel (Polycontrols Technologies). Courtesy of National Research Council Canada, Boucherville, Quebec, Canada



Fig. 4.14 Liquid nitrogen pump system with dual pumps (middle), liquid nitrogen tank (right), and controls and vaporizer (left). Courtesy of Air Products and Chemicals, Inc.

Traditional liquid nitrogen tanks can range in size from 5,700 to 75,700 L (1,500 to 20,000 gal). The tanks are most commonly rated at 17 barg (250 psig) maximum allowable working pressure but are normally operated at a pressure below this level, that is, 7–10 barg (100–150 psig), which is sufficient to provide adequate liquid supply to the cryogenic pump. Higher-pressure-rated tanks, for example, 28 to 41 barg (400 to 600 psig), are available for certain applications, but because the pressure re-

quirement for cold spray is above the critical pressure of nitrogen (32.6 bara, or 473 psia), just using product directly from a high-pressure tank is not suitable.

The specialized cryogenic storage tanks, which are normally of a vertical design, have an inner vessel that contains the liquid nitrogen (-195°C , or -320°F , at 0 psig, or 0 barg, at saturated conditions) and an outer carbon steel vessel, with vacuum and perlite insulation in between to minimize any product losses from ambient heat transfer into the liquid nitrogen product. Storage tanks come complete with piping controls to automatically regulate their pressure and often use a telemetry system to remotely monitor the tank level and alert the user and/or the supplier when a delivery is required. In some cases, the tanks may be elevated an additional 1 m (3 ft) to ensure an adequate suction head to the liquid pump to avoid cavitation issues.

The cryogenic pumps are reciprocating pumps specifically designed to handle the extremely cold liquid nitrogen while minimizing flash losses. The pumps are usually driven by electrical motors and have the advantages over warm gaseous compressors of low power consumption, single-stage pressurization, and lower capital and maintenance costs because they are compressing liquid rather than gaseous nitrogen. Various sizes and pressure ratings are available, but for this application, a pump capable of approximately 207 barg (3000 psig) is ordinarily adequate. The flow capacity of the pump should exceed the desired process flow rate by an amount sufficient to allow the pump to cycle on/off intermittently to refill the gas storage tubes. With a process flow rate of approximately 130 Nm^3/h (5000 scfh) of gaseous nitrogen (equivalent to approximately 3.4 L/min, or 0.9 gal/min, of liquid nitrogen) for a single cold spray system, a pump capable of 5 to 8 L/min (1.3 to 2.0 gal/min) is recommended. The available volume of gaseous storage should also be considered when sizing the liquid pump. The pump system comes with a control panel to monitor and control its operation. Often dual pumps are used for redundancy, and the control system can alternate between them to stagger operating hours, or run both at the same time if needed, and control the on/off sequence for filling the gas storage.

The most common ambient high-pressure vaporizers use stainless steel tubing with aluminum fins, which provide high surface area to transfer heat from the ambient air to convert the liquid nitrogen to a gas. This type of vaporizer requires no energy input to convert the liquid to a gas, instead relying on the high temperature difference between the ambient air and the cryogenic nitrogen. Various other types of vaporizers using fans, steam, or electric energy for enhanced vaporization are available if the overall parameters require it. Sizing of the vaporizer is in accordance with the pump output capacity, the duty cycle, and the local ambient conditions.

After vaporization, the nitrogen is typically stored in high-pressure gaseous storage tubes, also referred to as hydril tubes. One of the most common sizes for tubes is 7.3 m (24 ft) long and 0.6 m (2 ft) in diameter, with an internal volume of approximately 1.7 m³ (60 ft³) and rated for 169 barg (2450 psig) maximum allowable operating pressure. The hydril tubes are normally configured in a group of three and can be stacked as needed. Figure 4.15 shows a typical set of hydril tubes. The pump-control system fills the tubes to approximately 155 barg (2250 psig), with pressure switches controlling the pump operation. When the storage pressure reaches a predetermined low-level setting, the pumping cycle is initiated at a pressure set above the minimum customer supply pressure to refill the tubes. For cold spray operation, this could be in the range of 80 to 100 barg (1150 to 1450 psig). The pumps will cycle on and off at a frequency that depends on the sizing of the various system components and should be optimized to balance the run time and frequency of operation. Another alternative to hydril tubes for gas storage is the use of 16-packs of A-size cylinders connected together.

The final system component is a pressure-control manifold to regulate the delivery pressure from the tubes at the desired process feed pressure into the houseline. This normally includes a pneumatic regulator that must be specified to handle the desired flow rate. Adequate houseline pressure-relief valves should be included to provide protection for the downstream components.



Fig. 4.15 Typical arrangement of six-pack of high-pressure gas storage hydril tubes. Courtesy of Air Products and Chemicals, Inc.

The specification of the overall nitrogen supply system, including the liquid storage tank, pump capacity and pressure, vaporizer flow rating, and volume of high-pressure gas storage supply mode, is dependent on many factors, including the overall nitrogen volumes, the average and instantaneous flow rates for the process, the minimum customer house-line delivery pressure requirement, and the production operating schedule. The criticality of reliability of supply is also an important aspect to consider.

Because of the unique nature of these cryogenic supply systems, the industrial gas companies that produce and distribute liquid nitrogen typically design, install, own, and maintain these systems as part of a supply contract with the customer.

Gas safety is an important issue. The primary safety concern with gaseous nitrogen or helium is that they are asphyxiants, able to displace the normal oxygen levels in air under certain conditions. Because they are odorless, tasteless, colorless, and nonirritating, there are no warning properties. An oxygen-deficient atmosphere can cause dizziness, unconsciousness, and death. Oxygen monitors should be used for any areas determined to be confined spaces. Liquid nitrogen has the additional hazards that it can overpressurize when it expands to a gas if trapped in piping as a liquid, and it can cause cryogenic burns to personnel. The high pressure requirement of this application also brings additional safety concerns into consideration.

Proper construction materials must be selected for components because of the potential for embrittlement from the cryogenic temperatures of liquid nitrogen and the requirement that they withstand the high pressures. However, because nitrogen and helium are noncorrosive, special materials are not required. Material safety data sheets and standard design codes should be used when dealing with nitrogen.

CHAPTER 5

Cold Spray—Advanced Characterization

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MATERIALS CHARACTERIZATION is an inherent aspect of the cold spray coating evaluation process. Characterization of the as-sprayed microstructures enables the development of an understanding of the thermomechanical evolution of the coating and elucidates the bonding mechanisms both within the coating and at the coating-substrate interface. Evaluating the coating residual stress and the coating relaxation behavior after thermal treatments becomes imperative to establish the reliable functionality of the coating for the proposed application. Microstructural characterization methods including optical microscopy, scanning electron microscopy, transmission electron microscopy, electron backscatter diffraction, and electron probe microanalysis are integral to understanding the highly nonequilibrium process that enables the formation of thick adherent coatings via severe plastic deformation of metal powders. Microhardness, nanoindentation, and residual-stress analysis add to a more complete understanding of the formed coating.

This chapter elucidates the indispensable role of characterization in the development of cold-sprayed coatings and illustrates some of the common processes used during coatings development. Table 5.1 provides an exhaustive list of all the characterization techniques that can be used for cold spray coating characterization. The table also lists the key aspect of each technique and its relevance to cold spray coating characterization. Not all the techniques have been used to their optimum level in developing a complete understanding of the complex nature of a cold spray coating.

Table 5.1 Characterization techniques used for cold-sprayed coatings and their key attributes

No.	Characterization technique	Key aspect for cold-sprayed coating
1	Optical microscopy	Coating thickness, coating porosity, substrate-coating interface integrity, coating porosity after heat treatment
2	X-ray diffraction	Feedstock powder phase evolution, as-sprayed and heat treated coating phase formation, coating macro- and microstrain, coating relaxation behavior, presence of any coating texture
3	Scanning electron microscopy	Intersplat interactions in the sprayed coating before and after heat treatment, microcracks and micropores, coating fracture surface, inclusions and other phases in the coating or substrate-coating interface
4	Focused ion beam	Preparation-specific sections for examination in the scanning and transmission electron microscopes, coating splat interface or coating-substrate interface
5	Electron probe microanalysis	Precise chemistry, diffusion layers in a cold-sprayed coating, coating-substrate interface chemistry
6	Transmission electron microscopy	Phase identification, dislocation structure, recovery processes and recrystallization, coating chemistry
7	Electron backscattered diffraction	Coating texture, extent of recrystallization, deformation map in the substrate, nature of bonding in the coating and coating substrate, grain size and orientation
8	Electron channeling contrast	Dislocation structure, deformation characteristics
9	Residual stress	Residual stress in the as-sprayed coating, coating relaxation process monitoring
10	X-ray photoelectron spectroscopy	Chemical bonding, presence of oxides
11	X-ray fluorescence	Presence of oxide and nature of chemistry on coating surface
12	Auger electron spectroscopy	Surface chemistry of the coating
13	Raman spectroscopy	Phase transitions in the coating
14	Oxygen analysis	Feedstock powder characterization
15	Surface roughness	As-sprayed coating, distinguishing between process parameters, gas type
16	Microhardness	Screening tool for coating
17	Nanoindentation	Coating characterization, deformation
18	Bond adhesion test	Evaluating the adhesion and cohesion strength of the coatings

This chapter emphasizes the advanced microstructural characterization techniques that are used in high-pressure cold spray coating characterization, including residual-stress characterization. The chapter does not cover evaluation of the mechanical behavior, such as tensile strength, fatigue, creep, corrosion or tribological properties of the coating. It includes some preliminary screening of tool hardness and bond adhesion strength, as well as a distinction between surface and bulk characterization techniques and their importance for cold spray coatings. Details pertaining to all the characterization techniques can be found in several standard books as well as in the open literature and from equipment manufacturers. Some basic well-known references are cited for each technique (Ref 5.1–5.5). Each

section includes a note on the sample preparation for characterization, which is critical and must be followed for accurate results without any artifacts.

5.1 Optical Microscopy

Optical or light microscopy (OM) makes use of the visible or near-visible portion of the electromagnetic spectrum and is one of the oldest characterization techniques. With any cold spray coating, it is the first characterization process that is used to evaluate and optimize process variables.

To start with, an estimate of the as-sprayed coating thickness and coating porosity is evaluated, along with an assessment of the coating-substrate interface integrity. The easiest way to assess the coating formation as a function of various coating parameters, such as spray angle, standoff distance, raster speed, deposition efficiency, and powder feed rate, is to use the optical microscope. Practically all the reports on cold spray coatings will start with this characterization, which is fundamental to assessing the coating quality.

In most cases, OM plays an important role in optimizing the process parameters for obtaining dense, pore-free coatings. There exist reports of cold spray coating trials for several pure metals, such as aluminum, copper, titanium, tantalum, nickel, and magnesium (Ref 5.6–5.15), as well as alloys based on aluminum (2052, 6061, etc.), magnesium (AZ31B, ZE41A, etc.), nickel (IN718, IN625, IN738, etc.), and titanium (Ti-64, CP-Ti, etc.), with optical micrographs of the as-processed coating (Ref 5.6–5.18). The coating porosity is determined using the image analysis attached to the optical microscope. In most of the cases, the coating becomes denser with heat treatment, whereas in others it becomes more porous. A quantitative estimation of the porosity using image analysis attached to the optical microscope is usually the best way to characterize the coating density. The effects of process gas (helium versus nitrogen versus air) as well as of the various process conditions, such as standoff distance, speed, and deposition efficiency, are discerned from the optical microscope.

Figure 5.1(a) and (b) show representative optical micrographs comparing an ~0.3 mm (0.01 in.) thick titanium cold-sprayed coating, sprayed using nitrogen and helium gas in the as-sprayed condition (Ref 5.16). A clear distinction can be seen between the porous top region and the dense inner region between the two coatings, revealing an important aspect about the tamping effect of the two gases in the densification of the coating. Figure 5.1(c) and (d) illustrate measurement of coating porosity using image analysis of a pure copper coating (Ref 5.15). The optical micrographs in Fig. 5.1(e) and (f) reveal the coating interface and surface, respectively, of a WC-Co coating (Ref 5.11). Gulizia et al. (Ref 5.10) used

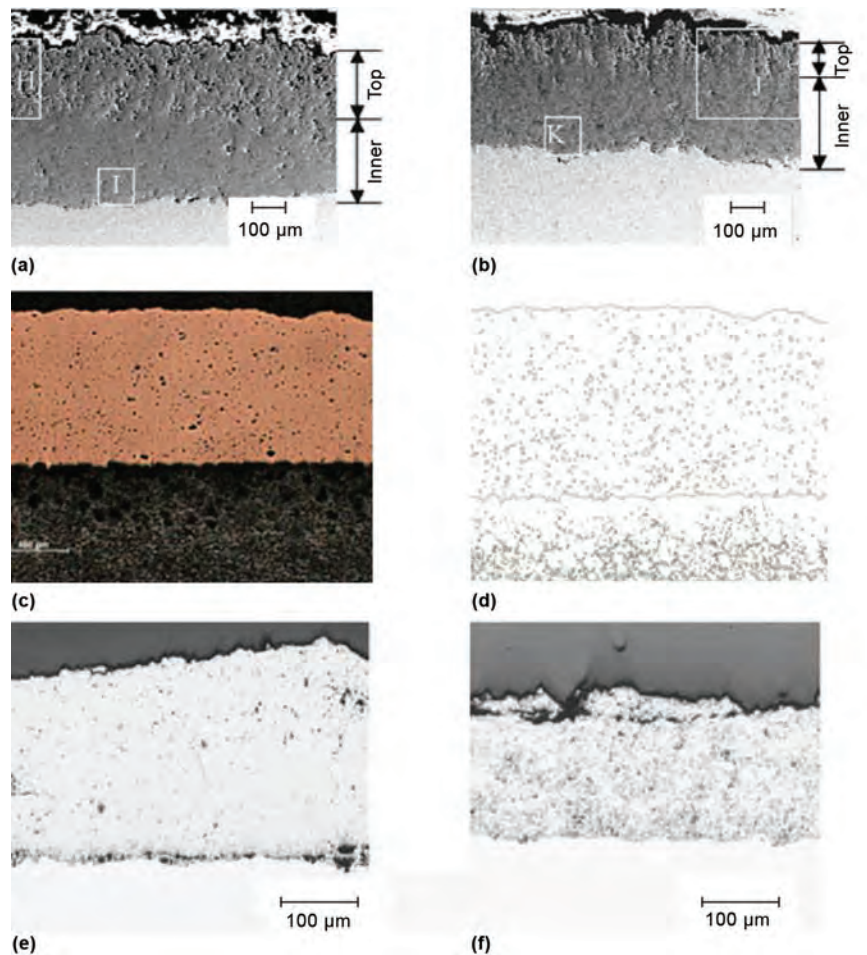


Fig. 5.1 Representative optical micrographs showing (a, b) comparison of overall coating thickness and top layer thickness between a nitrogen-sprayed and a helium-sprayed copper coating, respectively; (c, d) image analysis to evaluate porosity in pure copper coating; and (e, f) interface and top surface in a WC-Co cermet coating sprayed using nitrogen gas. Source: Ref 5.11, 5.15, 5.16

OM to map the process variables to obtain dense coatings, as shown in Fig. 5.2(a) and (b) for an aluminum coating, by etching an aluminum coating and mapping the microstructure evolution as a function of temperature. Van Steenkiste et al. (Ref 5.12) were able to observe the nature of particle deformation and use inputs from optical micrographs to do a numerical simulation, as shown in Fig. 5.3(a) to (c).

Sample preparation for OM is usually straightforward, involving metallography, namely cutting the coating either transversely or along the direction of spray, mounting the cross section using a resin, and grinding and polishing to yield a mirror finish. Because most of the samples are made of metallic or composite materials, mechanical abrasive cutting or

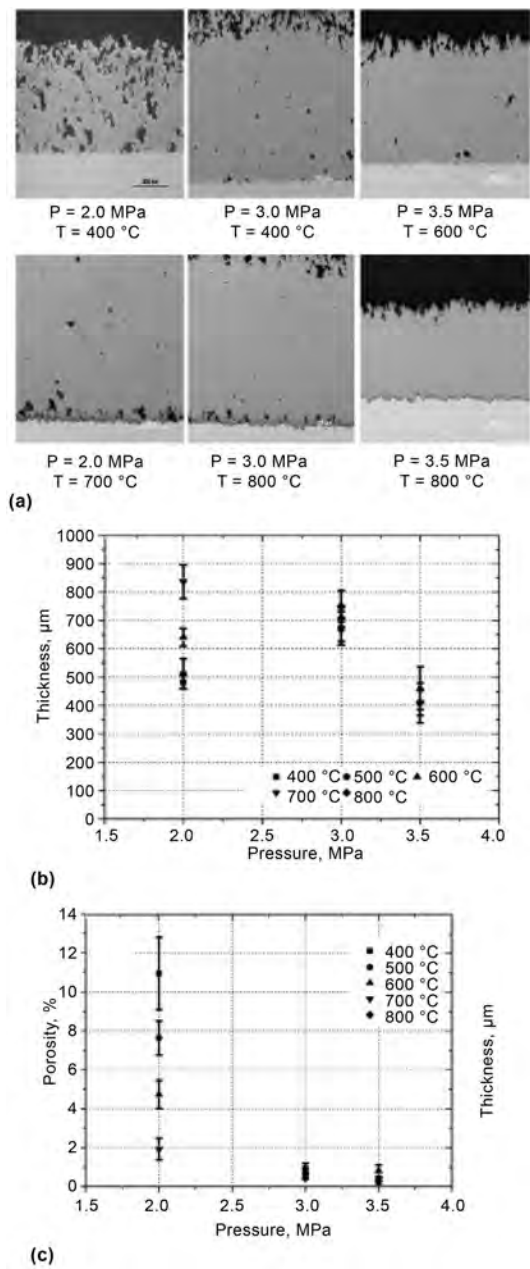


Fig. 5.2 (a) Optical micrographs depicting variation in porosity with processing parameters for a Ti-64 coating on a SS304 substrate. (b, c) Variation of porosity with thickness and gas pressure as measured from the optical micrograph. Source: Ref 5.10

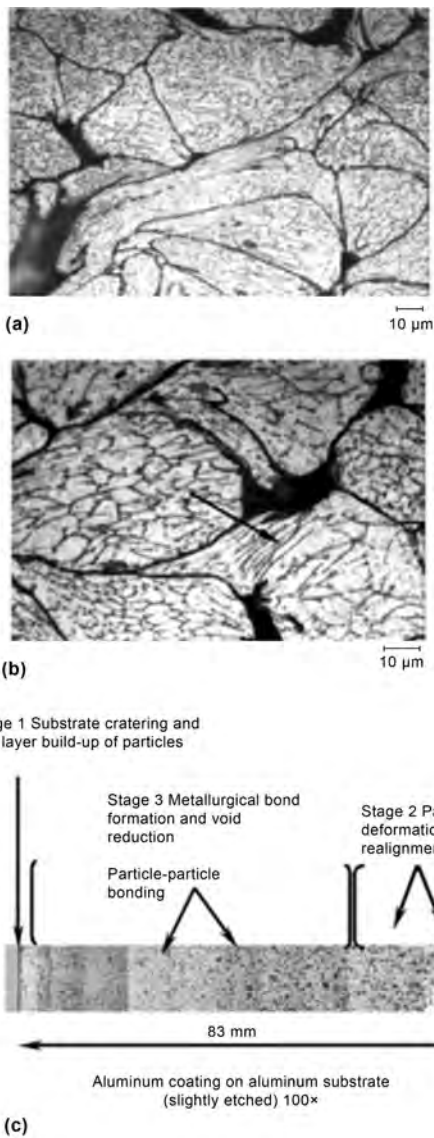


Fig. 5.3 Optical micrographs with etched aluminum coatings as a function of gas temperature at (a) 204 °C (400 °F) and (b) 315 °C (600 °F), revealing the extent of particle deformation. (c) Micrographs used to determine the nature of bonding of the coating. Source: Ref 5.12

electrodischarge machine wire cutting is typically used. However, in some cases, these have been found to result in delamination of the coating from the substrate, and therefore, waterjet cutting is recommended in order not to impart stresses during cutting. Typically, the samples are viewed in the bright-field mode to obtain images of the coating thickness. It is recommended that a dark-field mode be used to make a more quantitative assessment of the pores in the coating.

5.2 X-Ray Diffraction

X-ray diffraction (XRD) has been used as a versatile tool for preliminary characterization of the phases that evolve in cold-sprayed coatings. A collimated beam of x-rays with a wavelength of 0.5 to 2 Å is diffracted by the crystalline phases in the specimen according to Bragg's law. The diffraction pattern is used to identify the structural properties of the material, such as structure, lattice parameter, strain (which is measured with great accuracy from the diffraction peaks), epitaxy, and the size and orientation of the crystallites (Ref 5.1, 5.2, 5.4, 5.5). The probing depth is a few micrometers to tens of micrometers, depending on the absorption coefficient of the material for the particular wavelength of the x-ray probe.

The analysis for cold-sprayed coatings starts with the powder characterization, followed by the as-sprayed as well as the heat treated coatings (Ref 5.4, 5.19–5.24). Due to the severe plastic deformation that takes place during the high-pressure cold spray process, the characteristic diffraction pattern in the as-sprayed condition is usually one with broad peaks, as shown in Fig. 5.4(a) for an IN625 coating (Ref 5.25). The peak broadening in the as-sprayed coating as compared to the powders can be due to two factors: particle size broadening and broadening due to strain (nonuniform). The full width at half maxima (FWHM) of the diffraction peak is estimated from the Scherrer formula (Ref 5.26) for particle size broadening:

$$d = 0.9\lambda/\beta\cos\theta \quad (\text{Eq 5.1})$$

where d is the particle size, λ is the wavelength of the x-ray, β is the FWHM of the x-ray peak (in radians), and θ is the angle of the peak. Typically, the Scherrer formula is based on the assumption that the peak broadening is caused by crystallite size. The nonuniform strain-induced broadening effect of the FWHM is obtained by the Williamson-Hall (WH) plot, which is derived by the equation:

$$\varepsilon = \beta\cos\theta - A/2\sin\theta \quad (\text{Eq 5.2})$$

where A is expressed as $C\lambda/d$, where C is the correction factor (~ 1), and d is the particle size. Figure 5.4(b) shows the WH plot for the IN625 coat-

ing, measuring a grain size of 35 nm (Ref 5.25). Another key feature of XRD is its ability to identify the phases in the coating and distinguish any changes to the phase equilibria during the process of cold spraying. Figure 5.5(a) is an illustration of characterization done on a cold-sprayed titanium coating with progressive removal of layers from the coating (Ref 5.20). A comparison between the as-sprayed coating and α titanium indi-

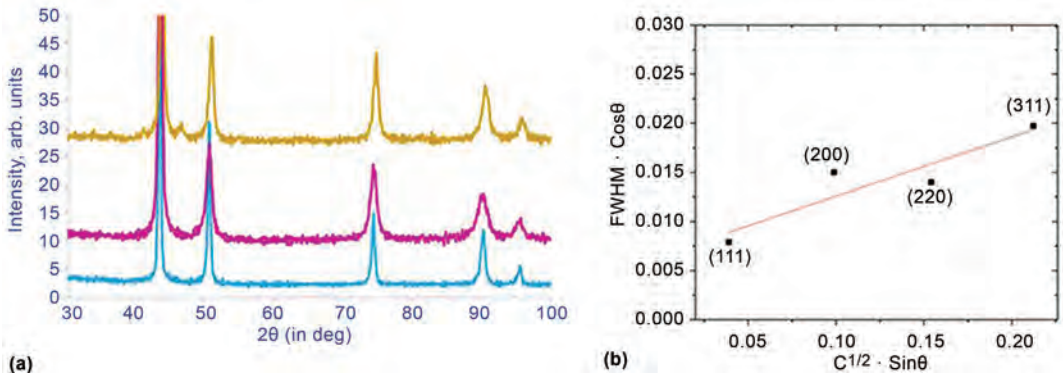


Fig. 5.4 (a) X-ray diffractograms comparing IN625 (nickel-base superalloy) powders and cold-sprayed IN625 coating reveal broadening of the diffraction peaks in the coating, indicative of macroscopic strain. (b) Hall-Williamson plot taken from the peak broadening data to calculate the extent of strain. FWHM, full width at half maximum. Source: Ref 5.25

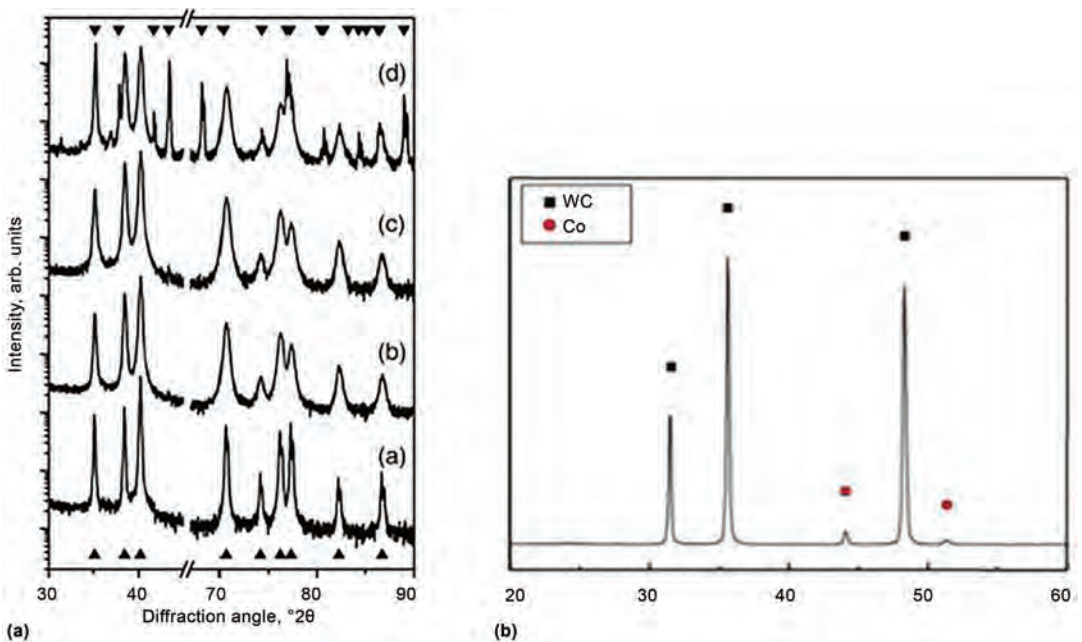


Fig. 5.5 X-ray diffraction patterns from (a) cold-sprayed titanium coating after removal of progressive layers from the coating compared with α titanium, indicating no phase transformation taking place in the coating, and (b) cold-sprayed WC-Co without any decarburization after the cold spray process. Source: Ref 5.11, 5.20

cates that there are no phase transformations taking place during cold spraying. Another example includes characterizing the absence of decarburization in a WC-Co coating, as shown by Kim et al. (Ref 5.11). In Fig. 5.5(b), a comparison is made between the powders and the cold-sprayed WC-Co coating to indicate the absence of any decarburization. Moridi et al. (Ref 5.19) were able to distinguish between a cold spray coating and the substrate for a titanium alloy using XRD, and Rokni et al. (Ref 5.22) showed an extensive peak broadening that is typically characteristic of cold-sprayed coatings in the as-sprayed condition. Upon heat treatment, the peaks become sharper, indicative of stress relaxation in the coatings (Ref 5.25). In all cases, the coating residual stresses diminish with heat treatment to a more tensile value, as reflected by a sharpening of the peak, as shown in Fig. 5.4(a).

A characteristic specific to cold-sprayed coatings is that they are nearly always crystalline with sharp diffraction peaks. X-ray diffraction is also used to identify phase formation during variations in the process, such as in the case illustrated in Fig. 5.6(a) and (b). Kim et al. (Ref 5.21) have done extensive characterization of cold spray versus warm spray using

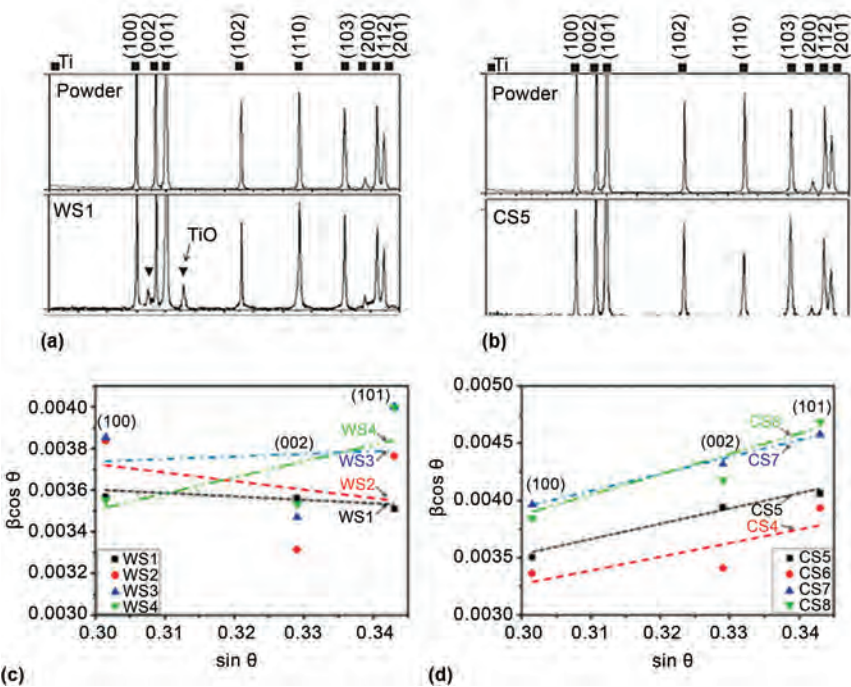


Fig. 5.6 X-ray diffraction patterns comparing (a) warm-sprayed and (b) cold-sprayed titanium coating, along with the respective starting powders, indicate the presence of TiO oxides along with the metal in the warm-sprayed coating. Williamson-Hall plots for the (c) warm-sprayed and (d) cold-sprayed coatings indicate a lower degree of strain in the warm-sprayed coating. Source: Ref 5.21

XRD, wherein the presence of oxides of titanium is prevalent in the warm-sprayed coatings, whereas it is absent in the cold-sprayed. They conclude that solid-state spraying can minimize or eliminate detrimental effects to the microstructure, such as oxide formation.

Figure 5.6(c) and (d) compare the WH plots between warm- and cold-sprayed titanium, indicating that the coatings contain more nonuniform strain as compared to the powder; however, between the two coatings, the cold-sprayed coating showed a higher level of strain than those in the thermally softened process of warm-sprayed coatings. The particle sizes indicated by the WH plots range between 38 and 40 nm.

The peak FWHM is also used to interpret the surface state of the material. Figure 5.7(a) shows a representative FWHM taken from the work of Ghelichi and Bagherifard (Ref 5.24) from their studies on Al7075 cold-sprayed coating onto an aluminum substrate. A big jump at the interface between the deposited material and the substrate is shown in Fig. 5.7(b), which represents the FWHM measured through the thickness of the coating into the substrate. In this case, by applying the de Keijser (Ref 5.23) method, the grain size of the material is found to range between 20 and 50 nm, from a convolution of the diffraction pattern.

Several reports have thus made use of XRD to characterize the powders, the coating in the as-sprayed condition, the extent of lattice strain, the phase transformations in the as-sprayed versus heat treated condition, and the grain size. Typically, flat samples are recommended in order to

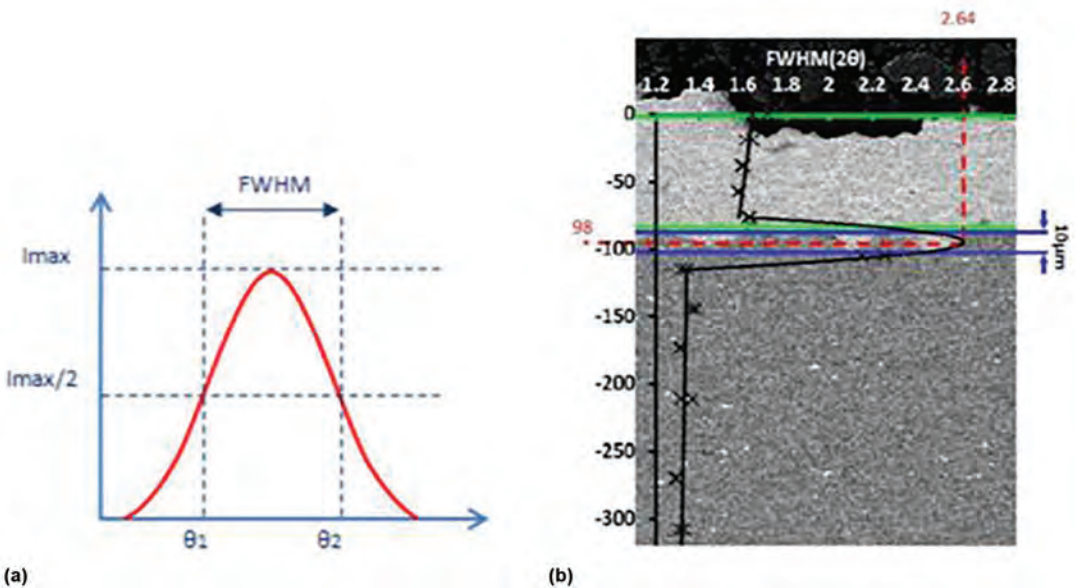


Fig. 5.7 (a) Full width at half maximum (FWHM) from an x-ray diffractogram peak corresponding to a cold-sprayed Al7075 coating. (b) Mapping the FWHM through-thickness of the coating and substrate for estimating grain size. Source: Ref 5.24

obtain precise values of lattice spacing from the x-ray diffractogram. Apart from this, no special care is needed during sample preparation. It is recommended that the top surface be slightly ground off so that any oxides that form on the surface do not lead to any artifacts or additional peaks in the XRD pattern.

5.3 Scanning Electron Microscopy

The scanning electron microscope is often the first analytical tool that is used when imaging features having a resolution that exceeds the resolution of the optical microscope. The image can be magnified up to 100,000 times, and it typically requires minimal sample preparation. Details of the scanning electron microscopy (SEM) can be found in several books. However, the key aspects of SEM that distinguish it from other analytical techniques are the depth of field of the equipment and the ability to obtain chemical composition information using energy-dispersive x-ray spectroscopy (EDS) or wavelength-dispersive spectroscopy (WDS).

The equipment possesses a lateral resolution of 1 to 50 nm in the secondary electron mode. Energy-dispersive x-ray spectroscopy can provide a rapid multielement analysis for $Z > 11$, with a detection limit of approximately 200 ppm. Wavelength-dispersive spectroscopy is based on the phenomenon of Bragg diffraction of x-rays incident on a crystal, and it yields a more precise quantitative estimate of the elements. Details pertaining to both these techniques can be found in Ref 5.1 and 5.2. A unique aspect of SEM is that it is able to image in both the secondary electron (SE) mode and the backscattered electron (BE) mode. Figure 5.8 shows a comparison of EDS and WDS spectra from a complex multielement glass (Ref 5.1).

In cold spray characterization, SEM is used right from the starting powder characterization. The feedstock powders are analyzed for particle size, size distribution, shape, and chemical composition prior to start of the cold spraying process (Ref 5.27–5.37). Figure 5.9(a) and (b) show representative scanning electron micrographs with two types of WC-Co feedstock powders used for cold spray coating (Ref 5.11), revealing an acicular and a spherical shape. Scanning electron microscopy is used prior to spraying to assess powder cross section (Fig. 5.9c, d) and particle size distribution (Fig. 5.9e, f) (Ref 5.27). Imaging can be done in either the SE or the BE mode, as shown in Fig. 5.9(g) and (h), respectively, taken from an aluminum coating. The SE imaging is typically used to reveal topography, while BE imaging is used to reveal atomic number contrast to reveal the phases in the coating. The effects of spray angle and deposition efficiency are analyzed using SEM microstructures of etched samples, as shown in several reports. For example, sometimes there is erosion of the nozzle during cold spray, especially while spraying hard materials such as MCrAlY or Inconel powders; the eroded material could end up embedded in the coating and be distinguished as an artifact.

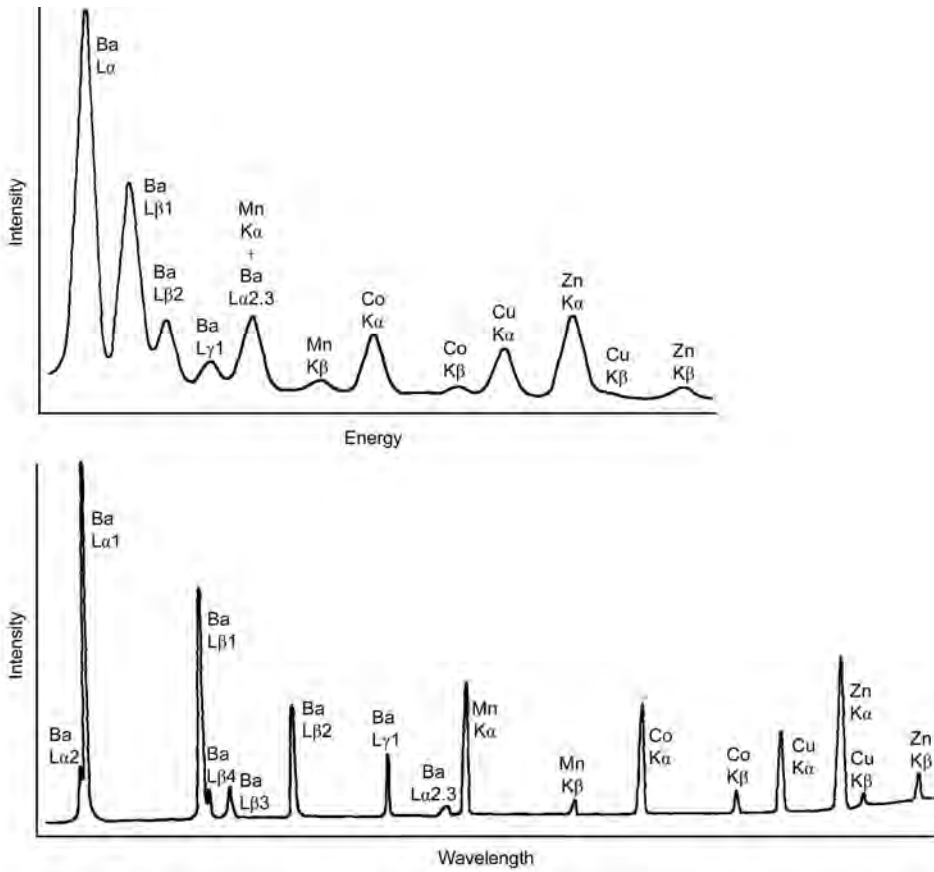


Fig. 5.8 Comparison of energy-dispersive x-ray spectroscopy and wavelength-dispersive spectroscopy spectra from a complex multielement glass. Source: Ref 5.1

One of the most extensive uses of SEM is in characterization of coating chemistry using EDS. Figure 5.10(a) to (d) show representative SEM micrographs of IN625 feedstock powders and cold spray coating, along with the corresponding energy-dispersive x-ray analysis pattern from the powder, and the coating chemistry (Ref 5.33). Often, elemental mapping is carried out, especially on the powders prior to spraying, to evaluate the level of segregation in the chemistry, as shown in Fig. 5.11(a) to (d) for the case of two types of MCrAlY powders (Ref 5.38). Characterization of coating porosity is carried out to provide feedback to achieve the optimum coating thickness for enabling a dense coating (Fig. 5.12), as described by Wong et al. for titanium coatings (Ref 5.37). The evolution of coating porosity with different feedstock powders and the surface topography of the powders are shown in Fig. 5.12.

Coating thickness and interface contour can be characterized in a manner that makes SEM an indispensable and versatile tool for evaluating the coating integrity in the as-sprayed condition, as well as in developing an

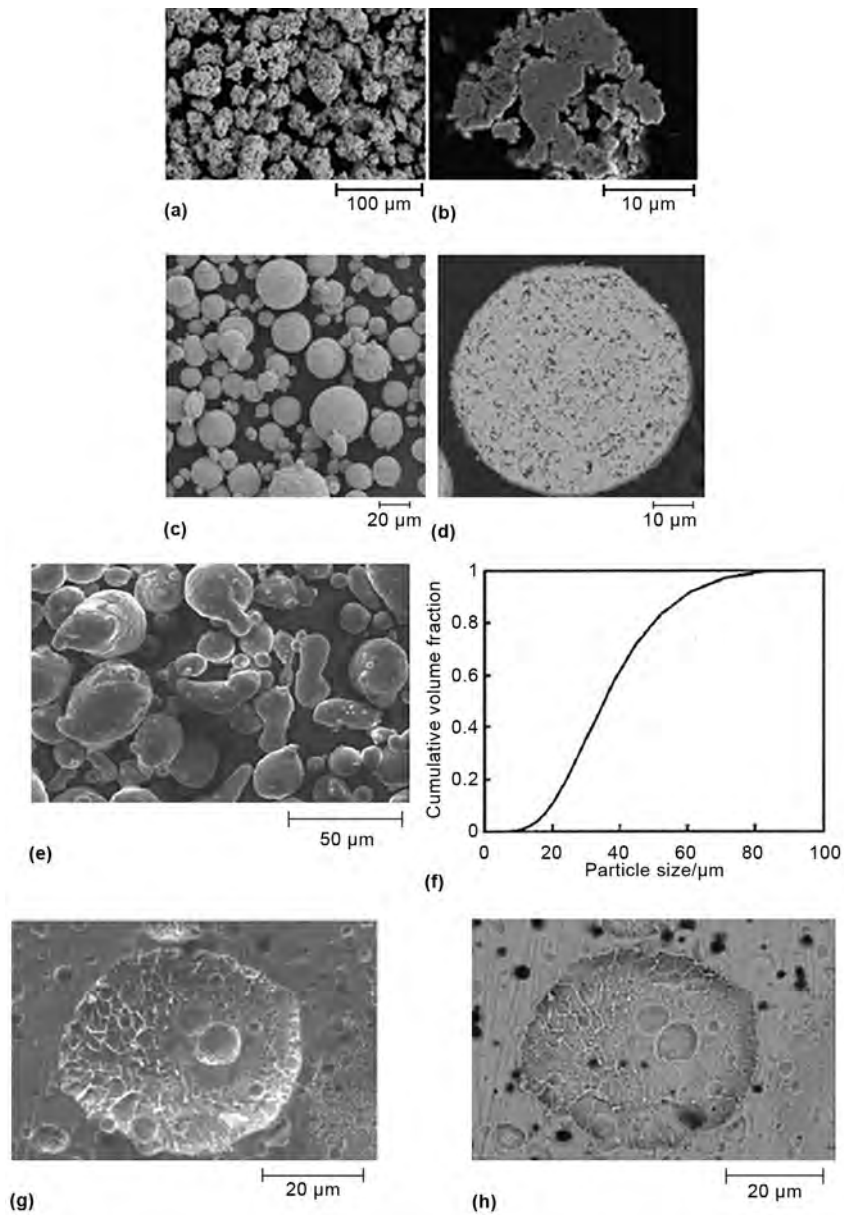


Fig. 5.9 Scanning electron micrographs showing powder morphology and cross-sectional structure from (a, b) two different feedstocks of WC-Co powders; (c, d) powder cross section, (e) morphology, and (f) size distribution of aluminum feedstock powder; and (g, h) secondary electron image and backscattered image of an aluminum coating. Source: Ref 5.11, 5.27

understanding of the bonding to the substrate. Substrate hardness has been found to play an important role in achieving good coating deposition. Figure 5.13(a) and (b) show the interface of a Ni-20Cr coating (Ref 5.33) on an AISI 4130 steel versus an aluminum substrate. The softer aluminum

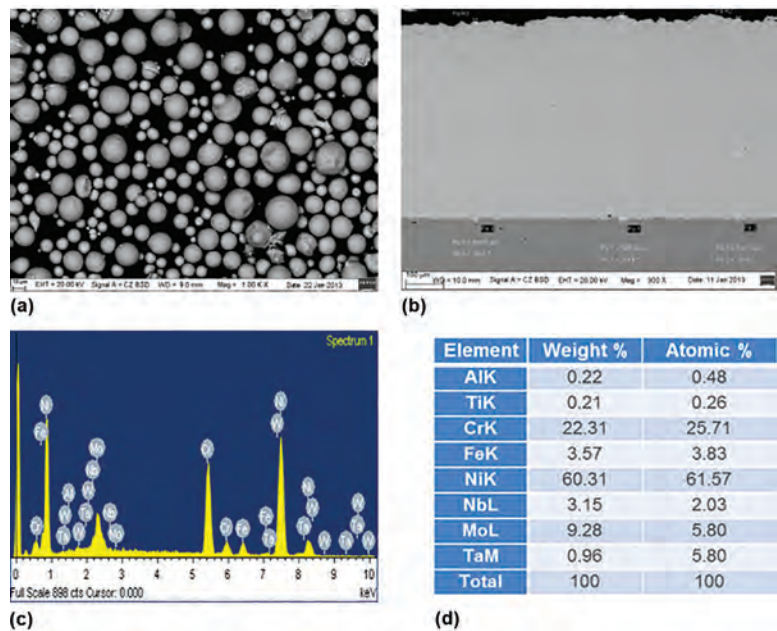


Fig. 5.10 Scanning electron micrographs showing (a) IN625 powder morphology and (b) as-sprayed coating. (c) Energy-dispersive x-ray analysis pattern and (d) listing of the elements from the spectrum in the coating. Source: Ref 5.33

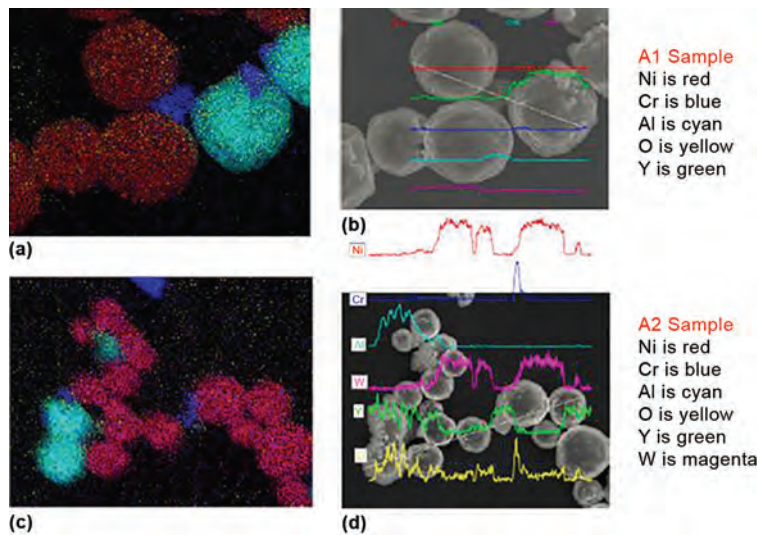


Fig. 5.11 Energy-dispersive x-ray analysis mapping along with scanning electron micrographs taken from an MCrAlY cold-sprayed coating to illustrate elemental segregation in the powders. (a, b) Powder type A. (c, d) Powder type B. Source: Ref 5.38

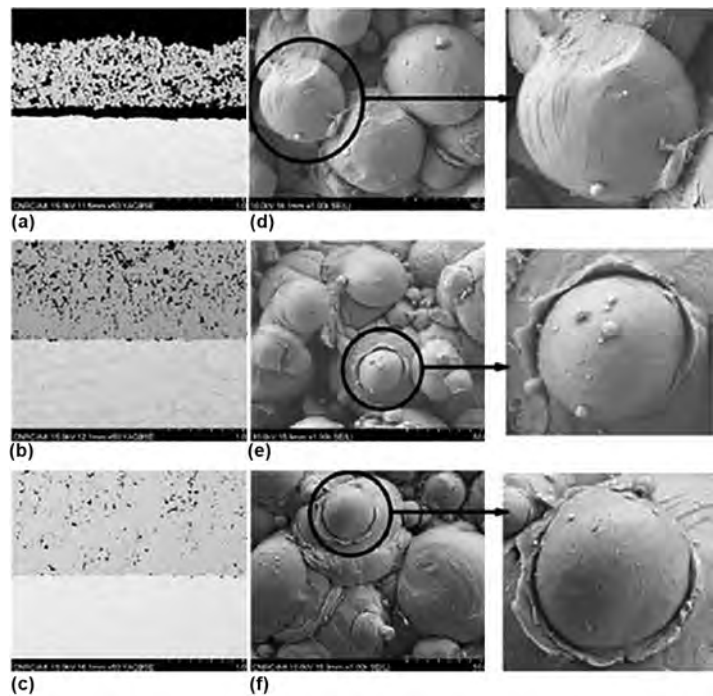


Fig. 5.12 Scanning electron micrographs showing powder morphology and cross-sectional structure from two different feedstocks of WC-Co powder. Source: Ref 5.37

substrate does not provide any resistance to the particles that impinge on it at high velocity, as shown by the first layer of particles, which undergo little or no deformation (Fig. 5.13b) as compared to the steel substrate (Fig. 5.13a). In each case, upon heat treatment, a thin diffusion layer forms along the interface, as shown in the scanning electron micrograph in Fig. 5.13(c). The nature of the interdiffusion layer is established by EDS analysis of the chemistry, as shown in Fig. 5.13(d) (Ref 5.33). In a similar way, SEM is used extensively to study the intersplat coating characteristics in the as-sprayed versus heat treated condition, as shown in Fig. 5.14(a) to (c) (Ref 5.13).

5.4 Focused Ion Beam Machining

Focused ion beam (FIB) systems are used in cold spray coating characterization selectively, to gather information on the nature of splat formation, single splats, multiple splats, or the coating-substrate interface (Ref 5.39–5.42). It resembles the SEM except that instead of using a focused beam of electrons to raster the sample surface, it uses a focused beam of ions (usually gallium) either to image the sample (using low-beam currents) or to remove material by sputtering it away (high currents).

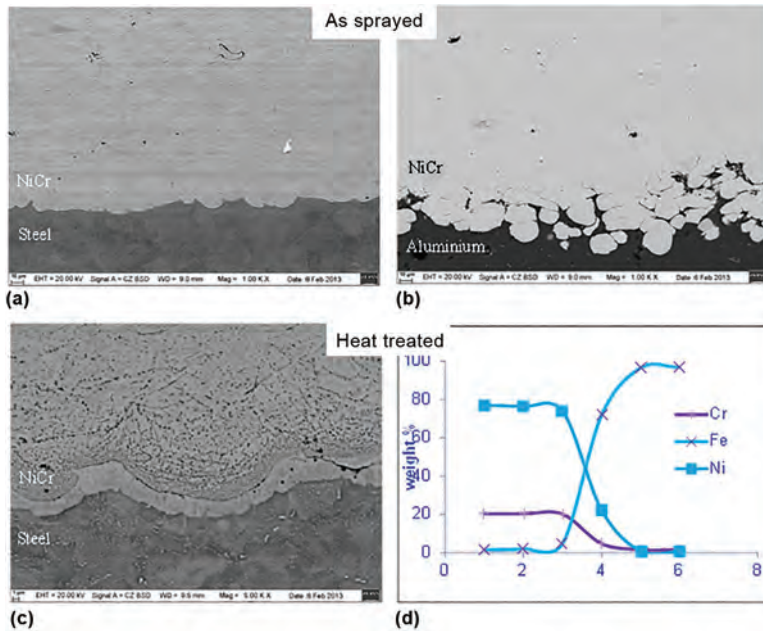


Fig. 5.13 Scanning electron micrographs taken from a NiCr cold-sprayed coating (using helium gas) on (a) AISI 4130 steel, (b) aluminum substrate, and (c) coating-substrate interface after heat treatment, revealing an interdiffusion zone. (d) Composition across the interface taken by energy-dispersive x-ray spectroscopy. Source: Ref 5.33

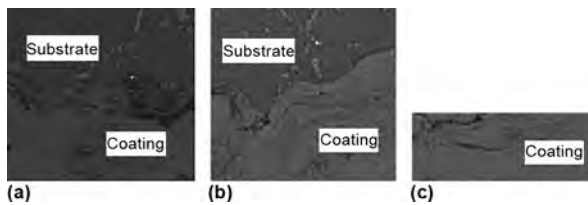


Fig. 5.14 Scanning electron micrographs of aluminum cold-sprayed coating on magnesium substrate. (a) Without heat treatment, air cooled. (b) 250 °C (480 °F), 1 h holding time, air cooled. (c) 300 °C (570 °F), 1 h holding time, air cooled. Source: Ref 5.13

King and Jahedi (Ref 5.39) studied the effect of particle size and bonding for aluminum and copper particles and were able to make use of FIB machining to prepare sample sections and then view and analyze them by means of SEM, as shown in Fig. 5.15(a). The particle-flattening ratios could be determined accurately using the FIB sections and used as inputs to feed into a model. Smaller particles were seen with a higher bow shock effect in the gas flow and exhibited a greater resistance to deformation on

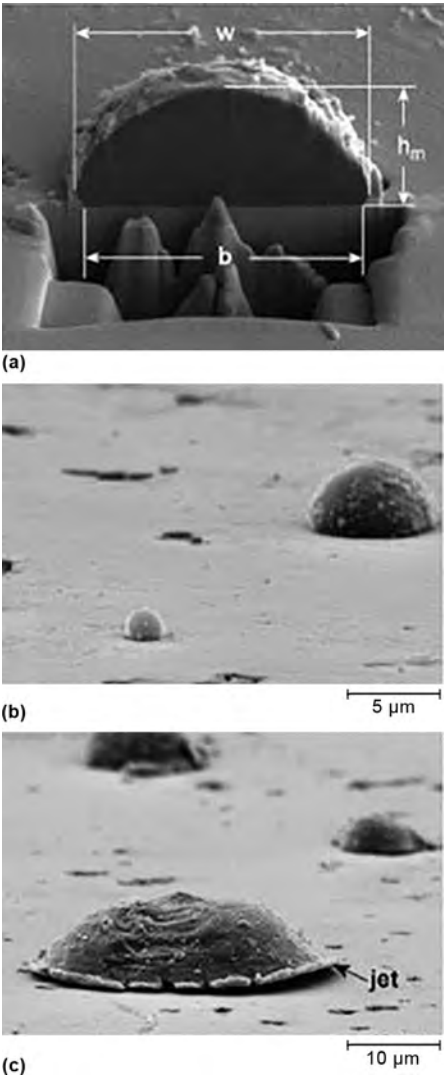


Fig. 5.15 (a) Focused ion beam/scanning electron microscopy image of aluminum particle dissected using Ga⁺ ions. (b, c) Secondary electron micrographs of aluminum particles adhering to ceramic (lead-zirconium titanate) surface. Source: Ref 5.39

impact. This result was further validated using an SE image with a stage tilt in the SEM >75° to precisely estimate the base and apex of the individual particles, as shown in Fig. 5.15(b).

The advantage of using FIB is to have location-specific characterization of the cold-sprayed coating. Sometimes, FIB is used to enable preparation of thin electron-transparent samples for transmission electron microscopy, as discussed in the next section.

5.5 Electron Probe Microanalysis

Electron probe microanalysis is a spatially resolved quantitative elemental analysis technique based on the generation of characteristic x-rays using a focused beam of energetic electrons. Further details on this technique can be found in Ref 5.1. Electron probe microanalysis is used to measure the concentration of elements at levels as low as 100 parts per million (ppm) and to develop lateral distributions by mapping, using both an energy-dispersive x-ray spectrometer and a wavelength-dispersive spectrometer (Ref 5.1, 5.2). Electron probe microanalysis has been used in cold-sprayed coating characterization mainly to understand the bonding mechanism at the coating-substrate interface. It is a valuable characterization tool for accurately understanding the type of bonding, as shown in the case of a Ni-20Cr cold-sprayed coating on an AISI 4130 steel substrate in the as-sprayed versus heat treated condition in Fig. 5.16 (Ref 5.43). It has been used to understand the coating relaxation process in the as-sprayed condition and after heat treatment in the vicinity of the substrate.

5.6 Transmission Electron Microscopy

The structure and phase equilibria of severely plastically deformed cold-sprayed coatings are studied using transmission electron microscopy

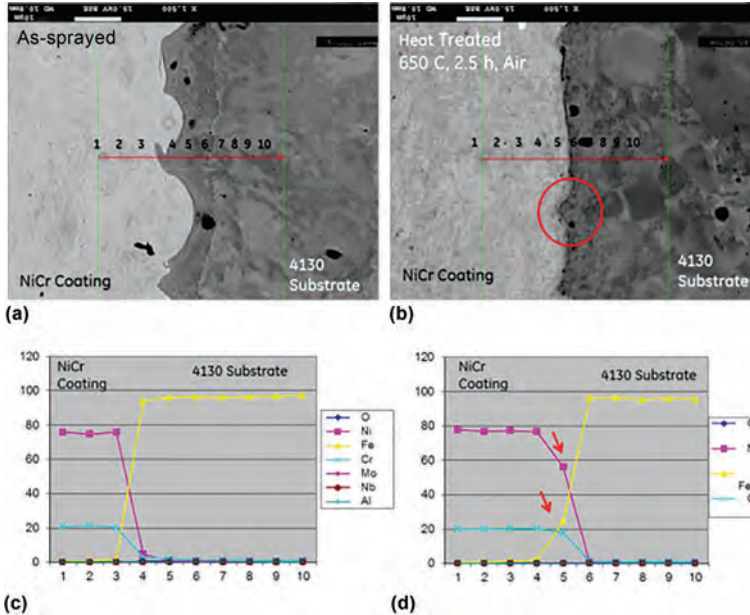


Fig. 5.16 Representative scanning electron micrographs showing Ni-20Cr coating on AISI 4130 steel substrate interface, (a) as sprayed and (b) after heat treatment. (c, d) Corresponding electron probe microanalysis elemental profiles indicating the interdiffusion of elements at the interface. Source: Ref 5.43

(TEM). Precise information about the atomic structure, microstructure, crystallinity, extent of deformation, dislocation density, precipitate formation, defects, recrystallization, and other characteristics can be quantified at high lateral resolution (at the angstrom level) using TEM. Like x-ray diffraction and electron backscatter diffraction, TEM can yield quantitative information about the phase equilibria and phase evolution in the coating as well as its bonding mechanism.

In TEM, a high-energy electron beam (100 to 300 kV) is used to penetrate the coating, and information from the transmitted and the diffracted beams is used to analyze the characteristics of both the coating and the coating-substrate interfaces. It is one of the most reliable techniques for acquiring very precise information about the characteristics of cold-sprayed coatings.

However, because the sample must be electron transparent, sample preparation is somewhat tedious. The sample size is a standard 3 mm (0.1 in.) diameter disc, with the electron-transparent region ranging between a few nanometers to a few micrometers. It is prepared through a series of process steps (Ref 5.2, 5.5). In some cases, especially involving a study of the characteristics of intersplat boundaries or the coating-substrate interface, a special sample preparation that can give TEM samples, using an FIB attached to an SEM, is used. Details of the FIB technique can be found in Section 5.4 in this chapter.

Typical magnification in TEM ranges from 500 to 100,000 $\times$. The nature of deformation in the as-sprayed condition and the extent of relaxation of the coating after heat treatment are studied by this technique. Transmission electron microscopy provides a means to obtain a diffraction pattern from the specimen, which enables identification of the phases in the cold-sprayed coating in a unique manner.

Cold-sprayed coatings are complex by nature, largely because of the severely plastically deformed structure of the atomized powders (which are obtained by rapid solidification). In addition, the high strain rates (10^6 to 10^8 /s) that enable the formation of the coating, the resulting adiabatic shear instability with abnormal heating at the interface, and the rapid solidification at the splat interface can combine to result in a complex dislocation structure. The coating-substrate interface microstructure and bonding mechanism are therefore complex as well, depending on whether the substrate is hard(er) or soft(er) compared to the coating material. Additionally, the scale of the sample area that is electron transparent for TEM evaluation will probably cover only one-tenth of one splat, and thus, several samples will need to be studied. For all of these reasons, there are not too many detailed studies on the TEM characterization of cold-sprayed coatings. This section presents representative TEM characterization of various coatings.

The TEM examination of the feedstock powders enables an understanding of the starting powder structure. Borchers et al. (Ref 5.44) reported a

TEM study of cold-sprayed copper (using nitrogen gas) to assess the bonding mechanism of these coatings. An analysis of the feedstock powder revealed that the particles had a dislocation density of $10^{12}/\text{cm}^2$ with an average grain size $> 5 \mu\text{m}$ (Fig. 5.17a, b). The analysis was able to reveal the grain size of the prior particles, an important result that could give insights into the nature of deformation during cold-sprayed coating formation and subsequent recovery processes.

In addition, the analysis was able to confirm the absence of oxides in the feedstock powders, as revealed from the diffraction patterns taken from the powders. In this case, a high-pressure nitrogen gas (2.6 MPa, or 360 psi; 570 m/s, or 1870 ft/s) was used to spray the coating. The coating structure has four distinctly different regions, comprising elongated grains ($50 \times 150 \text{ nm}^2$), nonequilibrium grain boundaries characterized by a high

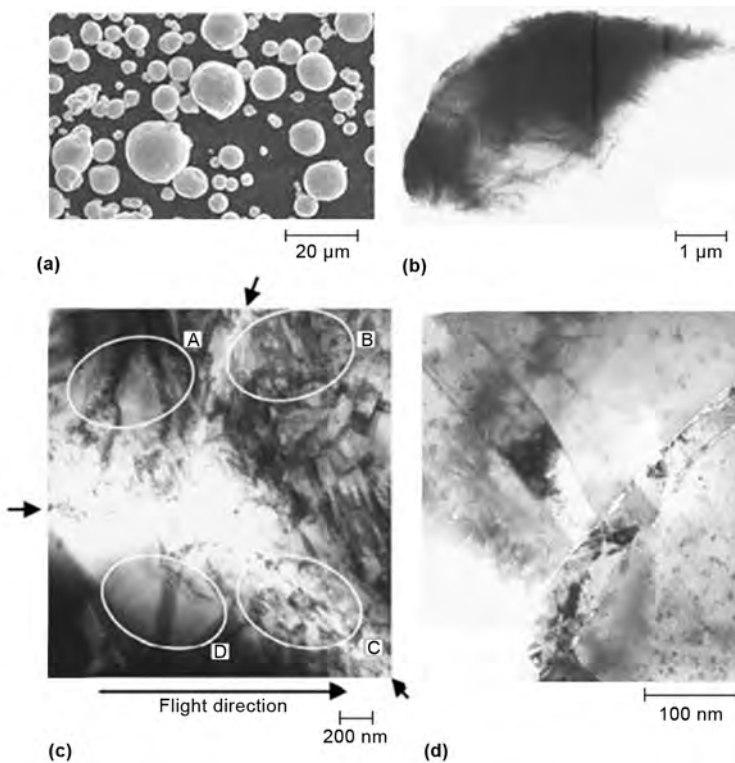


Fig. 5.17 (a) Scanning electron micrograph of the copper feedstock powder. (b) Transmission electron micrograph from powders showing a high dislocation density of $10^{12}/\text{cm}^2$. (c) Transmission electron micrograph of the cold-sprayed coating, showing the triple point of three particles and three different regions: grains $> 1 \mu\text{m}$ in diameter with a high dislocation density (region A), aligned elongated grains ($50 \times 150 \text{ nm}^2$) (region B), and equiaxed ultrafine grains $\sim 100 \text{ nm}$ in diameter (region C). (d) High magnification of a particle-particle interface showing a 50 nm copper layer indicative of a trapped jet, having a low dislocation density. Source: Ref 5.44

dislocation density, regions of very fine grains (~ 100 nm), and regions with somewhat large grains (>1 μm), as shown in Fig. 5.17(c). Borchers et al. also reported elongated grains (tens of nanometers wide by hundreds of nanometers long) and a particle-particle boundary having a 50 nm layer of copper, with a very low density of dislocations attributed to possible jet formation. They observed a strong tendency for grain refinement near the particle-particle interface, and they identified extensive dynamic recrystallization as the mechanism responsible for the formation of the observed dense microstructure and particle bonding, by comparing these microstructures with cold rolled copper. A model of deformation of copper powders to enable a dense coating was proposed by using the TEM microstructures, which is not likely to be obtained by any other characterization method. Figure 5.17(d) shows a closer view of a particle-particle interface, revealing a 50 nm layer of copper between the particles, evidence of a trapped jet that appears to be devoid of any dislocations.

Transmission electron microscopy is also used to characterize the mechanisms of bonding to different substrates, which can be uniquely obtained by no other characterization technique. In a fundamental study, Kim et al. (Ref 5.45) studied the deformation behavior of a single-particle impact of warm-sprayed titanium onto three different substrates of varying hardness as compared to the equivalent bulk titanium. Figure 5.18(a) to (c) show representative particle-substrate interface TEM bright-field electron micrographs to illustrate the bonding mechanism of cold-sprayed titanium to titanium (Fig. 5.18a); to aluminum, a softer substrate (Fig. 5.18b); and to zirconia, a harder one (Fig. 5.18c), by using the scanning TEM (STEM) mode. Details on STEM imaging can be found in other references (Ref 5.1, 5.2). The particle-substrate interface was characterized into two distinct regions: a well-bounded one near the periphery, and a rebounded region with a thin gap (a few micrometers) between the particle and the substrate at the center bottom of the particle (Fig. 5.18a).

Making use of the STEM mode in the TEM, they were able to distinguish the roles played by the different substrate hardnesses. In the titanium-titanium case, very fine grains (a few tens of nanometers) were seen at the lower portion, indicative of some dynamic recrystallization at elevated temperature, while the grain size near the upper region was characterized by grains measuring a few micrometers, representing the original particle. For titanium on a softer aluminum substrate, the deformation was concentrated on the substrate and not so much the particle; for the zirconia substrate, the titanium particle was flattened the most, with little deformation of the substrate (Fig. 5.18). Furthermore, high-resolution TEM lattice images reveal the contiguity of the interface, without any voids, as well as the jetting out of the particle induced by the impact, with evidence to indicate that there is a fresh surface created that can lead to metallurgical bonding. In some cases, the interfacial region showed an amorphous layer with nanograins (Fig. 5.18).

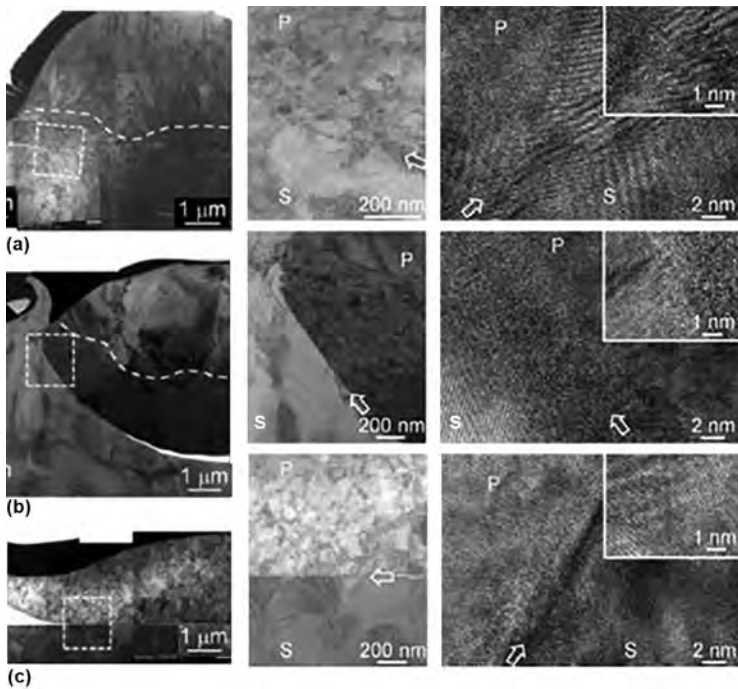


Fig. 5.18 High-resolution lattice images of a single titanium cold-sprayed particle on three different substrates: (a) titanium, (b) aluminum, and (c) ZrO_2 . P: particle; S: substrate. Source: Ref 5.45.

Balani et al. (Ref 5.46) have compared cold-sprayed aluminum coating microstructures using helium (100%) versus nitrogen ($\text{He-20\%N}_2$) process gases. They attribute the higher hardness obtained for the 100% He coating to a gradual smooth interface with a dislocation pileup and distributed oxides, as compared to a 20% N_2 coating, which exhibits a reduced compatibility at the interface, with associated subgrain formation. The TEM analysis of a Stellite 6 coating (Ref 5.47) reveals that under the high strain rates imposed by the typical cold gas spraying process, the coating remains in the high-temperature face-centered cubic phase, with a number of deformation twins in the microstructure. Despite the severe plastic deformation that takes place in a cold-sprayed coating, there was no shear activated deformation seen in the Stellite 6 coating, and it was found to remain as a cubic phase after cold spraying.

Ogawa and Seo (Ref 5.48) and Niki (Ref 5.49) report extensive studies on the interfacial structure of IN738 cold-sprayed coating on an IN738 substrate. Careful sampling of the coating-substrate interface was done using an FIB for the as-sprayed coating (using nitrogen gas) and for the same coating after heat treatment. Figure 5.19(a) is an optical micrograph to indicate the sampling section for the TEM. In the as-sprayed condition, the coating comprises crystal sizes of the order of tens of nanometers to hundreds of nanometers. There was no texture of preferential orientation; however, they were

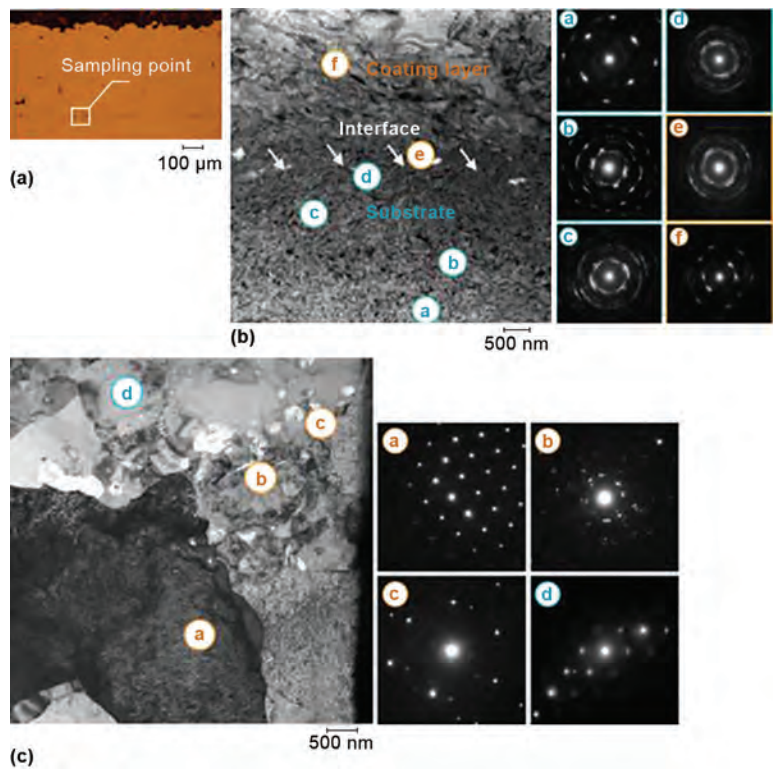


Fig. 5.19 (a) Optical micrograph of as-sprayed coating-substrate interface along with (b) corresponding transmission electron micrographs identifying phase evolution and deformation in vicinity of the coating-substrate interface, and (c) interface evolution after heat treatment. In both cases, this is demonstrated unambiguously by using selected area diffraction patterns. Source: Ref 5.48

able to pinpoint the severe plastic deformation of the coating and the substrate, which resulted in nanosized grains, from TEM bright-field imaging, as shown in Fig. 5.19(b). Further along the interface, the authors refer to columnar grains. Depending on the direction of the impact and the extent of deformation, there could be variations in the location of nanograins versus columnar grains with the span of a particular splat.

It was mostly concluded that the splat bottom was made of nanograins, while along the sides of a particle, accommodation of the shear strain results in columnar grains. However, they conclude that in the as-sprayed condition, due to repeated impact that takes place as the coating is built in thickness, the structure comprises a mixture of columnar grains and nanograins. Upon heat treatment, there is rampant grain growth, as shown in Fig. 5.19(c). There were still some pockets close to the interface with fine-grained structure (point B in Fig. 5.19b), to which possible poor adhesion of the coating to the substrate is attributed. In both cases, selected area diffraction patterns were used to identify the formation of nanograins close to the interface.

Recent studies by Srinivasan and Amuthan (Ref 5.25) on cold-sprayed IN625 have demonstrated some very different behavior in the cold-sprayed form as compared to its wrought counterparts. Detailed investigation of the coating in the as-sprayed versus heat treated condition revealed that cold-sprayed IN625 coatings were devoid of any strengthening precipitates and were thought to be a complete solid solution with a severe deformed structure both in the as-sprayed condition and after heat treatment.

Two distinct regions lying adjacent to each other demarcated the coating microstructure in the as-sprayed condition. Region I comprised fairly large grains with a severely deformed structure, and region II, between 0.5 and 1 μm , comprised mainly twins, as shown in Fig. 5.20(a) and (b). Upon

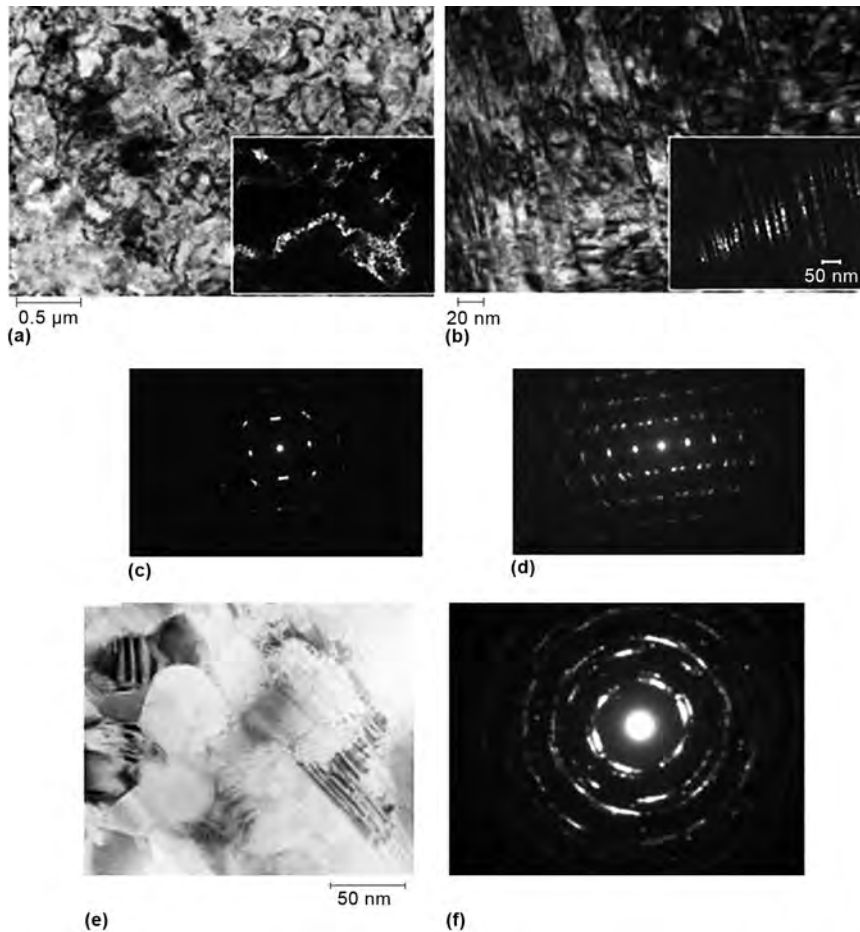


Fig. 5.20 Bright-field transmission electron micrographs showing representative microstructures of the as-sprayed IN625 coating, revealing two distinct adjacent regions: (a) region I, with $>1\ \mu\text{m}$ grains having a highly deformed grain structure, and (b) region II, with $<1\ \mu\text{m}$ grains displaying deformation twins. Inserts show dark-field transmission electron micrographs from respective regions. (c, d) Selected area diffraction patterns indicating occurrence of twins in region II. (e) Formation of nanograins after heat treatment at 650 $^{\circ}\text{C}$ (1200 $^{\circ}\text{F}$) for 2.5 h. (f) Corresponding diffraction pattern. Source: Ref 5.25

heat treating, the severe deformed structure underwent recovery, recrystallization, and grain growth, leading to strain-free grains (between 800 and 1200 nm), as shown in Fig. 5.20(c) and (d). However, in no instance did the cold-sprayed IN625 exhibit the γ'' -($\text{Ni}_3\text{Nb}(\text{Al,Ti})$) precipitate, and it was found to be devoid of the strengthening precipitate γ'' upon heat treatment up to 800 °C (1470 °F) for 100 h. There was also no occurrence of the equilibrium δ - Ni_3Nb phase upon heat treatment, and the coating remained a solid solution up to 800 °C for 100 h.

Superimposing the observed coating phase sequence on the time-temperature transformation diagram, as shown in Fig. 5.21, reveals that there is suppression of γ'' precipitation in the cold spray processing. It is rather remarkable to see the cold-sprayed coating display a modified phase evolution as compared to the wrought and heat treated bulk IN625. The difference is possibly due to a strain-induced transformation, with complete lack of any precipitation, unlike in the bulk counterpart. The TEM charac-

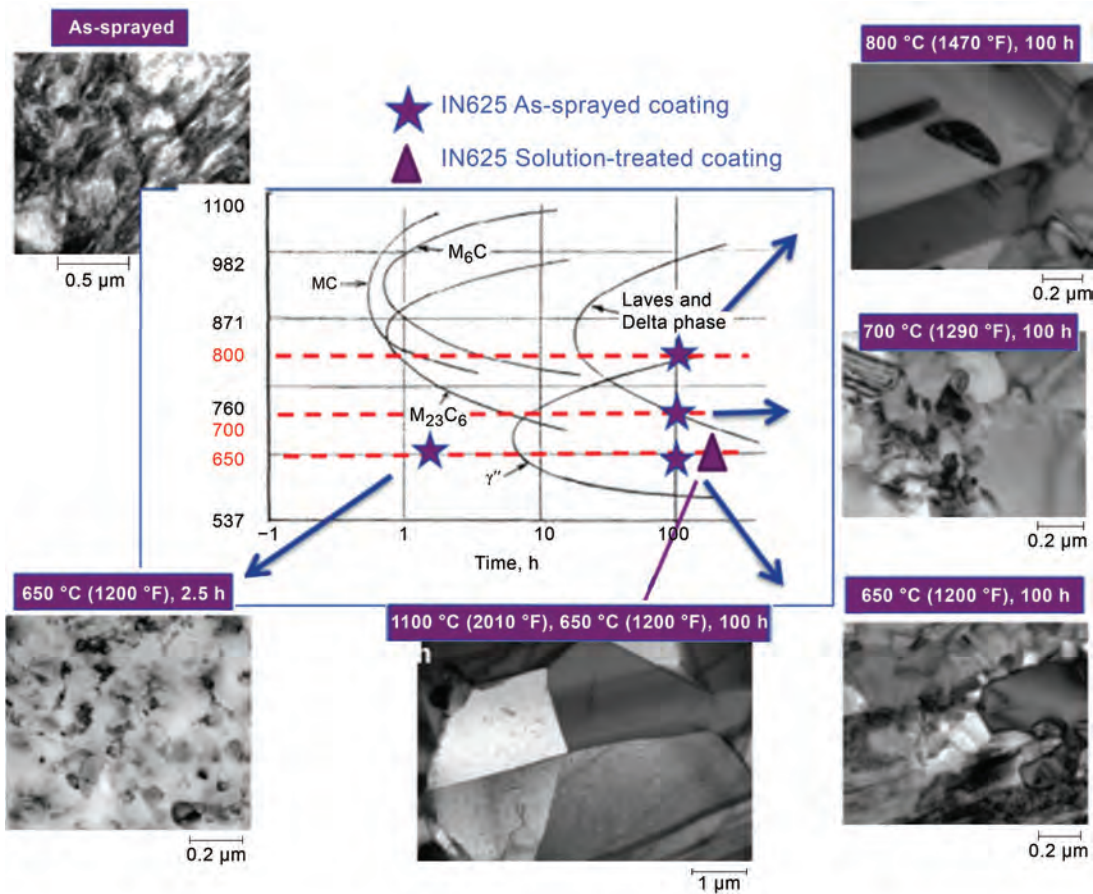


Fig. 5.21 IN625 cold-sprayed coating phase evolution superimposed on time-temperature transformation diagram for bulk IN625. Source: Ref 5.25

terization has been used to evaluate the thermal stability of the cold-sprayed coatings to map their recovery processes.

Overall, TEM is used as a valuable characterization tool to understand the powder characteristics, the cold spray coating deformation behavior both within splats as well as near the coating-substrate interface, the phase transformations in the as-sprayed and heat treated conditions, the phase equilibria of the coating under the operating conditions pertaining to the application of the coating, the coating recovery mechanism, and the thermal stability of the coating. This is probably the only characterization tool that gives precise quantitative information. However, as explained earlier, the sample preparation is somewhat cumbersome, and the region of observation is rather local; these factors should be borne in mind while using TEM as a characterization tool.

5.7 Electron Backscattered Diffraction

Electron backscatter diffraction (EBSD) is a characterization technique that enables the determination of crystal orientations, texture, boundary misorientations and deformation behavior, and bonding mechanism in cold-sprayed coatings. Although TEM provides adequate crystallographic information, EBSD is a microstructural crystallographic characterization technique performed by means of SEM that is able to sample large areas of samples and provide statistically significant data along with image quality. Especially in the case of cold-sprayed coatings with a nonuniform deformation, this technique is very suitable for providing valuable information on the nature of bonding. Pattern quality maps obtained by the Kikuchi pattern qualities show the local defect density and lattice strain. Sample preparation for EBSD involves metallography of the sample to yield a highly polished flat surface. Typical SEM accelerating voltages of 20 kV are used with step sizes of 50 to 500 nm to scan the coating with different grain sizes. Euler angle maps indicate locations with differing orientation by different colors (Fig. 5.22).

Figure 5.22(b) is a typical EBSD map showing the grain or crystallite size from aluminum feedstock powders to assess the initial crystallite size, taken from the work of Zou (Ref 5.50). In the EBSD map, each point is colored according to its crystal orientation. In this case, red corresponds to the [001] direction, blue to [111], and green to [101]. Characterization of the thermomechanical behavior of the cold-sprayed coatings has been carried out extensively using EBSD.

Electron backscatter diffraction, in conjunction with field-emission gun SEM, has provided insights into large areas of samples to elucidate the particle bonding, porosity, and so on and has provided statistically significant information on crystal orientation, including splat-boundary misorientation that can help elucidate the bonding mechanism and the complex thermomechanical history of the metal powder particles during cold

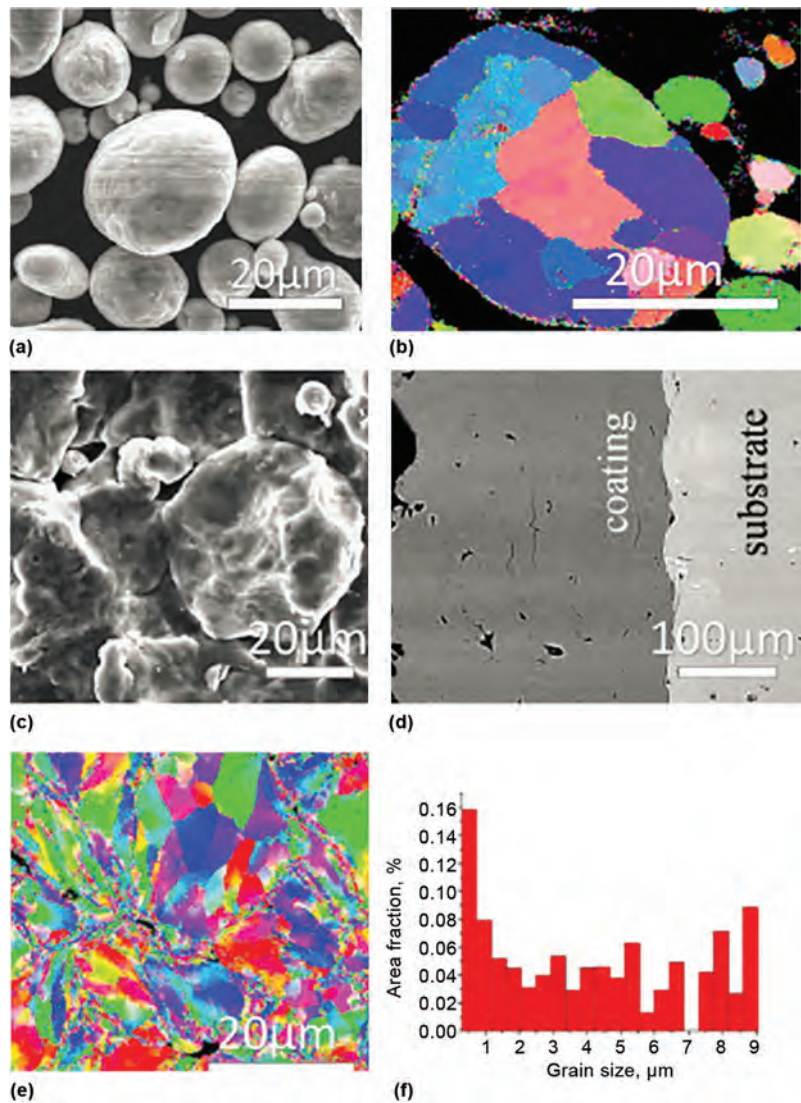


Fig. 5.22 (a) Scanning electron micrograph and (b) electron backscatter diffraction (EBSD) map of feedstock aluminum powder particles showing polycrystalline powder. (c) Scanning electron micrograph of top surface of cold-sprayed coating. (d) Coating cross section. (e) EBSD map of top surface. (f) Grain size distribution. Source: Ref 5.5

spraying (Ref 5.43, 5.50–5.55). Starting with the atomized powders, EBSD enables an understanding of the crystallite size as the lattice strain in the starting powder, by means of a Euler angle map. The as-sprayed coating (Fig. 5.22c, d) reveals a nonuniform deformation pattern, with some grains showing an equiaxed structure while others appear elongated. Regardless of whether the particles remain equiaxed or are heavily deformed, the particle-particle boundaries reveal ultrafine grains <100 nm.

Electron backscatter diffraction is also able to reveal the occurrence of nonuniform fine-grained structure, which can be attributed to dynamic recrystallization rather than static recrystallization.

The EBSD characterization of IN625 cold-sprayed coating is able to reveal several insights as to the nature of deformation within the splats, as shown in Fig. 5.23 (Ref 5.51). Figure 5.23(a) is a high-magnification SEM

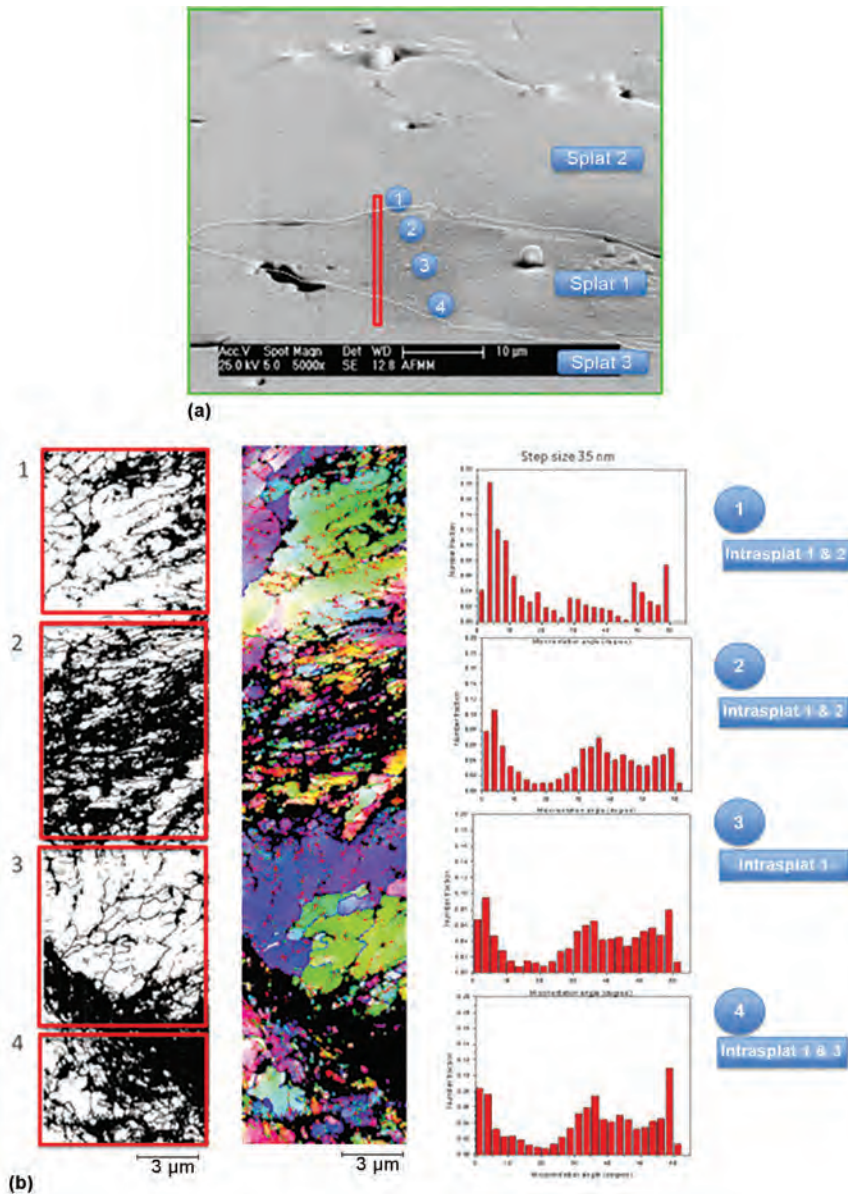


Fig. 5.23 (a) Scanning electron micrograph indicating boundary between two splats in an IN625 cold-sprayed coating. (b) Series of Euler images and image quality maps showing the nature of deformation in inter- and intrasplat locations. Source: Ref 5.51

micrograph focusing on the inter- and intrasplat locations, labeled “1” to “4” in the figure. Figure 5.23(b) is a series of Euler images as well as image quality maps taken from all the locations to indicate the degree of deformation that takes place in an IN625 coating. Figure 5.24, taken from the same coating, reveals details of change in grain orientation in response to the deformation, by way of the Euler angle map, which shows a change from the [110] to the [111] direction on impact. Figure 5.24(b) is an EBSD pattern from the AISI 4130 steel substrate showing two distinct deformation zones in the substrate, in the vicinity of the coating-substrate interface, in the case of hard particles on a hard substrate (Ref 5.43).

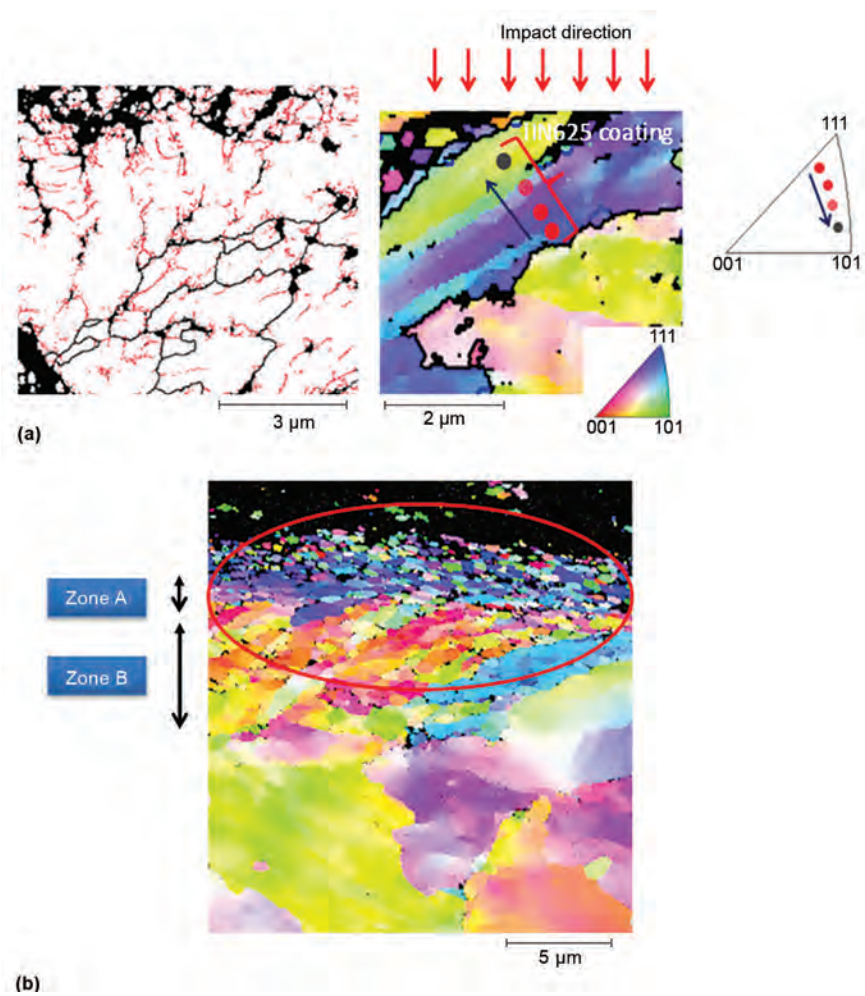


Fig. 5.24 (a) End-pattern quality maps from IN625 coating showing the change in orientation of the grain with respect to powder impact direction, indicative of the nature of deformation in these coatings. (b) Electron backscatter diffraction pattern from AISI 4130 steel substrate, indicating two distinct deformation zones in the as-sprayed condition. Source: Ref 5.43

Electron backscatter diffraction is also an indispensable tool in understanding the mechanical behavior of cold-sprayed coatings on different substrates, such as enabling an understanding of the fatigue response. The fatigue behavior of cold-sprayed coated materials is not well understood. In the case of hard metallic coatings, such as titanium- (Ref 5.56) and nickel-base alloys, there have been fatigue debits observed, whereas for soft materials such as aluminum and copper, it is reported that the compressive stress results in enhancing the fatigue properties (Ref 5.25, 5.57). Here, EBSD enables a detailed understanding of the deformation behavior in the substrate and is therefore able to substantiate the fatigue behavior.

5.8 Electron Channeling Contrast

Electron channeling contrast imaging (ECCI) is a technique that makes use of a convergent electron beam impinging on the surface of a crystalline material. The intensity of the backscattered electrons (BEs) depends on the orientation of the lattice planes inside the emission volume of the diffracted electrons. Hence, at any given point in the image, the BE yield is constant if the specimen is a monocrystal without any deformation. If, however, the grain has a different orientation or contains crystal defects such as stacking faults or dislocations, then the contrast changes and the resulting image is a channeling micrograph.

The theory of ECCI was developed by Howie, Joy, et al. in the late 1970s (Ref 5.58–5.60), and it was subsequently enhanced by several others. Electron channeling contrast imaging offers an angular resolution that is an order of magnitude smaller than that of EBSD and is particularly useful for observing complex deformation structure, such as twins and stacking faults. Zhang et al. (Ref 5.61), for example, have observed the dislocation structure in cold-sprayed copper to assess the complex nature of the cold-sprayed coating. An extra plane in the crystal generates strain, which induces a slight increase in the angle between the plane and the incident beam on one side of the dislocation line and a decrease of the angle on the other. This results in a change in the diffraction conditions and hence in the channeling/backscattering probability drive by the Block wave theory.

The ECCI offers a unique way of imaging dislocations in cold-sprayed coatings that enables an understanding of the dislocation arrangement as well as twinning, both of which play an important role during coating formation by means of deformation.

5.9 Residual Stress

Residual stress builds up during high-pressure cold spray coating. Characterizing the stress is paramount to assess the coating reliability during service operation. Residual stresses in cold-sprayed coatings are caused

by the plastic deformation of the powder particles, which, in turn, is caused by the peening effect of the incoming high-velocity particles that deform the underlying material. Because this process takes place at relatively low temperatures compared to thermal spray processes, this enables the deposition of ductile metal coatings to any desired thickness.

Residual stress can affect coating adhesion with the substrate, as well as the fatigue behavior of the substrate. Because the cold spray process is akin to shot peening in many ways, compressive stresses tend to develop in the coating (Ref 5.62–5.74). It is well known that compressive residual stresses are beneficial for fatigue behavior. Table 5.2 compares shot peening and cold spray coating processes. Significant peening stresses are generated during the impact of particles on the substrate and on previously deposited particles as the coating is built to the required thickness. Fatigue cracks initiate on the surface of a component, so normally, an overall compressive stress on the surface is a preferred state to enhance the fatigue life of the component. It is therefore imperative to characterize the residual stress of any cold-sprayed coating, both in the as-sprayed condition and at the application temperature.

There are two ways in which residual stresses are typically generated: as macrostresses that cover several grains and encompass the entire structure, and as more localized microstresses that cover individual grains or phases of the material. In both cases, residual stresses are those stresses that remain in the material after the external forces have been removed. Compressive stresses act by pushing the material together and are mathematically denoted as negative, while tensile stresses act by pulling the material and are denoted as positive.

Two nondestructive techniques have been used to measure residual stresses. One uses Stoney’s equation and determines the bending radius of the substrate, and the other uses XRD (Ref 5.64, 5.71). Only the latter is discussed here.

The traditional XRD method uses the $\sin^2(\Psi)$ technique, which is based on the measurement of the shift in diffraction peaks for different values of

Table 5.2 Comparison of cold spray versus shot peening characteristics

No.	Cold spray	Shot peening
1	Surface-modification process	Surface-modification process
2	Very high velocity, in the range of 300–1100 m/s (1000–3600 ft/s)	Shot velocity in the range of 50–100 m/s (160–330 ft/s)
3	Particles on impact deform plastically and develop coating surface on substrate	Rigid balls, do not stick to surface
4	Diameter of particles on the order of 5–40 μm	Steel balls used, size 1–2 mm (0.04–0.08 in.)
5	Requires process gas	No process gas
6	Additive process	Nonadditive process
7	Complex geometry can be sprayed	Flat surfaces give best results

the angle Ψ between the diffracting plane normal and the specimen surface normal (Ref 5.64, 5.71). In this method, a specific plane is selected and the interplanar spacing is measured from a θ to 2θ scan (from a standard Bragg-Brentano geometry) of the specimen at different tilt angles Ψ . Thereafter, the residual strain can be derived from the slope of a linear plot between the fractional change of the plane spacing (i.e., strain) and $\sin^2\Psi$. A biaxial stress model is then used to convert the measured strain to the stress.

X-ray diffraction is by far the best and most easily available versatile technique that can give accurate information about the through-thickness coating residual stress. Figure 5.25 is a schematic that shows how the layer-by-layer removal is performed to estimate the through-thickness residual stress. A few reports mention the shortcomings of the XRD technique in terms of the small sampling area as well as the need to account for the layer-by-layer relaxation and gradient for x-ray penetration, and they make use of neutron diffraction (Ref 5.73, 5.74) as more representative to determine residual stress in cold-sprayed coatings. Other methods include hole drilling (Ref 5.63) as well as the Barkhausen noise method (for ferromagnetic materials) (Ref 5.71).

Typically, all cold-sprayed coatings exhibit high compressive residual stress. In some cases, the compressive stresses are known to inhibit the formation of through-thickness cracks and improve bonding, as in alumi-

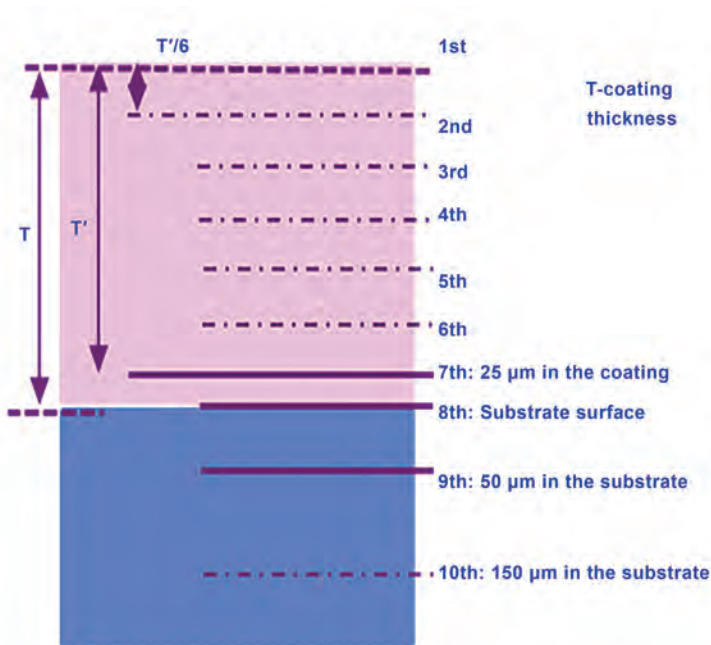


Fig. 5.25 Schematic of through-thickness residual-stress measurement in cold-sprayed coating by electropolishing and removal of layers

num and magnesium alloys (Ref 5.57, 5.70), whereas for harder metals (nickel, cobalt, etc.) (Ref 5.56), they have been known to have a reverse effect by inducing a debit to the fatigue strength of the coated component. Figure 5.26(a) to (d) show an example of the residual stresses in aluminum (Fig. 5.26a), aluminum alloy (Fig. 5.26b), copper and copper alloy (Fig. 5.26c), and magnesium and magnesium alloy (Fig. 5.26d), as determined by the XRD technique (Ref 5.57).

The effect of helium versus nitrogen gas in imparting coating residual stress and the effect of heat treatment or stress relaxation are determined for the case of IN625 with NiCr coating, as shown in Fig. 5.27(a) and (b) (Ref 5.69). Choi et al. (Ref 5.74) have compared the effect of grit blasting on the residual stress of an aluminum coating on an aluminum substrate. It appears that the coating has a compressive stress after grit blasting, which is balanced after the application of a cold-sprayed coating. The average through-thickness stress in their coatings is hardly within the standard deviation of the XRD measurement system, ranging between 50

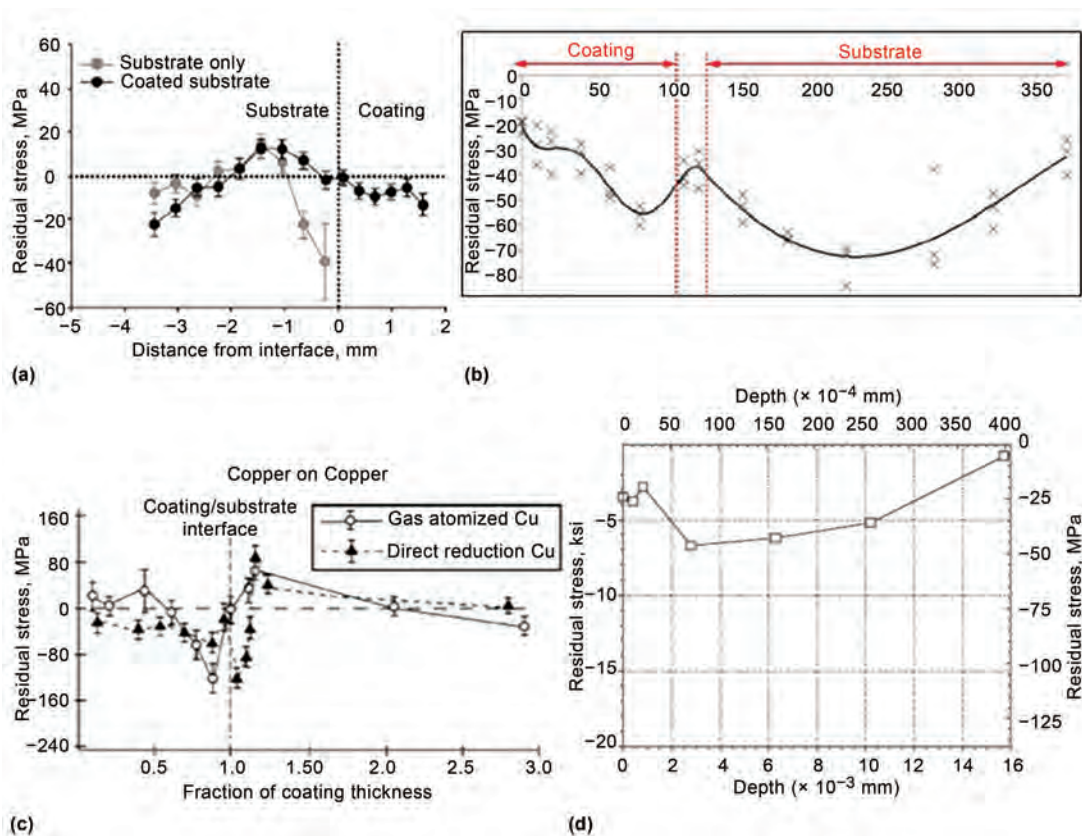


Fig. 5.26 Residual stress measured by means of x-ray diffraction $\sin^2\Psi$ method on various cold-sprayed coatings: (a) aluminum, (b) aluminum alloy, (c) copper alloy, and (d) magnesium alloy. Source: Ref 5.24, 5.57

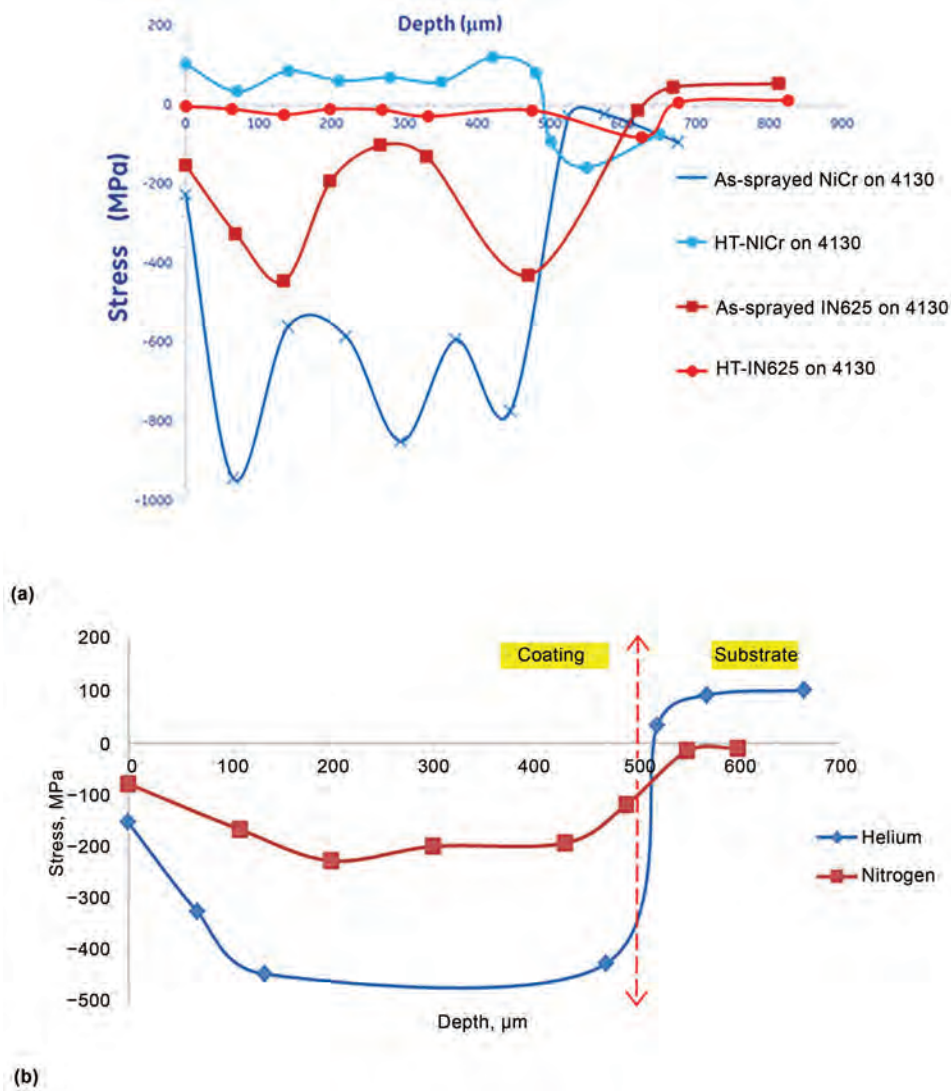


Fig. 5.27 Through-thickness residual stress in a cold-sprayed IN625 and Ni-20Cr coating (a) in the as-sprayed versus heat treated (HT) condition and (b) using helium versus nitrogen as process gas, in each case measured using the x-ray diffraction $\sin^2\Psi$ method. Source: Ref 5.69

and 80 MPa (7 and 12 ksi) in compression. Some reports have recorded the beneficial effect of these compressive stresses in improving the bonding, while others, especially for hard materials such as Inconels and MCrAlY, have reported the contrary, with debits to the bonding and fatigue properties, depending on the substrate material properties.

Mahmoudi-Asl (Ref 5.57) studied the residual stress in a cold-sprayed magnesium AZ31 alloy, compared the stress in the as-sprayed and stress-relieved conditions, and compared the experimental values with those of

the stress state obtained by means of finite-element modeling. The overall study was to predict and measure the effect of cold-sprayed coating on the fatigue behavior of a self-mated magnesium alloy. Luzin et al. (Ref 5.73) used neutron diffraction to determine the residual stress of thick coatings (~ 0.5 mm, or 0.02 in.). Neutron diffraction is nondestructive and is considered the most direct way to measure stress, especially because it is phase sensitive and the stresses can be assessed for each phase independently. Additionally, no specific sample preparation is required for neutron diffraction. The study evaluated copper and aluminum coatings on aluminum (aluminum-magnesium alloy) and copper substrates. There have also been reports of using the in situ coating property sensor to evaluate the deposition stress of the coating as the coating is deposited (Ref 5.62). Thus, regardless of the method used, it is important to characterize the coating residual stress in the as-sprayed condition as well as at the application temperature to assess the overall reliability of the coating.

5.10 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique to determine the elemental and chemical state on the surface of the coating. In XPS, soft x-rays bombard a sample material, causing electrons to be ejected (Ref 5.1, 5.2). Based on the kinetic energy of the ejected photoelectrons, the chemical state of the sample can be determined, and the relative concentration of the elements can be determined from the relative photoelectron intensities. X-ray photoelectron spectroscopy typically probes to a depth of 2 to 20 atomic layers and, depending on the material, can be used to probe depths of 5 to 50 Å. It thus serves as a valuable tool in cold spray characterization to determine the oxidation or nitridation state of the coatings.

In general, a higher inlet gas temperature and hence a higher substrate temperature is found to be beneficial for cold-sprayed coatings. However, when trying to achieve these conditions in practice, there can be excessive oxidation and nitridation of the resultant coatings. X-ray photoelectron spectroscopy has been used to very accurately determine the temperature effect on the coatings. Figure 5.28 illustrates this application for a commercially pure titanium coating, showing the effect of substrate temperature. The influence of particle temperature can also be determined using XPS when an external gas heater is used to heat the particles (Ref 5.37). X-ray photoelectron spectroscopy is also a very useful technique to determine the surface contamination in cold-sprayed coatings.

5.11 X-Ray Fluorescence

X-ray fluorescence (XRF) is a nondestructive method used for elemental analysis of materials. Relevantly, it has been used for cold-sprayed feedstock powders to provide accurate estimates of the chemistry, espe-

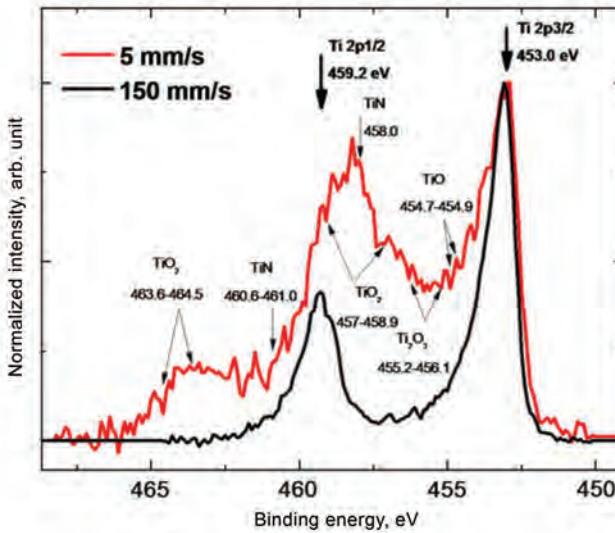


Fig. 5.28 Comparison of surface characteristics of helium-sprayed versus nitrogen-sprayed titanium coating for oxidation and nitridation characteristics. Source: Ref 5.37

cially the oxygen and nitrogen levels, because coating chemistry is known to affect mechanical properties.

With this method, an x-ray source is used to irradiate the specimen and cause the elements in the coating powders to emit or fluoresce their characteristic x-rays. A detector is used to detect the emitted x-ray peaks for quantitative estimation of the elements present. All elements except hydrogen, helium, and lithium can be detected using XRF. It is possible to determine very accurate values of elemental information using this method. Details of XRF can be found in other well-known references (Ref 5.1, 5.2).

The impurity levels and the moisture/oxygen content in the powders can lead to significantly poorer coatings, despite optimized parameters, especially because adsorbed moisture can lead to significant powder-feeding issues and hence premature degradation of the formed coating. In this application, XRF can provide precise information about the starting powder chemistry. Figure 5.29 is an example of using XRF to characterize the amount of copper in a mixture of copper-chromium powders taken at different ratios, as a function of the coating thickness (Ref 5.75).

5.12 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is a surface characterization technique that enables determination of the elemental composition and chem-

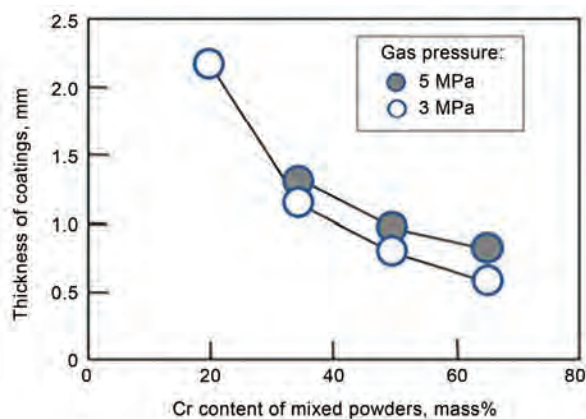


Fig. 5.29 Relationship between chromium content of mixed powders and thickness of coatings, as evaluated by x-ray fluorescence spectroscopy. Source: Ref 5.75

istry of the sample surfaces. More details can be found in well-known references (Ref 5.1, 5.2). It makes use of a focused electron beam to create secondary electrons near the surface of a solid sample. Some of these have energies characteristic of the elements and, in many cases, of the chemical bonding of the atoms from which they are released. Typically used in combination with ion sputtering to gradually remove the surface, AES can be used to characterize the sample through-thickness and hence the chemistry and bonding through the sample depth. The high spatial resolution of the process allows microanalysis of high lateral resolution (300 Å), semi-quantitative elemental analysis, and accurate chemical bonding information, including semiquantitative standardless analysis. It has been very useful in analyzing fractured cold-sprayed samples to evaluate the oxygen levels across the coating fracture surface, as shown in Fig. 5.30(a), which indicates peaks of aluminum, carbon, and O_2 . After removal of a surface layer using ion beam milling, the Auger spectrum was devoid of oxygen and carbon, as shown in Fig. 5.30(b), which confirmed the presence of an oxide layer of 31 nm thickness in the as-deposited condition (Ref 5.76).

5.13 Raman Spectroscopy

Raman spectroscopy is a structural characterization tool used for evaluating the arrangement of bonding in a material. An intense monochromatic light beam is applied to the sample, with the result that the electrical field of the incident radiation distorts the electron clouds that make up the chemical bonds in the sample, which have a particular energy. On reversal of the field, the wave passes, the distorted electron clouds relax, and the stored energy is reradiated. Most of the stored energy is reradiated at the

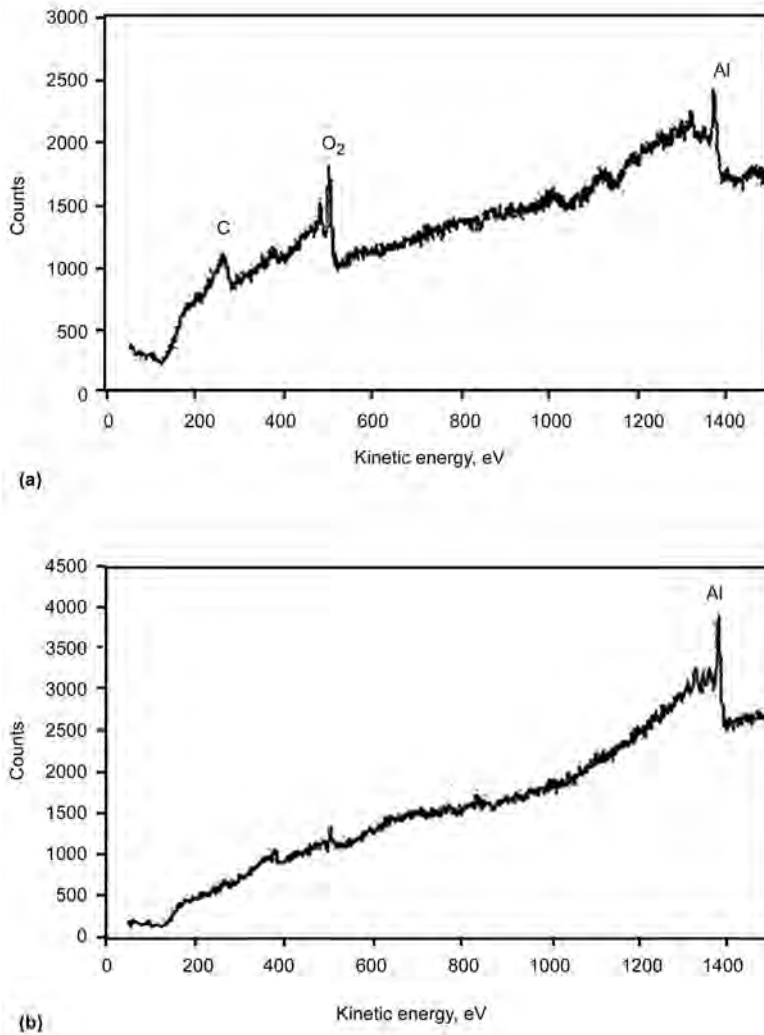


Fig. 5.30 Auger electron spectroscopy of the fracture surface of an aluminum cold-sprayed coating (a) in the as-sprayed condition and (b) after ion beam milling, revealing the surface layer chemistry. Source: Ref 5.76

same frequency of the incident exciting light; this phenomenon is called Rayleigh scattering. However, a small portion is transferred to the sample itself, exciting vibrational modes that appear as weak side bands in the spectrum at frequencies less than the incident beam. These are the Raman lines characteristic of the material.

Kliemann et al. (Ref 5.77) carried out micro-Raman spectroscopy to detect phase transitions in ceramic TiO₂ coatings. Figure 5.31 shows the intensities obtained from a cold-sprayed coating of TiO₂ starting with an anatase powder. The presence of both rutile and anatase forms of TiO₂ in the starting powder is clearly established, the two forms being distinguished by their

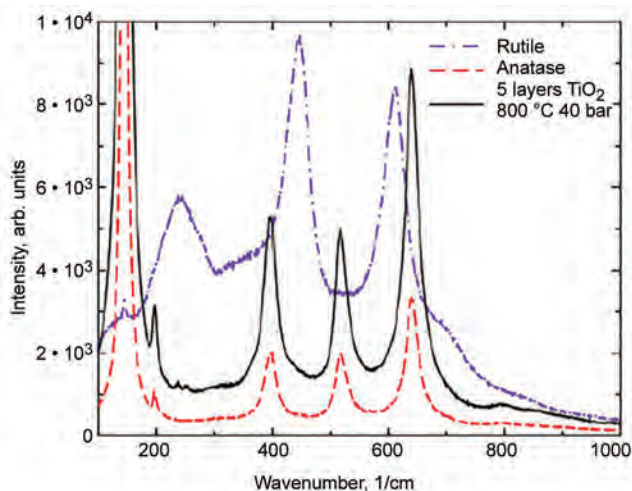


Fig. 5.31 Raman shift of TiO_2 coating sprayed using nitrogen at 4 MPa (580 psi) compared with Raman spectra of rutile and anatase. Source: Ref 5.77

individual patterns in the Raman spectrum. However, in the cold-sprayed coating is seen 100% anatase structure, regardless of the gas temperature.

5.14 Oxygen Analysis

One of the key features that distinguish cold spray coating from thermal spraying is the lack of oxidation during the spray process. However, if the starting powders contain oxygen, then it becomes difficult to avoid subsequent oxidation in the coating. It is therefore important to characterize the oxygen content in the coating, starting with the powders, prior to the start of spraying.

A LECO analyzer is specifically designed to estimate very minute (5 to 10 ppm) traces of oxygen and nitrogen as well as hydrogen in samples. Especially for materials and alloys prone to oxygen pickup, such as titanium alloys (Ref 5.78), it is imperative to characterize for oxygen level. Because titanium can dissolve up to 13 wt% oxygen, it is important to know how much oxygen exists in the coating in order to interpret the mechanical properties as well as the bonding characteristics with the substrate. Figure 5.32 provides an example of the measured oxygen levels in warm- and cold-sprayed coatings, using the inert gas fusion method. Others have detected the oxygen using high-resolution energy-filtered TEM (Ref 5.46) and have found that most of the oxygen exists near the interface of the substrate/particle or particle/particle boundaries. Inert gas fusion (Ref 5.79) is also used to determine the oxygen content in the coatings.

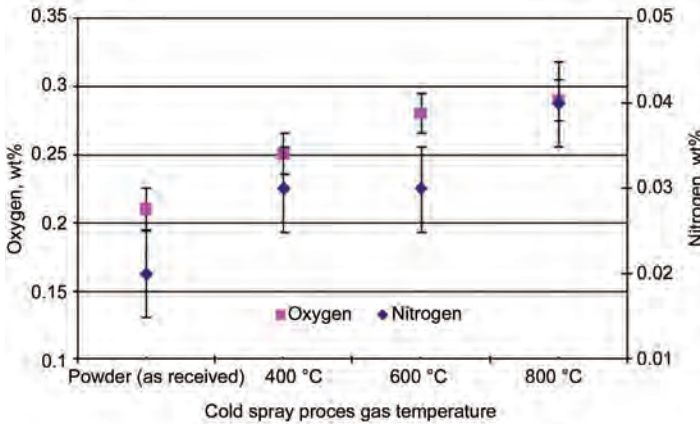


Fig. 5.32 LECO analysis of oxygen and nitrogen at different cold spray gas temperatures in titanium and Ti-64. Source: Ref 5.78

Typically, the oxygen content of the cold-sprayed coating is largely determined by the oxygen content of the original powder.

5.15 Surface Roughness

The first step in any coating process is characterization of the surface. Roughness (R_a) is the average of the deviation from the average height of a surface profile. This can be measured using a simple handheld surface profilometer (a mechanical profiler with a spring-loaded stylus) or by more sophisticated methods such as interferometry (using an optical profiler), atomic force microscopy, or scanning tunneling microscopy. A review of all the various surface profilometer techniques is given in popular books (Ref 5.80). Very simple to use, a profilometer run on a cold-sprayed coating is an indirect indicator of the extent of deformation and bonding of the powder particles in the coating. In many instances, nitrogen coatings have a higher roughness than helium-sprayed ones, as shown in Fig. 5.33(b) (Ref 5.33).

Coating surface roughness is a combination of many factors, such as powder size distribution, morphology, as well as the process parameters. Surface roughness is considered an indirect indicator of the coating density and coating process integrity and is used as a characterization tool during coating process optimization. Figure 5.33(c) and (d) show the variation of coating roughness with deposition efficiency and microhardness, respectively, for a cold-sprayed titanium coating (Ref 5.81). Furthermore, in applications that involve direct use of cold-sprayed coatings without any machining, the coating roughness could play an important role in determining the reliability of the coating life and the fatigue properties.

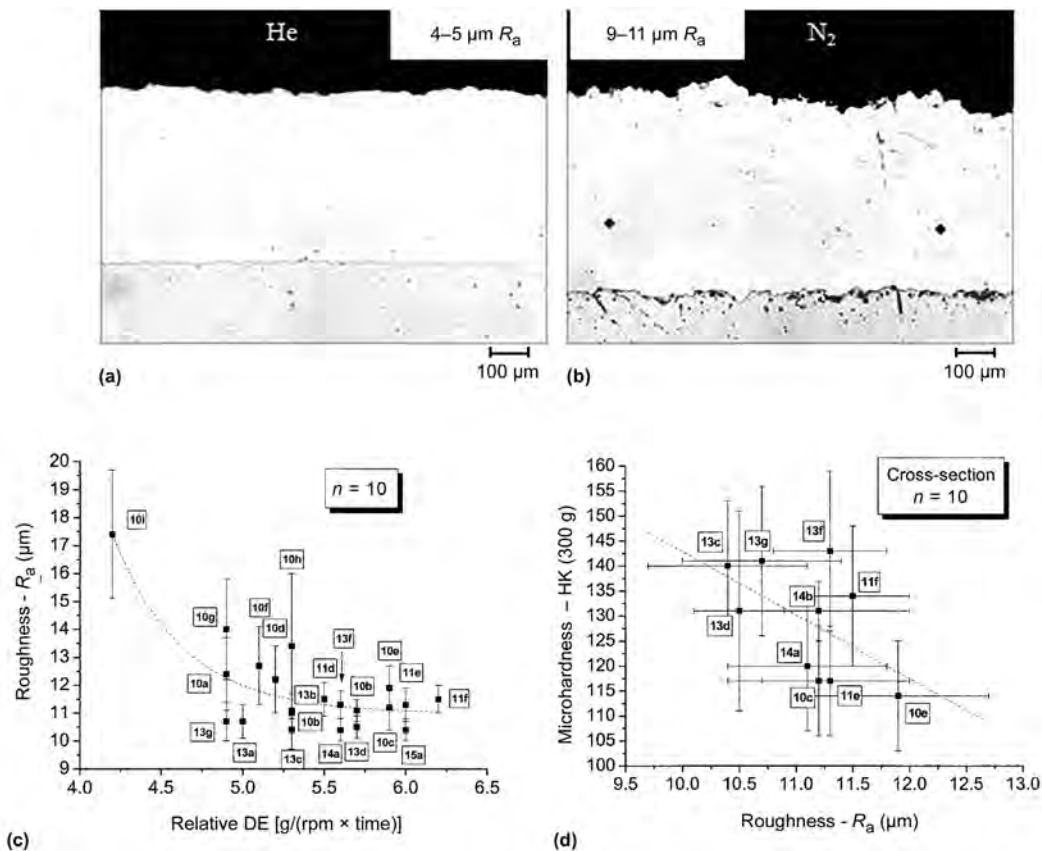


Fig. 5.33 Root mean square surface roughness (R_a) measurements. (a, b) Optical micrographs showing variation in surface roughness from a helium-sprayed (4 MPa, or 580 psi, and 600 °C, or 1110 °F) versus nitrogen-sprayed (5 MPa, or 725 psi, and 800 °C, or 1470 °F) IN625 coating on AISI steel. The insets in the micrographs indicate the average surface roughness measurement. (c) Roughness versus deposition efficiency (DE) of a cold-sprayed titanium coating. (d) Microhardness versus roughness for a titanium coating. Source: Ref 5.33, 5.81

5.16 Microhardness

A quick screening of the mechanical properties of a cold-sprayed coating is done by using the microhardness. Details about microhardness can be found in Ref 5.3. Microhardness is another ubiquitous tool for coating characterization to assist in optimizing the coating for a given set of parameters. Because cold-sprayed coating thickness ranges from 0.25 mm (0.01 in.) to as much as 12 mm (0.5 in.), Knoop and Vickers hardnesses are typically used to characterize the coating hardness, the latter being more suitable for thicker ($>25\ \mu\text{m}$) coatings. Vickers microhardness is measured using loads ranging from 50 g to 1 kg (2 to 35 oz), depending on the expected coating hardness. An average of ten measurements is recommended to span the thickness of the coating, as shown in Fig. 5.34(a).

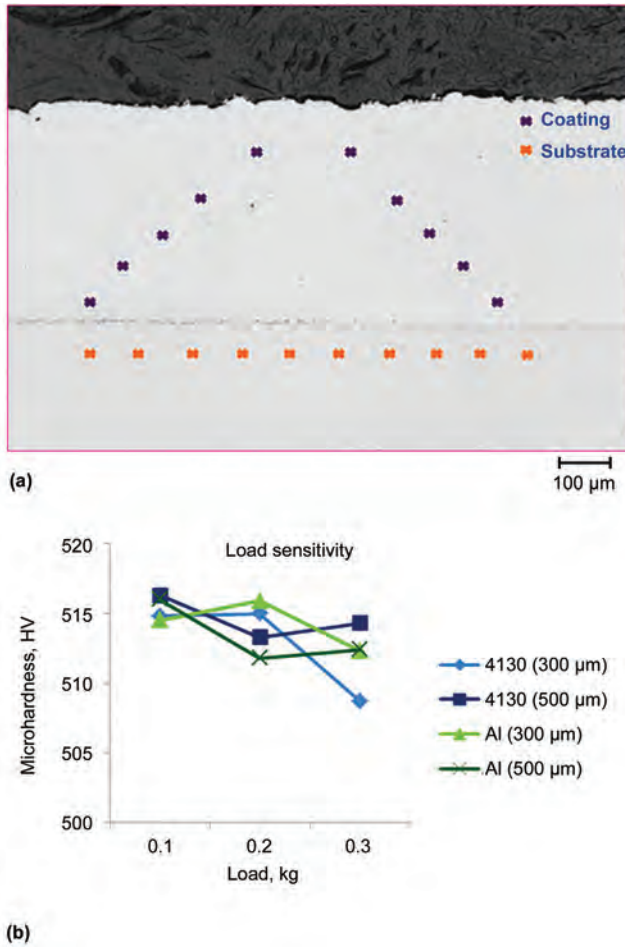


Fig. 5.34 (a) Schematic showing a possible method for hardness measurement in the cold-sprayed coating and substrate. (b) Load sensitivity analysis of coating microhardness. Source: Ref 5.33

It is also recommended to measure the substrate hardness at a location away from the vicinity of the interface, as indicated in Fig. 5.34(a). The dwell time of the indent is typically 10 to 15 s. In case of a softer coating and, especially, a softer substrate, such as pure aluminum, a lower load is used, <50 g. For harder substrates, a higher load, >100 to 500 g (3.5 to 18 oz), is typically used. The Vickers microhardness is calculated by using the standard formula:

$$HV = 1.854F/d^2 \quad (\text{Eq 5.3})$$

where d is the mean of the two diagonals of the impression on the sample, and F is the applied force in kilogram force.

It is usual to correlate the coating process parameters, extent of porosity, and so on by using the coating microhardness. Typically, cold-sprayed coatings tend to display at least 20 to 30% higher hardness than their bulk wrought counterparts. Due to the severe deformation that takes place in the cold spray process, a complex strain hardening is expected, and therefore, nearly all cold-sprayed coatings tend to have a 20 to 40% higher hardness in the as-sprayed condition than their wrought counterparts (Ref 5.19, 5.29–5.34). A study on the load sensitivity reveals that these coatings show a behavior that is invariant under the applied load, as shown in Fig. 5.34(b) for NiCr coatings on AISI 4130 steel (Ref 5.33). Hardness does not usually vary much with coating thickness, as shown in Fig. 5.35(a) for the case of an IN625 coating on an AISI 4130 steel substrate. The dotted lines indicate the substrate hardness.

Upon heat treatment, the hardness in many cold-sprayed coatings increases, sometimes reaching as much as 30 to 40% higher than in their as-sprayed condition, contrary to what happens in most work-hardened materials, in which recovery processes tend to lower the final hardness.

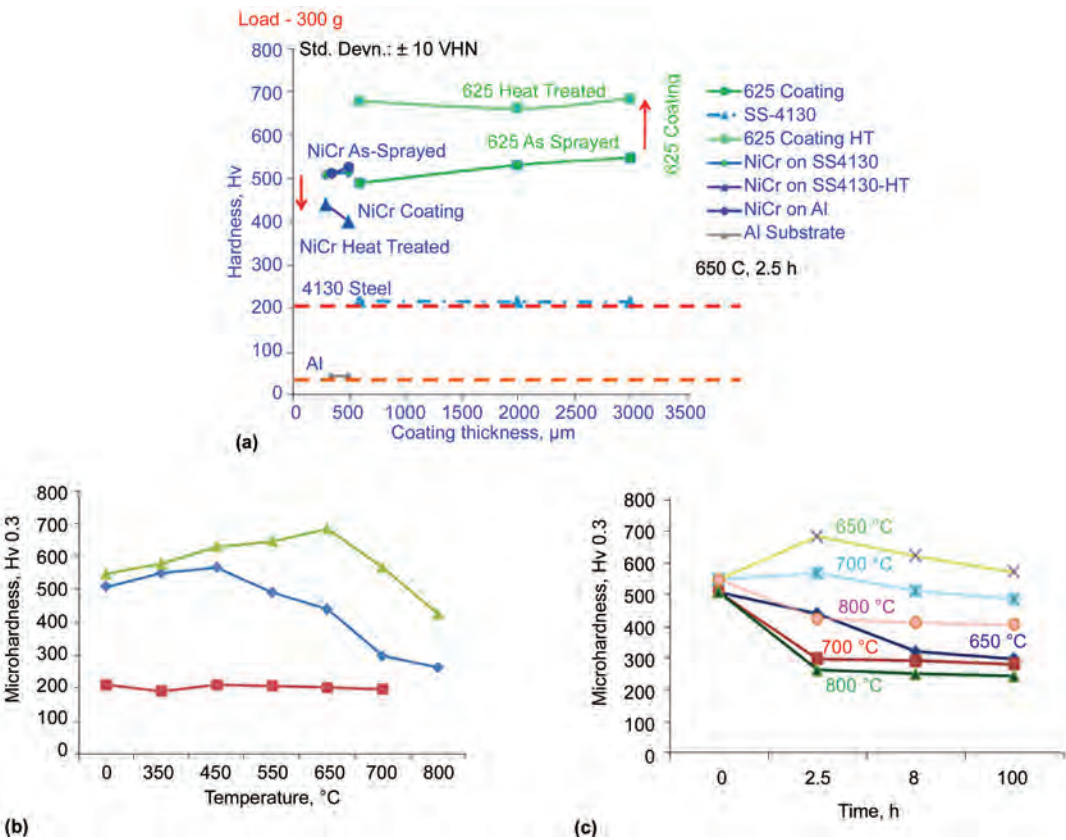


Fig. 5.35 Microhardness as a function of (a) coating thickness, (b) temperature, and (c) time for IN625 coatings on AISI steel substrate. Source: Ref 5.33

An example is shown in Fig. 5.35(b), taken from the IN625/NiCr cold-sprayed coating, which shows a steady increase in hardness up to a certain temperature, above which it drops off to a lower value. The coating hardness with time is shown in Fig. 5.35(c) for the same IN625 coating.

5.17 Nanoindentation

Nanoindentation is mainly used to extract the hardness and elastic modulus of the coating. Conventional indentation techniques, including the standard microhardness tests, involve measurement of the size of a residual plastic impression in the specimen as a function of the indenter load. From the area of contact, the hardness of the material is inferred. In a nanoindentation test, the size of the residual impression is often only a few micrometers, and thus, direct imaging becomes difficult. Here, the depth of penetration beneath the specimen surface is measured as the load is applied to the indenter. From the known geometry of the indenter, the size of the area of contact is determined.

A nanoindentation test is usually performed as a depth-sensing indentation test with a diamond Berkovich indenter that has a nominal edge radius of 100 nm. The hardness and elastic modulus are measured at loads ranging between 1 and 500 mN, at a loading/unloading rate of 200 $\mu\text{N/s}$. Data are analyzed using the Oliver-Pharr method (Ref 5.82). Figure 5.36(a) shows an example of the hardness-versus-displacement curve, and Fig. 5.36(b) shows a modulus displacement curve after a series of nanoindentation tests were made on a Cu-10wt%Zn cold-sprayed coating (Ref 5.15).

Nanoindentation testing is a valuable tool to characterize the extent of plastic deformation and recovery in cold-sprayed coatings. Figure 5.36(c) is a plot of the nanohardness of a copper-nickel composite coating that makes it possible to distinguish the relative fractions; Fig. 5.36(d) is an image quality map taken using EBSD, combined with corresponding nanohardness, which is able to help deduce that static recrystallization takes place in cold-sprayed copper (Ref 5.53). The sample surface must be absolutely flat and polished prior to carrying out nanoindentation tests.

5.18 Bond Adhesion Strength

There exist several methods to evaluate and quantify the adhesive or cohesive properties of cold-sprayed coatings. Some of the more popular testing methods are the bond test, tubular tensile test, lap shear test, lug shear test, and splat adhesion test using a scratch tester.

For the bond adhesion test, the adhesion strength of the coatings is evaluated using a fairly well-established standard, in accordance with ASTM C 633 (Ref 5.83). This involves bonding the coated coupon with an adhesive having a much higher (at least 10 times higher) adhesive strength and

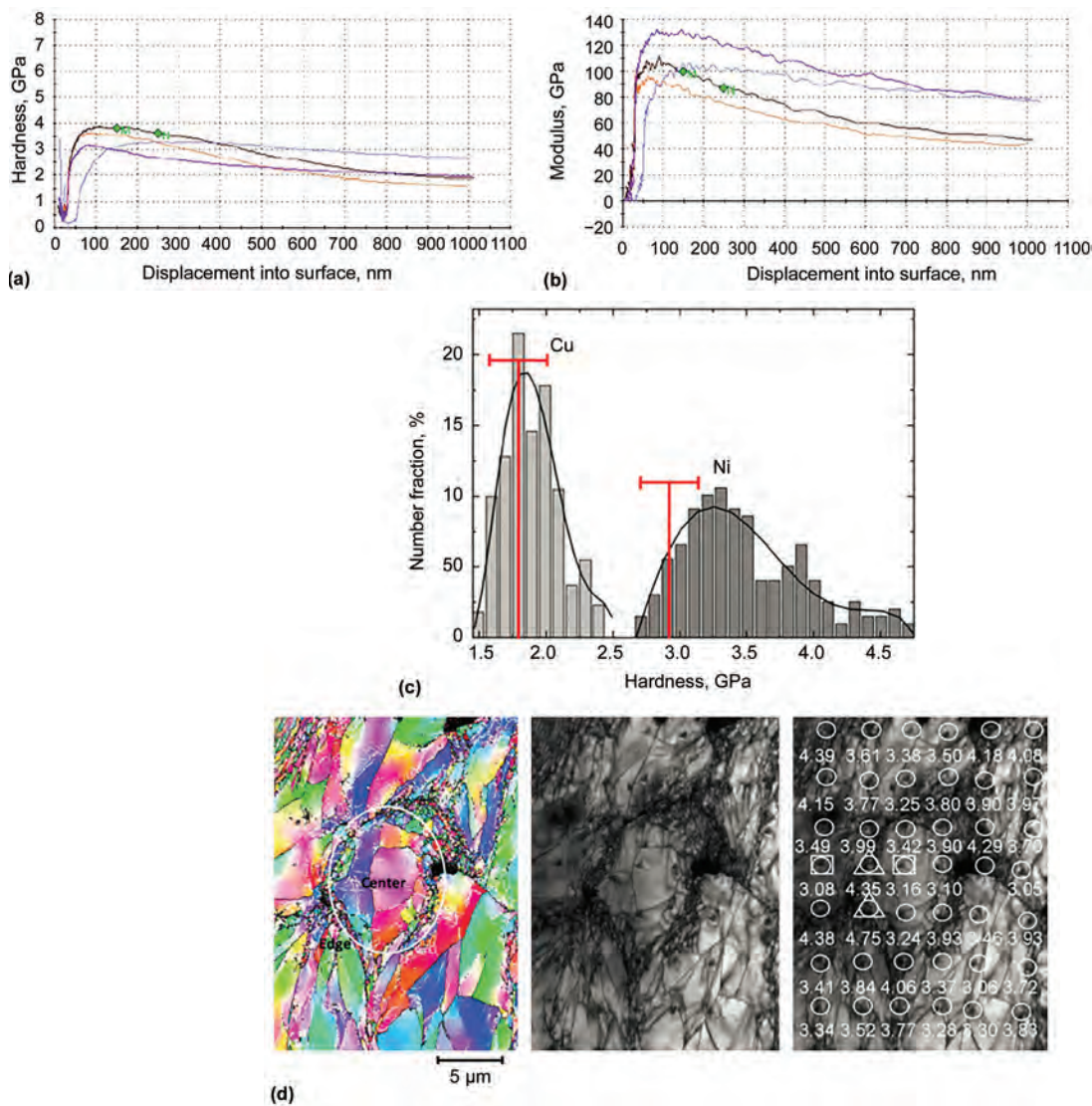


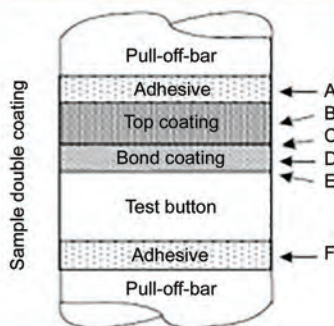
Fig. 5.36 Nanoindentation of cryomilled Cu-10Zn cold-sprayed coating showing (a) hardness and (b) modulus of elasticity. (c) Nanohardness of as-sprayed copper and nickel coatings, with hardness (superimposed red line) of the feedstock powders. (d) Electron backscatter diffraction characterization of the cross section of nickel coating after nanoindentation. Source: Ref 5.15, 5.53

pulling in uniaxial tension. The sample coupon is 25.4 mm (1 in.) in diameter and 5 to 6 mm (0.20 to 0.24 in.) thick; it is glued using glue with a strength of approximately 70 MPa (10 ksi) and pulled in a universal tensile testing machine. Care is taken to grind the edges to ensure proper adhesion of the coating to the glue. The tensile adhesion strength is defined as the maximum force to failure divided by the surface area of the coating. Figure 5.37(a) shows the setup used for tensile adhesion testing.

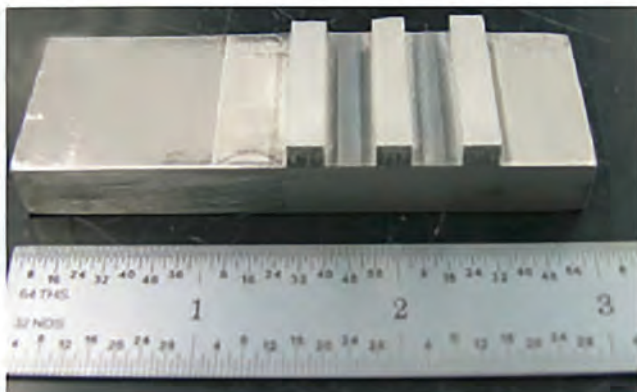


- A = Adhesive
B = Top coat
C = Interface top coat - bond coat
D = Bond coat
E = Interface bond coat - substrate
F = Adhesive

Note: For single coatings
number C and D not available



(a)



(b)

Fig. 5.37 (a) Bond adhesion strength test setup (ASTM C 633) along with a schematic showing various coating failure modes. (b) Triple-lug shear test setup. Source: Ref 5.79, 5.84

The cohesive strength of the coating is typically evaluated using a tubular tensile test (Ref 5.19). This method is easy to carry out and provides information on the cohesion quality of the coating.

Figure 5.37(b) reveals the test setup used for the triple-lug shear test to evaluate the coating bond adhesion strength, especially for thick (>1 mm, or 0.04 in.) coatings. The setups used for the other tests, such as lap shear and lug shear, can be found in other references (Ref 5.79, 5.84, 5.85), respectively. Several other tests are carried out to evaluate the coating adhesion strength, especially of single splats, such as the scratch test and the cavitation erosion test (Ref 5.86, 5.87).

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CHAPTER 6

Powder Production Techniques for High-Pressure Cold Spray

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RECENT GROWTH of high-pressure cold spraying (HPCS) applications on the industrial scale have forced global powder producers to face this challenge and develop specific powders for cold spray applications. Also, the range of metals and alloys that can be cold sprayed is rapidly increasing, which creates a demand for developing new powder manufacturing processes that enable cost-effective production of specific cold spray powders.

Due to the nature of the cold spray process, there are several properties that the powder must have. In general, powder properties have a strong influence on two process phenomena: powder feeding/spraying and layer deposition. Powder feeding/spraying is mainly influenced by the physical properties of the powder, such as particle shape and size distribution.

6.1 Key Powder Properties

The required particle size distribution is specific to the cold spray equipment used and varies in the range of 5–200 μm .

The powder must flow freely through the feeding system, creating a continuous feed into the spray nozzle. Flowability of the powder is directly linked with the shape of particles, surface conditions, and particle size distribution. For the cold spray process in general, the particles should be spherical, with surfaces free of satellites and a narrow particle size distribution. Many materials have a strong tendency to react with oxygen and thereby create surface oxides, which also may affect the interaction between particles (e.g., agglomeration behavior) and influence particle deposition. It was proved that using powders with low oxygen contents in cold spraying resulted in both improved deposition efficiency and higher coating density (Ref 6.1).

Particle size distribution affects the cold spray process the most. On one hand, a high content of very fine powders below 5 to 10 μm decreases the deposition efficiency (DE), increases the coating porosity, and causes nozzle clogging and powder-feeding inhomogeneity. On the other hand, a high content of coarse particles also has a negative effect on the DE because the particles are too coarse to be deformed/deposited. Therefore, both fine and coarse particles must be separated from the feedstock powder.

Particle size distribution cannot be specified with exact numbers. For HPCS, the 10 to 32, 15 to 38, and 20 to 45 μm particle size distributions are the most common.

6.2 Powder Manufacturing

Inert Gas Atomization. Atomization is one of the basic procedures for manufacturing metal powder with the desired properties for cold spraying. In essence, it is the breakup of a molten stream into droplets, which are then cooled to form solid particles (Ref 6.2).

The process uses gas flow to disintegrate a liquid stream, which is represented by melt flow. In general, any gas that does not react with the melt (e.g., air, nitrogen, argon, or helium) can be used for this disintegration. However, because of its relatively low price, nitrogen is the most common gas used for manufacturing of powders if low oxygen content is required.

An atomizing unit can be divided into three basic parts: a vacuum furnace with controlled atmosphere, an atomizing chamber, and a powder-collection system (Fig. 6.1). All the parts must be vacuum tight.

Melting of the feedstock can be performed by any of several heating techniques; the most common is induction heating. The melting and atomization chambers are connected, and the melt is transferred from the melting chamber into the atomization chamber, where the atomizing process itself takes place.

The gas acts on the melt flow by shear stress, which causes a pressure increase inside the stream (Ref 6.3) (Fig. 6.2). The liquid stream explodes if the pressure acting on it exceeds a certain value and causes the stream

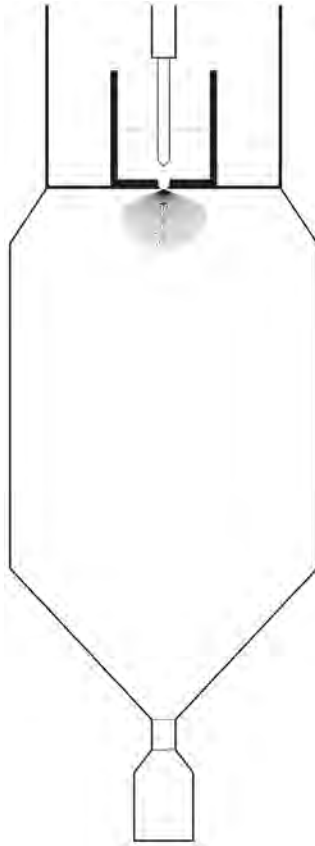


Fig. 6.1 Inert gas atomizer for induction heating with ceramic or graphite crucible. Courtesy of Impact Innovations GmbH

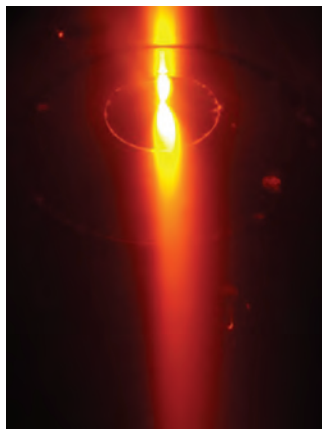


Fig. 6.2 Disintegration of melt stream by gas flow inside atomizing chamber. Courtesy of SAFINA, a.s.

to break up into small drops. These drops travel through the chamber, where the heat is continuously removed from them, which results in solidification into solid particles. These particles are collected in the bottom part of the atomization chamber or the cyclone, and a two-flap system allows continuous removal of the powder during this process. Exhaust gas escapes the chamber via a piping system with a built-in cyclone and filter system for complete separation of very fine powder from the gas flow.

One of the advantages of the gas atomization process is the flexibility in powder properties. A wide range of particle sizes can be produced by changing the process parameters, which are adjustable within the range from 5 μm to more than 500 μm . The more energy brought into the system, the finer the resulting particles. In practice, this can be achieved either by increasing gas flow and gas pressure or by decreasing melt flow. Metals in the liquid state are characterized by high surface tension and low viscosity. Therefore, overheating of the melt results in finer powder. Particles produced by gas atomization have near-spherical shape, which differs from particles manufactured by water atomization.

The metal feedstock for inert gas atomization differs and can be in the form of granules, rods, or wires. Depending on the metal chemical properties, different melting technology must be used. According to the melting technology, the inert gas atomization techniques used for cold spray powder production are the following:

- Crucible melting
- Crucible-free melting
- Wire-feed melting

Crucible melting of the feedstock can be performed by any of several heating techniques; again, the most common is induction heating. Once the material is fed into the crucible, the furnace is evacuated and flooded with protective gas. The metal feedstock is melted in a ceramic or graphite crucible in the melting chamber. The molten metal is transferred from the crucible in the melting chamber to the atomization chamber via the nozzle, whereupon it is subjected to high-pressure gas coming out of the atomizing nozzles (Fig. 6.1, 6.2).

Crucible-Free and Cold-Wall Melting. Because of the chemical reaction between the ceramic melting crucible and the molten metal, refractory and reactive materials cannot be atomized in pure form. To overcome this issue for these materials, crucible-free melting technology is used. In this process, metal rods are melted via induction coil without using a crucible. The prealloyed metal rods are slowly moved at constant rotation into the induction coil, where the metal melts. The melt from the rotating rod flows freely into the atomization nozzle system and is atomized by inert gas (Fig. 6.3).

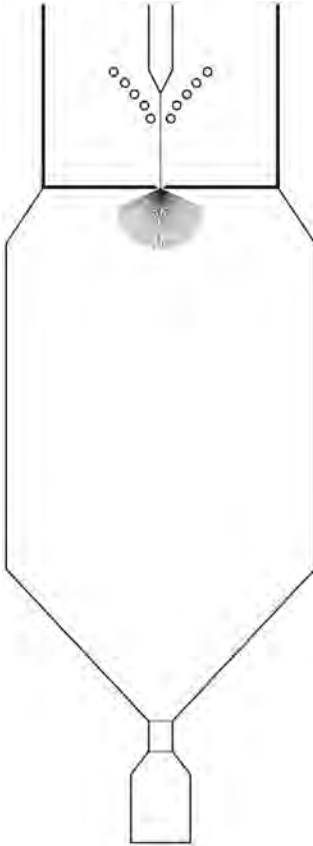


Fig. 6.3 Crucible-free atomization in induction coil melting. Courtesy of Impact Innovations GmbH

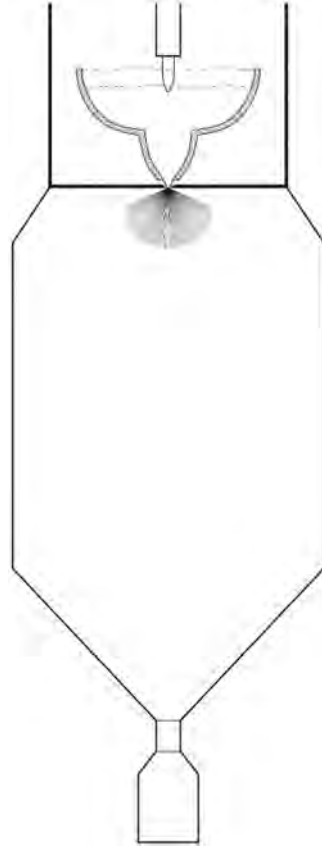


Fig. 6.4 Crucible-free atomization in plasma-torch-heated water-cooled copper crucible. Courtesy of Impact Innovations GmbH

Typical materials atomized by the crucible-free melting process are refractory and reactive materials, including titanium, titanium-base alloys, iron-base alloys, zirconium, and others.

For the production of ceramic-free powders and for the atomization of reactive and/or high-melting alloys, a plasma-torch-heated water-cooled (cold-wall) copper crucible can also be used (Fig. 6.4) (Ref 6.4, 6.5).

Wire-Feed Plasma. Another crucible-free technology uses wire feed-stock and plasma atomization (Fig. 6.5). Using a wire has many advantages over the typical gas atomization process, the most significant of which is that the metal feedstock and, more importantly, the melt do not come into contact with cold solid surfaces. Three direct current plasma torches are placed in a specific geometry so that the plasma jets converge on the metal wire. The supersonic nozzles installed at the exits of the torches ensure a maximum gas velocity to successfully atomize the metal wire. By using argon plasma as the atomizing medium and heat source, a

lower gas flow rate can be used, because the heated gas has a higher velocity and thus a stronger atomization force is applied. Additionally, using a hot atomizing gas instead of a cold one prevents the particles from rapidly freezing together into irregular shapes. The plasma enables the melt to be highly superheated, and the resulting cooling ensures complete spheroidization. Another advantage of plasma atomization technology is that almost any metal can be atomized (Ref 6.6).

Centrifugal atomization (Fig. 6.6) is an atomization process in which the feedstock is melted in a crucible and the melt is then poured onto a spinning water-cooled plate or disc. The spinning disc creates centrifugal force, which overcomes the surface tension so that the melt flow is fragmented into droplets. The droplets cool down, and spherical particles are created. The size of the particles depends on the speed of the disc or plate rotation. The atomization process is performed under an inert atmosphere to avoid the oxidation of the droplets/particles.

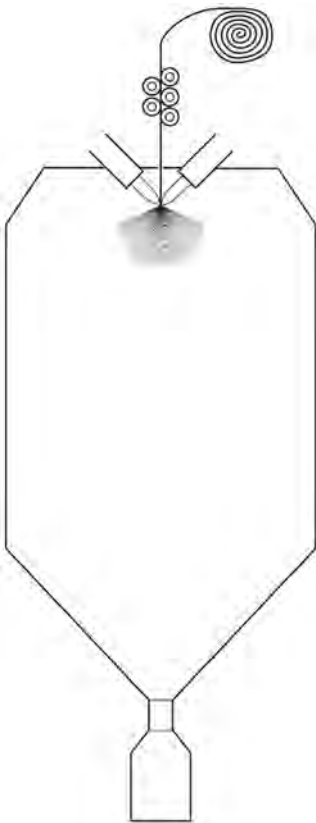


Fig. 6.5 Wire-feed plasma atomization. Courtesy of Impact Innovations GmbH

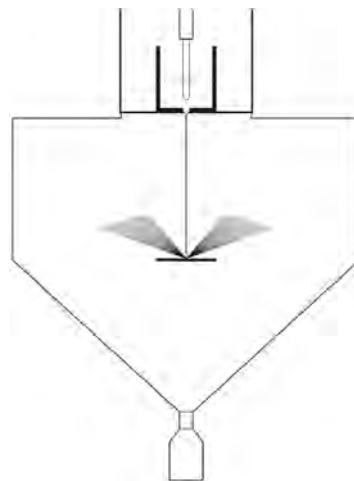


Fig. 6.6 Centrifugal atomization. Courtesy of Impact Innovations GmbH

This method is especially suitable for low-melting-point metals such as aluminum, magnesium, lead, zinc, and tin—in general, any metal with a melting temperature below 800 °C (1470 °F).

Mechanical alloying (MA) is a solid-state powder-processing method involving repeated welding, fracturing, and rewelding of powder particles by grinding in a container (Ref 6.7). This method allows production of advanced and nanostructured materials starting from blended elemental powder mixtures with unique advantages in material chemistry and microstructure.

High-Energy Ball Milling. A wide range of ball mills of various types can be used for powder production of alloys. Powder particles produced by MA do not usually meet the morphology and flowability targets for spraying deposition processes. Powders produced by high-energy ball milling are usually angular in shape because of flattening during high-energy impacts between particles and mill balls. The cold gas spraying process requires good-flowing powders that are roundish in shape and fall within a specific particle size distribution, generally in the range of 15 to 40 μm . Powders that are irregular in shape or too small will reduce the ability of the powder to flow, causing either clogging problems or scarce deposition with greater coating porosity.

Secondary low-energy milling to improve the morphological characteristics of MA ball-milled powders has been adopted for cold spray powder, which helps improve yield in the particle size window without affecting the material properties and composition. This method, when integrated into the powder classification system post-MA, has the effect of eliminating fine agglomerated particles; removing sharp edges, particularly for brittle materials; and delivering more flowable and spherical particles with high efficiency.

The output of this combined process is MA powder (Fig. 6.7) in the micrometer-sized range (15 to 45 μm), roundish in shape, and consisting of stable aggregates that can be effectively used in cold spraying.

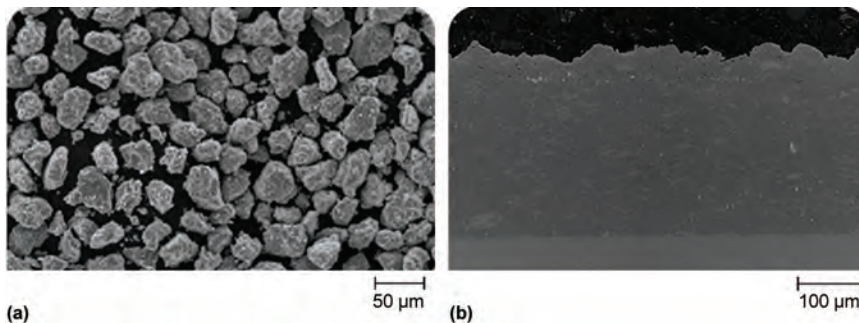


Fig. 6.7 (a) Example of mechanically alloyed powder. (b) Microstructure of titanium nano-composite coating. Courtesy of MBN Nanomaterialia S.p.A.

High-energy ball milling is able to generate numerous variants of alloys and nanocomposite materials and structures to promote different synthesis effects, depending on the materials and process conditions used.

The following material classes have been successfully developed by MA for cold gas spraying:

- *Cermet and reactive materials*: WC-Ti, Ti-SiC, Ti-TiC nanocomposites, Fe-Cu-alumina
- *Metal composites*: immiscible alloys, such as tungsten-copper
- *Intermetallic alloys*: alloying of two or more materials to form a fine dispersion of intermetallic phases in a metallic matrix, such as nickel-tin

Plasma Retreatment. One of the processes that can be used to transform the powder particle shape from irregular or flake to spherical is remelting the powder at high temperature. The feedstock material for this process can be agglomerated powders produced by spray drying and sintering techniques, angular powders produced by conventional crushing methods, or powders chemically reduced from compounds or solutions.

The remelting process by induction plasma technology leads to powder densification and spheroidization. It essentially consists of in-flight heating and melting of feed material particles followed by cooling and solidification under controlled conditions.

6.3 Classification

Particle size and distribution has a very strong influence on the cold spraying process itself. The general rule for reaching the maximum DE is to have as narrow a particle size distribution as possible. Practically, of course, compromise is inevitable in order to achieve a reasonable production yield. There does not exist one universal size range for each type of powder, cold spray equipment, and application, so it is important to have flexible equipment for powder classification.

The technique most commonly used for powder classification is screening. Movement of the screen can be performed in different ways, but most often two of them are used: vibration and tumbler screening. The efficiency of separation can be increased by additional cleaning of the mesh cloth (ultrasonic, air, rotating brushes, etc.). However, the use of the screening machine is limited by the size of particles to be screened. The screening process with standard stainless steel mesh cloth is more suitable for coarser particle classification with size 60 μm and coarser. Finer powder with size of approximately 50 μm can be processed by screening, but additional cleaning of the mesh cloth is required. Fine powders with particle size smaller than 40 μm are very difficult to screen because of the interactions between the particles, which have a strong tendency to stick together and clog the mesh cloth even when cleaning is used.

The efficiency of separation rapidly decreases with decreasing particle size, and a sharp division cannot be obtained. Therefore, it is recommended that very fine powders be processed with a different technique. The most suitable is the air classification process.

Air classification uses such powder characteristics as size, shape, and density to establish a clear division point and produce a particle size distribution that is uniform and homogeneous. Particles are fed into the system and entrained by air. Powder is subsequently separated into two portions by a classifying wheel. Coarse particles are rejected by the wheel and fall down under gravitational force, whereas fines continue through the wheel into the cyclone, where they are separated from the air flow. The content of fines can be adjusted by wheel speed and by material and air throughput. For metal powders, the typical working range for an air classifier is from 5 to 50 μm (based on copper powder; the exact range for other materials may differ because of their various densities). A typical powder before and after air classification is shown in Fig. 6.8.

6.4 Powder Packaging

Packaging is the last production step in powder manufacturing, and its importance can easily be underestimated. The type of packaging must be chosen appropriately for the material properties. The packaging material must protect the powder inside from contamination and must not react with it. If the powder tends to react with oxygen and create surface oxides, sealing should be used in combination with air evacuation followed by flooding with protective gas. Such protection can be further improved by the use of special materials that provide a diffusion barrier against further oxygen migration.

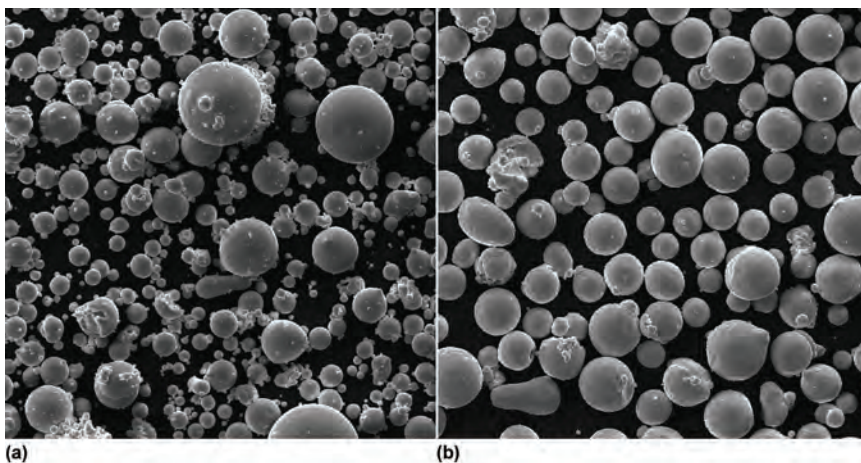


Fig. 6.8 Comparison of scanning electron microscope images of the powder (a) before and (b) after the classification process. Courtesy of SAFINA, a.s.

6.5 Powder Characterization

Once the powder is produced, it is important to characterize all its properties. Based on the results of analysis, the behavior of the powder during follow-up processes can be predicted. One of the major characteristics for powder description is the particle size distribution. In principle, two different methods can be used for the measurement of particle size distribution: sieve analysis and laser diffraction.

Sieve analysis is well known and widely used in industry (both dry and wet methods). It is stable and repeatable for coarse powders. Disadvantages of the testing method are linked to the limits of the technology, because sieving becomes increasingly inefficient the further the particle size drops below 50 μm . This effect can be countered to a degree by additional cleaning of the mesh cloth with compressed air. Sieve analysis assumes that the particles to be measured have near-spherical shape, so particles with irregular or needlelike shape can distort the results.

Laser diffraction is more advantageous in the range of very fine powders (below 15 μm) and is therefore commonly used for determination of the lower division point after classification. Laser diffraction, even more than sieve analysis, depends on the particle shape, so the less spherical the particles, the less accurate the results.

A scanning electron microscope gives the best indication of the actual particle size. This method also allows the investigation of particle properties that are otherwise difficult to measure, for example, roundness of particles and tendency to form satellites.

Apparent density (also called bulk density) is defined as weight per unit volume of material. This value is especially important for processes with volumetric feeding systems, in which increasing this parameter leads to improved deposition rates. Standard equipment for the analysis is the Hall funnel, which can be used for determination of either apparent density or flowability.

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CHAPTER 7

Cold Spray Coating Applications in Protection and Manufacturing

E. Calla, GE Power

COLD SPRAY (also called cold gas dynamic spray, or CGDS) coatings technology has the potential to provide surface enhancement for applications in sectors such as defense and aerospace, oil and gas, power generation, medical, automotive, electronics, and railways. Nanostructured materials, composites, and multilayered functionally gradient materials are generally difficult to produce but can be deposited by cold spraying. Lower process temperatures and the formation of the deposit by high-velocity impact result in surface cleaning and adiabatic shear phenomena. These improve the adhesion of the deposits and significantly reduce the in-flight oxidation of sprayed particles while depositing dense layers that are compacted by the successive impacts of incoming particles. Coating applications can be classified into the following broad categories:

- *Structural*: use of coatings for structural applications, such as joining or additive manufacturing (Ref 7.1–7.4)
- *Functional*: use of coatings to change the physical characteristics of the material, for example, conductive tracks (Ref 7.5–7.7)
- *Surface enhancement* (Ref 7.8–7.10)

Coatings for corrosion protection, wear mitigation, erosion resistance, thermal management, conducting layers, dielectric coatings, food processing, and heat conduction are covered in this chapter. Apart from new-make applications, cold-sprayed deposits are an important aspect of repair and refurbishment of scratched, dented, worn, and/or expensive parts, and the advantages and benefits discussed in this chapter are of interest to those applications as well. The chapter is therefore organized according to the function of the coatings in question rather than their specific application by industry. The chapters that follow discuss certain industry-specific applications of cold spray, and its application specifically to repair and refurbishment is discussed in Chapter 11, “Cold Spray Applications in Repair and Refurbishment for the Aerospace, Oil and Gas, and Power-Generation Industries,” in this book.

The results described in this chapter are focused on the manufacture of new parts, although, as noted, they are also applicable to repair and refurbishment, particularly for aviation, energy-generation, and oil and gas sectors. Deposits for new-parts manufacturing have such applications as additive manufacturing; enabling near-net shape products; functional layers for oxidation, corrosion, and wear; and so on.

Key features of the cold spray process that render it well suited for industrial applications include:

- *The production of dense, pore-free coatings:* Typical densities are > 99%, and values of 99.9% are possible.
- *The close resemblance of the results to bulk materials:* Tensile and other material properties akin to those of bulk materials can be obtained, making such coatings suitable for structural applications.
- *The ability to obtain thick metallic coatings:* Because the deposits are compressively stressed, thicker layers (up to 13 mm, or 0.5 in.) can be deposited without debonding.
- *The ability to achieve superior corrosion and wear properties:* Higher density and the absence of inflight oxidation/reaction result in excellent corrosion performance.
- *Better adhesion with the substrate.* Bonding is due primarily to surface film rupture and adiabatic shear, not to mechanical interlocking.
- *The ability to deposit a wide variety of metals/alloys and some cer-mets:* These can be deposited on a variety of substrates, both metallic and nonmetallic.
- *Very high deposition efficiencies:* Deposition depends on high-velocity impact of the sprayed particles; once the critical velocity is exceeded by the feedstock, deposition takes place.
- *Fewer safety concerns:* There is no combustion or hot plasma required in the process, and because the process uses N_2 , helium as the process gas, no combustible gases, such as H_2 , are involved.
- *Little or no postcoating finishing:* As-sprayed coatings have a smoother finish than those deposited by other methods.

- *Little or no posttreatment for management of thermal stresses:* Deposition occurs in the solid state, there is no heat-affected zone as there is in welding, and deposits are compressively stressed, so postdeposition heat treatment is usually not required.

As noted, dense and oxide-free coatings deposited by cold spraying also produce layers that have mechanical properties similar to bulk materials. This enables the cold-sprayed deposits to be used to make free-form parts or to enhance some functionality that does not exist on the part (Ref 7.7, 7.11–7.13). For example, such deposits can provide conducting layers on aluminum heat exchangers, using electrically conducting tracks deposited on nonmetallic substrates to make electrically conducting pathways that can act as circuits (Ref 7.6, 7.7, 7.14). The ability of cold spray to deposit dense, oxide-free coatings expands the range of applications of these coatings, because the coating microstructure and properties can be controlled and tailored for particular applications. The ability to deposit clean metallic coatings is used in applications requiring corrosion/oxidation protection, erosion/wear protection, additive manufacturing, and fabricating free forms. Some of these applications are described in the sections that follow.

7.1 Oxidation Protection

A key application of cold spray has been to deposit MCrAlY coatings (“M” stands for either nickel, cobalt, or a combination of both) on turbine parts. The MCrAlY coating is used as a stand-alone oxidation-protection layer or as a bond coat for the deposition of a ceramic thermal barrier coating. Lack of in-flight oxidation/phase change and deposition of dense coatings has enabled deposition of layers where the feedstock chemistry is well preserved in the coating and, consequently, more aluminum is available to form the protective Al_2O_3 layer (Ref 7.15, 7.16). Numerous studies have investigated MCrAlY bond coats and their behavior under oxidation and thermal cycling tests (Ref 7.9, 7.16–7.21). MCrAlY coatings typically consist of gamma-beta structure. Gamma is the Ni (or Co) solid solution and beta is the Ni (Co)-Al phase. In MCrAlY coatings, β acts as the reservoir for aluminum and provides the aluminum for thermally grown oxide (TGO) formation. Retention of β for longer durations improves the coating life by making the TGO stable for longer times and preventing the formation of faster-growing nickel oxides.

Richer et al. compared the 1000 °C (1830 °F) oxidation characteristics of CoNiCrAlY deposited by cold spray, high-velocity oxyfuel (HVOF), and air plasma spray (APS) (Ref 7.19). The oxygen content and porosity of the starting powder and the coatings is shown in Table 7.1. The MCrAlY coatings produced by cold spraying can have <1% porosity. Mass gain measurements after oxidation at 1000 °C (1830 °F) are shown in Fig 7.1.

Table 7.1 As-deposited MCrAlY coating properties by various spraying techniques

Material	Coating porosity, %	Oxide content, wt%
Feedstock powder	N/A	0.03 ± 0.03
Cold spray coating	1.0 ± 0.3	0.10 ± 0.05
High-velocity oxyfuel coating	0.5 ± 0.1	0.75 ± 0.23
Air plasma spray coating	5.3 ± 0.5	3.82 ± 0.70

N/A, not applicable. Source: Ref 7.19

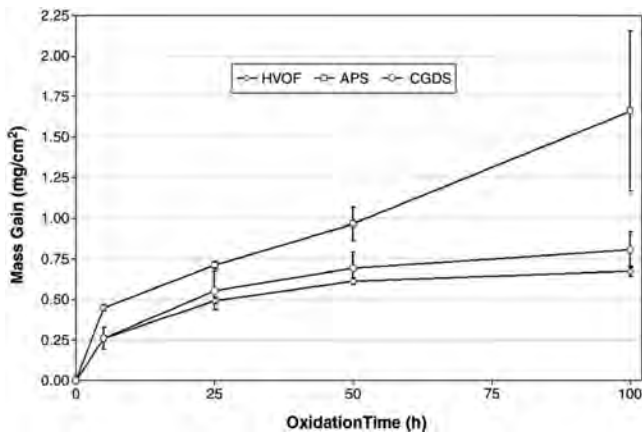


Fig. 7.1 Mass gain measurements as a function of oxidation time at 1000 °C (1830 °F) for CoNiCrAlY coatings deposited by high-velocity oxyfuel (HVOF), air plasma spray (APS), and cold gas dynamic spray (CGDS). Source: Ref 7.19

It was found that mass gain was highest for APS coatings. The HVOF coatings showed the presence of Cr_2O_3 , which was not observed in the cold spray coating after 100 h of oxidation. Formation of Cr_2O_3 suggests that the HVOF coating was depleted of aluminum and did not have any further reservoirs of aluminum to maintain the TGO. The CGDS CoNiCrAlY seems to offer benefits over HVOF-sprayed coatings in longevity of the bond coat. It was also concluded that lower porosity will result in lower oxidation rates (Fig. 7.2).

In another study, Bonadei and Marrocco (Ref 7.9) characterized the depletion of the β phase after isothermal oxidation in cold-sprayed coatings and low-pressure plasma-sprayed (LPPS) CoNiCrAlY + Re coatings. Figure 7.3 shows a schematic of the bond coat after high-temperature isothermal exposure, illustrating the depletion of the β layer and the formation of TGO, the inner and outer depletion zones, and the interdiffusion zone in the coating after isothermal oxidation. Microstructural images of cold-sprayed CoNiCrAlY showing the β phase can be seen in Fig. 7.4. It is reported that the β phase covers the entire coating before isothermal

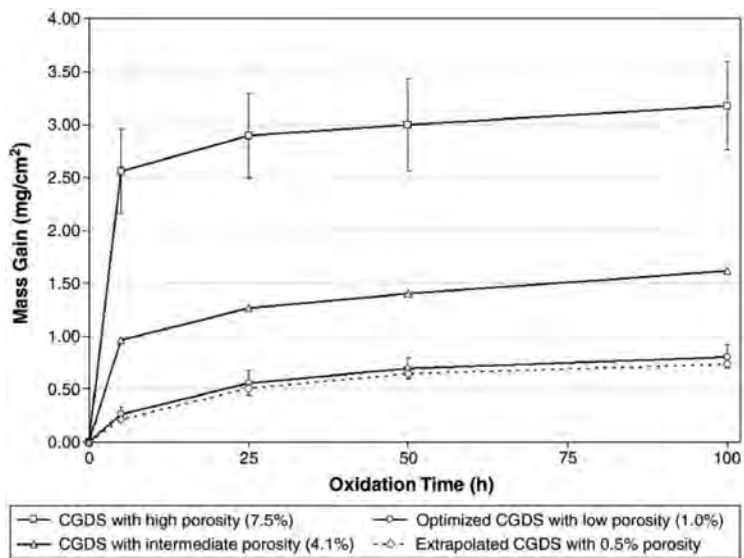


Fig. 7.2 Mass gain measurements as a function of oxidation time at 1000 °C (1830 °F) for cold gas dynamic sprayed (CGDS) CoNiCrAlY coatings showing the influence of coating porosity on overall oxidation rate. Source: Ref 7.19

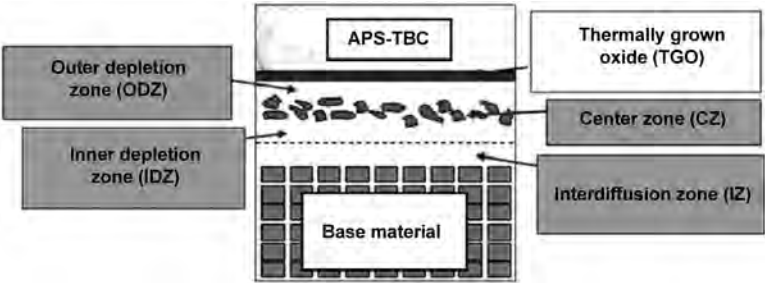


Fig. 7.3 Schematic of bond coat layer after high-temperature isothermal exposure. APS, air plasma spray; TBC, thermal barrier coating. Source: Ref 7.9

oxidation testing. The β is consumed during oxidation tests as aluminum from β diffuses through the coating to build and maintain the TGO. Over time, the diffusion of aluminum decreases the thickness of the β layer. The benefits of cold spraying over HVOF to deposit bond coats could be due to the better retention of aluminum that results from solid-state deposition and the absence of in-flight oxidation during spraying (Ref 7.20, 7.22). The aluminum content of APS, HVOF, and cold-sprayed coatings was measured in various locations by Chen et al., with the following results: APS, 9.6 to 17.9%; HVOF, 14.7 to 23.2%; and cold sprayed, 15.4 to 20.8% (Ref 7.22). It was observed that APS and HVOF coatings had regions that were oxidized, with APS coatings showing significantly higher

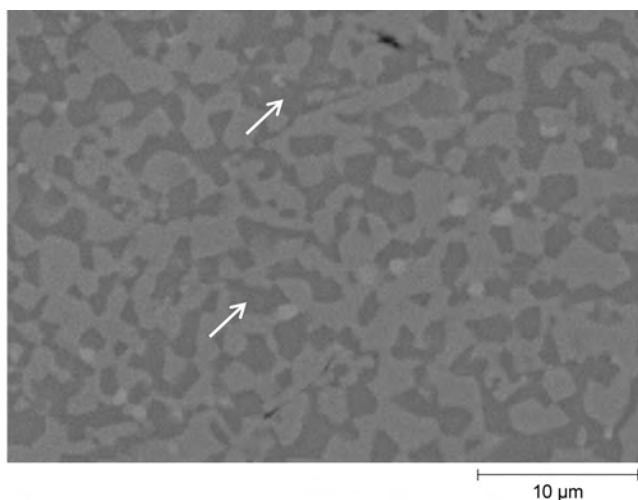


Fig. 7.4 CoNiCrAlY coating after diffusion heat treatment. Aluminum-rich β phase is seen as the dark phase in the matrix (white arrows). Source: Ref 7.9

oxide contents. Cold-sprayed coatings did not show oxides in the microstructure; however, some discontinuity around splat boundaries was seen, resulting from insufficient deformation of the feedstock particles.

Li et al. compared the performance of cold-sprayed and LPPS CoNiCrAlTaY with an 8YSZ coating deposited on top for thermal cycling performance (Ref 7.17). Thermal cycling was carried out by heating the sample to 1150 °C (2100 °F) in 2 min, holding for 27 min, and then rapidly cooling to a temperature lower than 80 °C (175 °F) by blowing air for 4 min. Oxygen content measurements were carried out using a LECO R0-316 oxygen determinator. The oxygen content of MCrAlY powder and coating (weight percent) was 0.055 in the starting powder, 0.095 in the cold-sprayed bond coat, and 0.18 in the LPPS bond coat.

Results of thermal cycling are shown in Fig. 7.5. It was observed that cold-sprayed bond coats had higher life in thermal cycling than LPPS bond coats (49 ± 10 versus 23 ± 2). It was concluded that cold spraying is an attractive method to deposit bond coats for thermal barrier coatings. The improvement in thermal cycling behavior of the cold-sprayed bond coat was attributed to the smoother surface of the cold-sprayed coating and the uniform and smooth TGO that was formed. The feedstock powder for LPPS and cold spray trials was in the size range of 5 to 37 μm . The smoother surface of the cold-sprayed coating is explained by the fact that the coarser fraction of the feedstock particles did not take part in the deposition process. The coarser particles do not exceed the critical velocity, and thus, they tend to bounce off from the substrate on impact. There may be some peening effect from the coarser particles as well. Both these phenomena could lead to smoother surfaces. The substrate surface-preparation technique used in the experiments is not described.

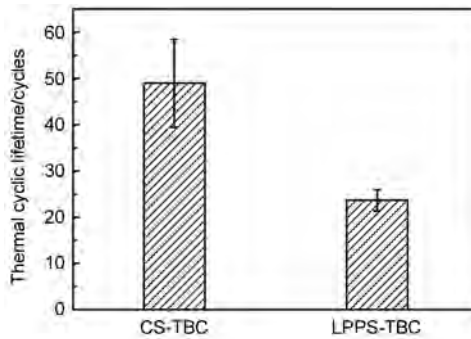


Fig. 7.5 Thermal cyclic life of thermal barrier coatings (TBCs) with the bond coats deposited by cold spraying (CS-TBC) and low-pressure plasma spray (LPPS-TBC). Source: Ref 7.17

7.2 Corrosion Protection

A diverse range of applications, including SS316 coatings, Al/SiC coatings on aluminum-magnesium alloys, Ni-20Cr for boiler tubes, and MCrAlY coatings for hot corrosion protection of iron-base superalloys, have been the subject of active research (Ref 7.8, 7.10, 7.23–7.28). TWI Ltd. (Ref 7.28) investigated the corrosion properties of Inconel 625, nickel, aluminum, titanium, WC-Co, NiCr-Cr₃C₂, and Stellite 6 cold sprayed on carbon steel. All the coatings passed the salt spray test.

Al-Mangour et al. (Ref 7.23) cold sprayed a blend of SS316 and L605 alloy (Co-20Cr-15W-10Ni alloy) on mild steel to evaluate corrosion behavior and tensile strength for medical implants. The tensile and corrosion test results from this study are shown in Fig. 7.6 and 7.7. The application was to reduce the cost and difficulty of manufacturing associated with L605 alloy, which has high melting temperature and strength. The optimum ratio of cobalt-chromium to SS316 that produced coatings with low porosity and acceptable strength and corrosion performance was at 33.3%. Annealing of the brittle, as-sprayed deposits was necessary to improve the density and the toughness. The corrosion rate of the cobalt-chromium alloy blend with SS316 is similar to the bulk value and lower than that of SS316 with higher strength. It was concluded that SS316 material mixed with cobalt alloy shows mechanical and corrosion characteristics that are suitable for the development of a new class of biomaterials.

Couto et al. (Ref 7.25, 7.29) characterized WC-12Co, WC-17Co, and WC-25Co cold-sprayed coatings sprayed on Al7075-T6 substrates and observed that the coatings were dense and the electrolyte (3.5% NaCl) did not penetrate through the coating to reach the substrate after 16 h of testing. Salt fog testing in accordance with ASTM B 117 of WC-25Co coatings did not show any evidence of pitting after 500 h of testing. Corrosion performance of cold-sprayed Ni-20Cr, Ni-50Cr, and MCrAlY coatings

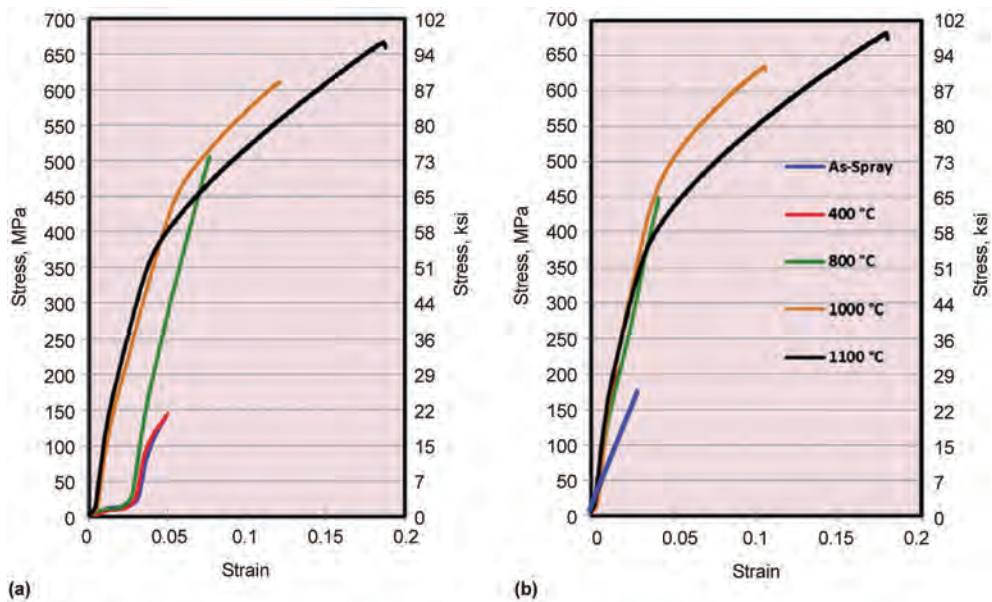


Fig. 7.6 Effect of heat treatment temperature on tensile properties of (a) 25% Co and (b) 33.3% Co coatings. Source: Ref 7.23

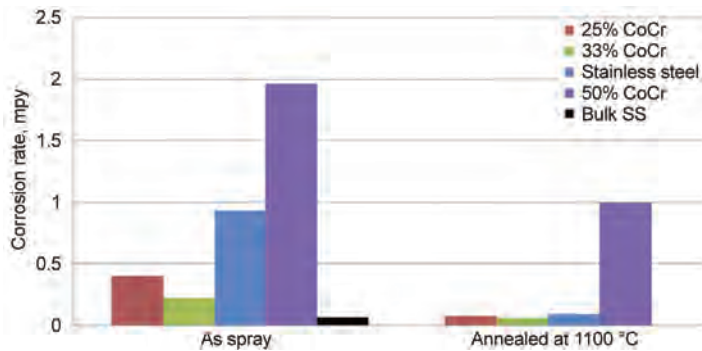


Fig. 7.7 Corrosion rate comparison (in mils per year, or mpy) between as-sprayed coating and after annealing at 1100 °C (2010 °F). Source: Ref 7.23

has been investigated for boiler tubes and waste incinerator plants (Ref 7.10, 7.26, 7.30, 7.31). In a study (Ref 7.30) of cold-sprayed Ni-20Cr applied on boiler steel, SA 516 (0.19C-1.07Mn-0.020S-0.25P-0.010Si-bal Fe) was subjected to corrosion tests at 900 °C (1650 °F) in Na₂SO₄-60%V₂O₅ for 50 cycles. The weight-change data from this study are shown in Fig. 7.8. The cold-sprayed Ni-20Cr coating was found to be protective, because it resulted in 87.2% lower weight gain of the steel in corrosion testing. Uncoated steel showed spalling and peeling of the oxide

film, probably due to the formation of nonprotective Fe_2O_3 oxide film. The authors attribute the protective capability of Ni-20Cr coating to the formation of stable oxides of nickel and chromium. Kalsi et al. (Ref 7.10) investigated hot corrosion performance of cold-sprayed NiCrAlY and NiCoCrAlY coatings in a Na_2SO_4 -10%NaCl environment at 900 °C. The coatings were deposited on iron-base alloy Superfer 800H and subjected to thermal cycling at 900 °C after applying a layer of Na_2SO_4 -10%NaCl on the surface. The coupons were examined visually after 50 cycles, and weight change was determined. Coated coupons had lower weight gain, looked cleaner, and were deemed to be more effective in providing protection to the substrate.

In another study (Ref 7.32–7.34), cold-sprayed Ni-50Cr and NiCoCrAlY were investigated for use in a chloride-based environment in a waste incineration plant. Nickel-base superalloy Superni 75 (1Fe-20Cr-0.3Ti-0.1Al-0.1C-bal Ni) coupons were cold sprayed with Ni-50Cr and exposed to flue gases in a waste incinerator plant at an average temperature of 900 °C. Visual inspection and weight gain measurements were carried out after every cycle, comprised of 100 h of exposure followed by 1 h of cooling. Testing was carried out for ten complete cycles (1000 h of exposure interspersed with 10 h of cooling). The weight gains are shown in Fig. 7.9(a), and the microstructure of the coupons after testing can be seen in Fig. 7.9(b). The coating is effective in providing corrosion protection in the aggressive chlorine-base environment at high temperatures. The dense, strongly adhering, and oxide-free coating lowers the corrosion rate (mils per year) of the substrate from 41.03 to 18.69 in the highly corrosive real service environment of the waste incinerator plant. The corrosion-protection ability of cold-sprayed Ni-50Cr is attributed to a dense, oxide-free coating that provides a barrier to penetration of corrosive media

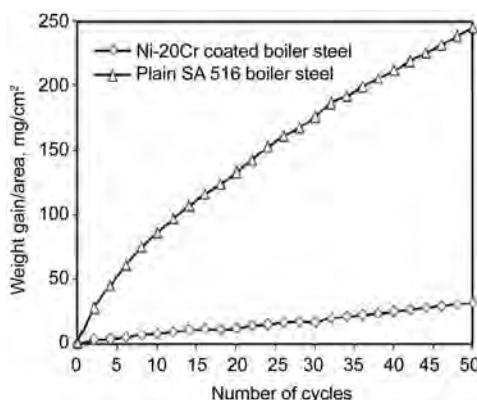


Fig. 7.8 Weight gain vs. number of cycles plot for coated and bare boiler steel exposed to hot corrosion for 50 cycles in a Na_2SO_4 -60% V_2O_5 environment at 900 °C (1650 °F). Source: Ref 7.30

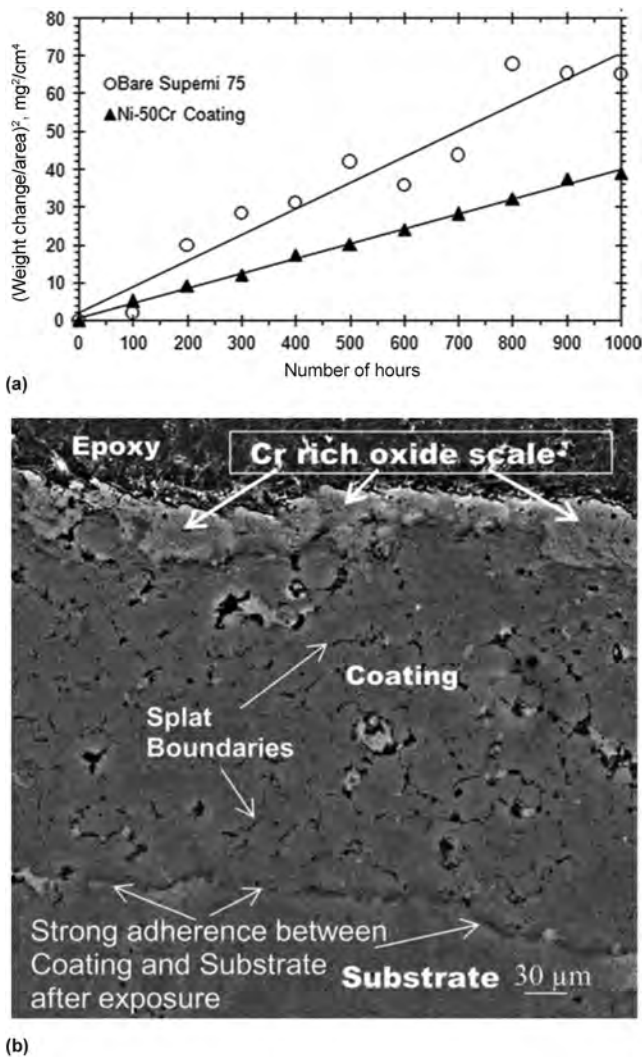


Fig. 7.9 (a) $(\text{Weight gain/area})^2$ vs. time plots for uncoated and cold-sprayed Ni-50Cr-coated superalloys after 1000 h of exposure in an incinerator environment. (b) Scanning electron microscope (backscattered electron) images across cross section for hot-corroded, cold-sprayed Ni-50Cr coating after 1000 h of exposure in the real service medical waste incinerator plant environment. Source: Ref 7.34

to the substrate and higher amounts of active chromium that are available to form the protective Cr_2O_3 oxide layer on Ni-50Cr.

There have been reports on the use of cold-sprayed titanium for corrosion protection of aluminum/aluminum-magnesium alloys (Ref 7.35), although these investigations are aimed at optimizing the cold spray parameters to achieve the dense microstructures that are expected to be effective in corrosion-protection application. Aluminum-base coatings

(e.g., aluminum-magnesium, Al-SiC) are also widely cited for use as anodic layers or for applications requiring wear protection along with corrosion protection (Ref 7.24, 7.36, 7.37). Cold-sprayed tantalum, because of its excellent ability to protect from aggressive environments at high temperatures, has been studied for aluminum, copper, and steel substrates (Ref 7.38). The dense coating produced by cold spray is a suitable barrier for protection against aggressive environments, and corrosion performance similar to that of bulk coatings has been observed.

Hydroxyapatite (HAP) and titanium composite coatings for biomedical implants have been studied for corrosion properties and found to be suitable because of the absence of oxidation of titanium during the spray process. Postspray heat treatment is required to manufacture HAP/titanium coatings with good corrosion and mechanical properties for biomedical applications (Ref 7.39).

Cold spraying of WC-CoCr (Ref 7.25, 7.40, 7.41) has been investigated for wear as well as corrosion protection. The higher density of deposits and lack of in-flight reactions are cited as the reasons for the improvement in corrosion properties associated with the application of the coating. Couto et al. (Ref 7.25, 7.42) characterized cold-sprayed WC-Co for corrosion and observed that the cold-sprayed layer was a good corrosion-resistant barrier, because the corrosive fluid did not penetrate the coating, and the coupons did not show pitting after 500 h of electrochemical testing in 3.5% NaCl solution.

7.3 Wear and Erosion Protection

Wear-protection coatings are usually formed by spraying ceramics or cermets. Cermets use hard particles in a metallic matrix. Cermets contain metallic phases of cobalt, chromium, nickel, aluminum, or iron and hard phases of WC, Cr₃C₂, Al₂O₃, ZrO₂, TiO₂, or other ceramics. Oxide coatings and some metallic coatings have also been used for wear/erosion protection.

Metals and alloys have long been known to be amenable to cold spraying, but it is only recently that spraying of cermets has been attempted. Spraying of ceramics without a metallic phase in the feedstock has not yet been reported, because ceramics tend to fracture on impact. It is necessary for feedstock particles to undergo deformation on impact to form a conformal layer on the substrate. The wear/erosion coatings produced by cold spraying fall into the following broad categories (Ref 7.24, 7.25, 7.29, 7.43–7.49):

- Spraying of cermets, where CoCr or aluminum is used as the metallic matrix with reinforcement by ceramic particles
- Cold working during deposition to improve wear properties and deposition of nanograined feedstock

Spraying of cermets, reported by many researchers, has the aim of replicating the success of HVOF spraying of cermets, particularly WC-CoCr. This research has had limited success so far, because the coatings formed have lower hardness and are not fully consolidated. Work hardening of the metallic matrix hinders the formation of dense, well-adhered microstructures, because the carbide particles do not find a soft layer in which to embed. Moreover, the absence of thermal softening allows the carbide phase to constrain the deformation of metallic phase, so that higher amounts of metallic phase are required for successful deposition of a coating. Wear performance is impaired by the higher amounts of metallic phases that are required to successfully form the coatings. The deposition efficiency also remains low, and the cost of coating deposition turns out to be very high.

One niche area where cold spraying of carbide cermets is more successful is in depositing nanograined carbides with higher strength. Ji et al. (Ref 7.50) sprayed a multimodal-particle-sized mix of WC particles in which nanometer-sized WC was blended with micrometer-sized WC and sprayed on SS316 and WC coupons. Dense and hard coatings were produced for wear applications (Fig. 7.10). White arrows in the images indicate the presence of smaller WC particles along with cobalt binder. These deposits have higher strength and benefit from the negligibility of the heat input in cold spraying. Deposition is made possible by controlling the feedstock size and carefully optimizing the spray parameters (Ref 7.29, 7.42, 7.50–7.52).

Several examples are available for the deposition of aluminum-base matrix composites with SiC, B₄C, and so on (Ref 7.36, 7.41, 7.49, 7.53, 7.54). When blends of aluminum-base alloys with hard ceramic phases are sprayed, there seems to be an optimal ratio of matrix to hard phase with which the coatings give the best wear performance with low porosity and high hardness. The optimal hard phase content depends on the processing conditions, particularly the gas used and the type of hard phase. There is also a loss of the hard phase during spraying, and only a small fraction of

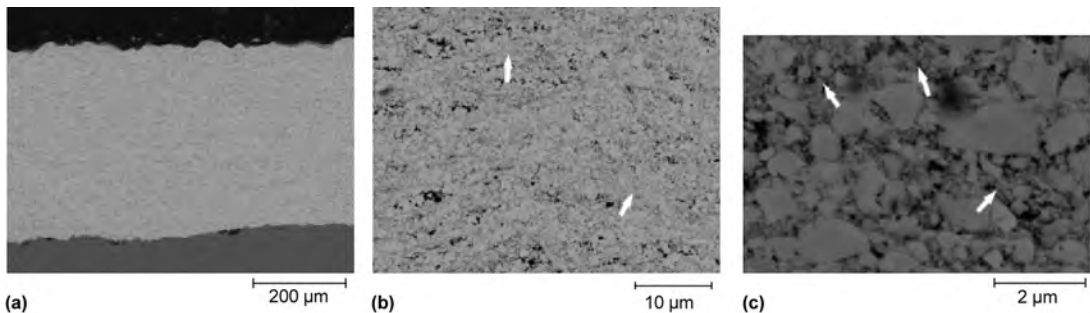


Fig. 7.10 Cold-sprayed WC-12Co; (a) low magnification; (b) and (c), high magnification. Image shows small carbide particles in Co matrix (white arrows). Source: Ref 7.50

the original feedstock composition can be retained in the final coating. Figure 7.11 shows retention of SiC in Al5056-SiC composite coating with different levels of SiC mixed in the feedstock before spraying (Ref 7.54). At 15% SiC in the feedstock, the deposit has higher (~21%) SiC. The authors attribute this increase to the loss of feedstock during spraying being higher for Al5056 particles when SiC content is lower, that is, the retention of SiC is higher for lower concentration of SiC. Figure 7.12 shows the wear rates and coefficients of friction measured in this study. Higher SiC content seems to have a beneficial effect on wear rate. Lower temperatures and higher velocities help in the spraying of nanograined or amorphous feedstock. Higher amounts of cold working also lead to the formation of a fine grain size during the deposition process (Ref 7.7).

Figure 7.13 describes the wear rate of cold-sprayed copper produced using cryomilled and conventional feedstock. Cryomilling produces nanograined feedstock powder, and cold spraying retains the nanometer-

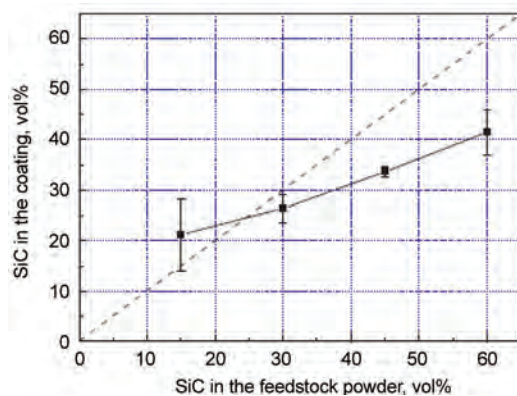


Fig. 7.11 Retained SiC phase as a function of starting powder composition. Source: Ref 7.54

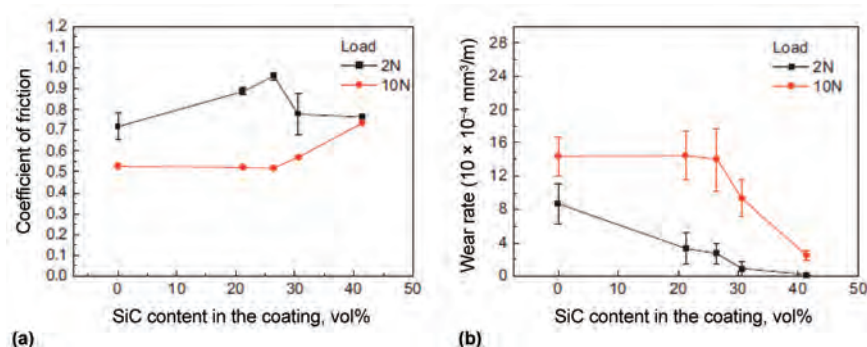


Fig. 7.12 (a) Coefficient of friction and (b) wear rate of Al5056 and Al5056-SiC coatings. Source: Ref 7.54

sized grains in the coating microstructure (Ref 7.46). The wear rate of coatings produced using cryomilled feedstock was reported to be lower than that of the coatings produced using conventional feedstock. The lower wear rate is attributed to strengthening due to grain refinement in the coating and the propensity of finer grains to form oxides during wear testing, which forms a surface layer along with copper. Finer grain size has more dislocations in the microstructure that provide nucleation sites for oxides and enhance diffusion rates of oxygen; this condition promotes the formation of a more stable surface layer.

Yandouzi et al. (Ref 7.53) sprayed Al-12Si + B₄C powder after blending (called MM) and blending followed by cryomilling (called CM). Cold spraying and pulsed gas dynamic spraying were used to deposit these materials. Pulsed gas dynamic spraying is a modification of the cold spray process in which the deposition is performed in pulses rather than continuously. The microstructures and hardness of the coatings are shown in Fig. 7.14 and 7.15, respectively. The microstructures show dense, well-adhered coatings with the B₄C phase uniformly distributed in the matrix. The hardness values depend on the feedstock powder; higher B₄C results in higher hardness. The wear resistance of the coatings produced using cryomilled feedstock was improved significantly (Fig. 7.16).

Grain refinement strengthening can be a significant means of enhancing the wear properties of cold-sprayed materials. Copper-, aluminum-, cobalt-, nickel-, and iron-base materials have been cold sprayed to improve wear properties. Cold spraying of quasicrystal (QC) materials has been explored because it is expected that the sprayed materials will not undergo phase change (Ref 7.49, 7.55). Guo et al. (Ref 7.49) studied the properties of Cu-8wt%Sn powder blended with QC powder Al_{59.1}Cu_{25.6}Fe_{12.1}B_{3.2} coatings. Mixtures of Cu-8Sn with three different QC fractions (19.5, 36.8, and 57.6 vol%) were mechanically blended and used as initial pow-

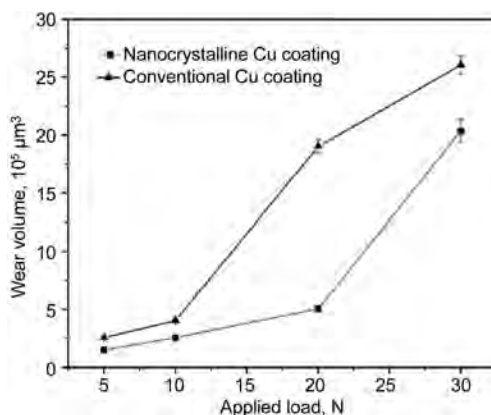


Fig. 7.13 Wear rate of cold-sprayed copper produced from cryomilled and noncryomilled feedstock. Source: Ref 7.46

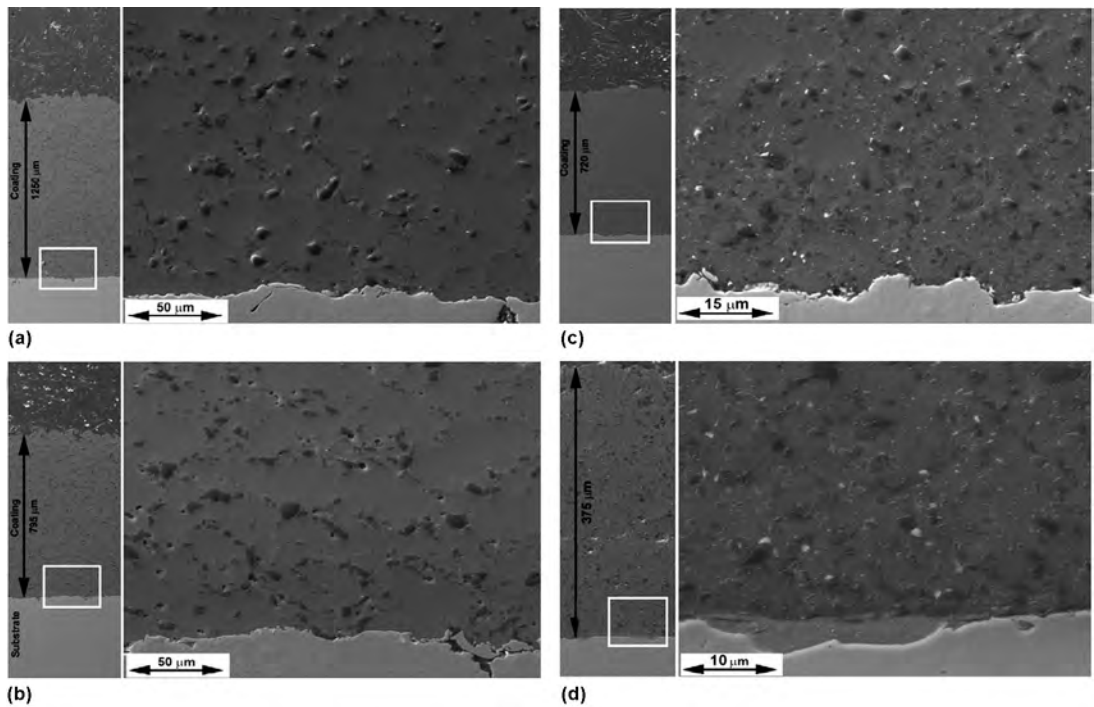


Fig. 7.14 Scanning electron microscope images showing the microstructure of composite coatings on SS316L substrate. (a) and (b) MM coating sprayed by cold spray and pulsed gas dynamic spray (PGDS), respectively. (c) and (d) CM coatings sprayed by cold spray and PGDS, respectively. Each image consists of a box on the left side with a corresponding higher magnification image of the box on the right side. Source: Ref 7.53

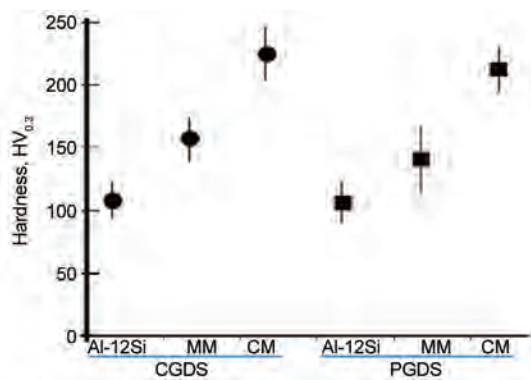


Fig. 7.15 Hardness of cold gas dynamic sprayed (CGDS) and pulsed gas dynamic sprayed (PGDS) coatings. Source: Ref 7.53

der feedstock for coating deposition. The deposits had 30 to 40% lower QC phase than the starting powder, and it was observed that the density and hardness of deposits increased with increasing volume fraction of the QC phase. The QC phase is lost by rebound and fracture of the larger-sized portion of the QC powder. The mechanism of coating formation was

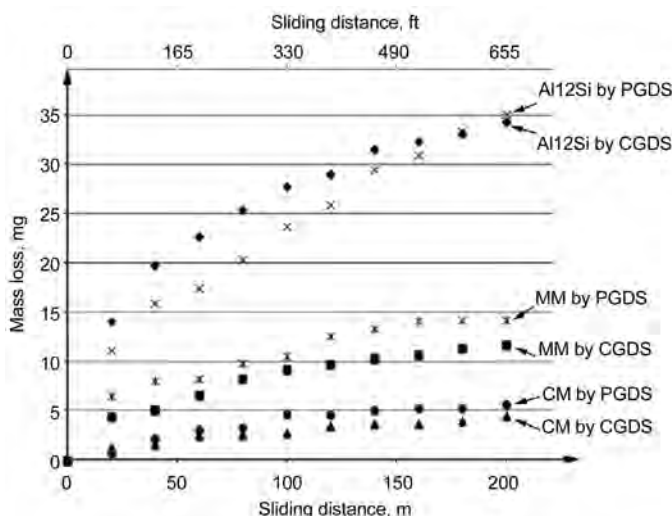


Fig. 7.16 Sliding wear test of Al-12Si + 20% B₄C coatings. MM and CM feedstock show significant benefits over Al-12Si coatings. PGDS, pulsed gas dynamic spray; CGDS, cold gas dynamic spray. Source: Ref 7.53

the embedding of the QC phase in the softer Cu-8Sn matrix, and the higher hardness is due to flattening of the matrix by the impacts of the QC phase. It is also likely that the embedding of the QC phase is not very efficient for higher volume fractions. The wear rate decreased slightly for 19.5% QC phase; however, for higher amounts of QC phase, the wear rate was higher. This latter phenomenon was attributed to debonding of the QC particles that can cause severe abrasion. Kiz et al. cold sprayed Al₉₄Fe₃Cr₃ and Al₉₄Fe_{2.5}Cr_{2.5}Ti₁ feedstock containing 30 vol% QC particles in the size range of 100 to 200 nm. The x-ray diffraction peaks of the coating showed retention of the QCs in the microstructure and higher hardness in the coatings. Such coatings are expected to provide good corrosion and erosion properties up to 300 °C (570 °F).

Yoon et al. (Ref 7.56) investigated the tribological properties of iron-base bulk metallic glass (BMG). The feedstock of Fe_{68.8}C_{7.0}Si_{3.5}B_{5.0}P_{9.6}Cr_{2.1}Mo_{2.0}Al_{2.0} (at.%) was prepared by inert gas atomization and cold sprayed after optimizing the parameters. The BMG coatings were subjected to pin-on-disc testing and compared to bearing steel and steel-backed sintered (SBS) bearings. The hardness of the BMG coating was increased by work hardening during the deposition process, and the wear performance was better than that of the steel bearing but inferior to that of the SBS bearing. The key finding in this study was that the deposition of dense BMG coatings may be further optimized for use in wear and corrosion applications.

Cold spraying of Stellite 6 is of interest because Stellite can be used to improve wear as well as high-temperature oxidation/corrosion (Ref 7.57). Stellite 6 is the most commonly used Stellite in the nuclear power industry, and it consists of approximately 12.6 wt% $(\text{Cr}_{0.80}\text{Co}_{0.15}\text{M}_{0.05})_7\text{C}_3$ carbides (M = tungsten as well as residual elements) in a Co-23Cr-4.5W solid-solution alloy (Ref 7.47, 7.58). There have been reports on cold spraying of Stellite where dense coatings were produced with hardening of the deposits by cold work (Ref 7.47). The wear rate of cold-sprayed Stellite 6 was found to be lower than that of HVOF-sprayed Stellite 6. The coatings were also tested for high-temperature oxidation and corrosion; it was concluded that the coatings may find applications in high-temperature environments up to 900 °C (1650 °F). Further improvements in wear properties were observed when alumina was co-sprayed along with Stellite 6 to incorporate up to 33% alumina in the top layer of the cold-sprayed deposit.

7.4 Functional Coatings and Additive Manufacturing

The production of coatings for functional layers is possible with cold spraying, because clean and dense layers can be deposited (Ref 7.6, 7.7, 7.27). One of the first applications of cold spraying was deposition of copper on aluminum heat sinks to provide soldering leads; these are now in mass production (Ref 7.6). Figure 7.17 shows a picture of this application. Production of conducting tracks for automotive applications has been investigated by cold spraying; the research effort has focused on investigating the thermal stability and electrical properties of a copper and tin underlayer with a top layer of copper deposited on a variety of polymer substrates (Ref 7.7). The as-sprayed electrical resistivity of the tin + copper layer was reported to be $27.09 \text{ n}\Omega \cdot \text{m}$, which, after annealing at 500 °C (930 °F), was reduced to $21.16 \text{ n}\Omega \cdot \text{m}$. Annealed bulk copper sheet resistivity was measured to be $16.76 \text{ n}\Omega \cdot \text{m}$. In the medical field, cold spray has been demonstrated to apply HAP without compromising its integrity (Ref 7.27). Cold-sprayed $\text{NiO-Al}_2\text{O}_3$ has been deposited to a thickness of 50 μm for use as a catalytic layer for steam reforming of methane to produce H_2 (Ref 7.59). The coating was found to have adequate adhesion for the application and remained active for H_2 production after 100 h.

Another application for cold spraying is in additive manufacturing, in which parts can be gradually built up by adding material, in contrast to machining, in which material is removed to form the final shape. (Its application specifically in the automotive industry is discussed in Chapter 8, “Cold Spray Applications in the Automotive Industry,” in this book.) Cold spraying has a narrow spray plume, typically 3 to 5 mm (0.1 to 0.2 in.) wide; the narrow spray plume allows better control of the spray path and less overspraying. The gun mounted on a robot can be programmed to move along complex paths and deposit thick deposits that can be sprayed in a variety of shapes to make free forms or parts by additive manufactur-

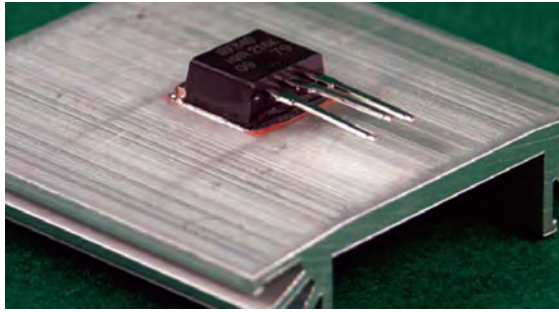


Fig. 7.17 Soldered power transistor on an aluminum heat sink with a cold-sprayed copper layer. Source: Ref 7.14

ing (Ref 7.60, 7.61). The final part can be finished with minimal machining/grinding postmanufacturing. There are reports on fabrication of aluminum/aluminum-alloy parts by cold spraying.

Cormier et al. investigated the formation of near-net shape pyramidal fins by cold spray deposition to enhance heat transfer in recuperating preheaters in microturbines and as heat exchangers in electronic devices (Ref 7.5, 7.62). Pyramidal fins provided additional surface area for heat extraction and thus improved the heat-exchange efficiency. This production method can enable better efficiency of microturbines and more compact packaging of electronic devices. A picture of a pyramidal fin is shown in Fig. 7.18. A wire mesh was used to mask the surface, and aluminum was deposited through the wire mesh to form the pyramidal fins. Wire mesh size and grid pattern can be varied to create pyramidal fins of different shapes and sizes. Cold-sprayed pyramidal fins were found to improve the heat-transfer efficiency. Joining by cold spraying has been explored by Cadney et al. (Ref 7.3). A schematic of the freeform and joint produced using cold spraying is shown in Fig. 7.19.

Much attention has been focused on additive manufacturing of titanium and its alloys, because of the high cost of titanium and the difficulty of fabricating titanium-base parts through conventional routes (Ref 7.4, 7.60, 7.63–7.65). Researchers at the Commonwealth Scientific and Industrial Research Organisation in Australia studied the cold spray deposition of titanium and optimized the parameters to obtain dense coatings that can be used for fabrication of parts (Ref 7.65). Binder (Ref 7.4) investigated cold gas spraying of titanium and found that it produced mechanical strength and electrical conductivities comparable to those of solid material of similar purity. The cold-gas-sprayed titanium layers, for the first time for a powder metallurgical process, achieve almost 100% of the tensile strength, over 90% of the fatigue strength, and 97% of the electrical conductivity of solid material and demonstrate impressively the suitability of cold gas spraying as a production process for titanium components that meet the high demands of the aviation industry. The parameter optimization study

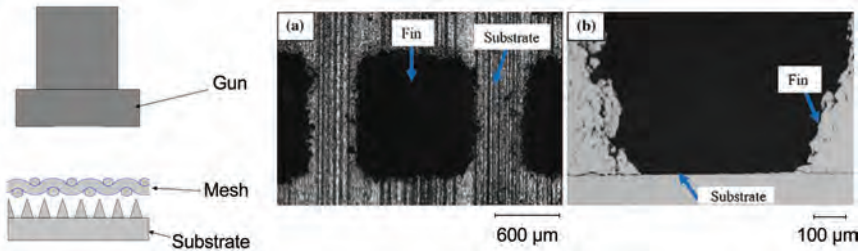


Fig. 7.18 Typical pyramidal fin prepared by cold spraying. Image at left illustrates the masking technique. Microstructures show (a) top view and (b) cross section of typical fin deposition. Source: Ref 7.5

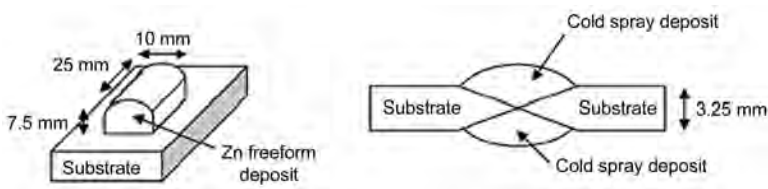


Fig. 7.19 Freeform and joining through cold spraying. Source: Ref 7.3

enabled the derivation of generalized layer quality parameters, which can allow optimization of the layer, and is also applicable to other materials.

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CHAPTER 8

Cold Spray Applications in the Automotive Industry

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THE COLD SPRAY (or cold gas dynamic spray, CGDS) process is a novel technology that can deposit metals or metal-ceramic composites under atmospheric conditions by accelerating feedstock particles above supersonic (300 to 1200 m/s, or 1000 to 3900 ft/s) speeds using a converge-diverge de Laval nozzle (Ref 8.1–8.8). Because the cold spray process can produce thick deposits up to bulk scale with advanced mechanical properties (e.g., high density, high strength, high hardness) and without oxidation, phase transformation, or decomposition of feedstock materials, there have been a number of studies on the application of the cold spray process to various industrial fields (Ref 8.9–8.12). In particular, the application of the cold spray process to the automotive industry is being increasingly investigated. Such cold spray application research for the automotive industry can be broadly divided into three parts: additive manufacturing (AM) of components, fabrication methods, and protective coatings.

In the global industrial field, AM technology is expected to drive rapid progress and to bring innovations in manufacturing processes (Ref 8.13, 8.14). Especially in the automotive industry, the potential value of CGDS as an AM technology is thought to be very high (Ref 8.15) because, with it, bulk-scale deposition can be rapidly achieved with good mechanical properties (Ref 8.16–8.19). Cold gas dynamic spraying is one of the few

metal and metal-ceramic composite deposition methods in bulk scale without any phase transformation and chemical/physical property change. Thus, CGDS additive manufacturing technology will occupy a critical position in the automotive industry, even though the research is in its early stages.

Also, the cold spray process has been researched as a new fabrication technology in various fields of industry (Ref 8.20–8.25). That is, the cold spray process can produce numerous forms of thick deposit up to almost bulk scale with good mechanical properties, and the manufacturing time can be much reduced by leaving out the unnecessary bonding process between the final product components. Cold spray thus has great potential as a fabrication technology for components.

Consequently, cold spray can be an alternative coating process to the protective coating method for automotive components. In the case of the thermal spray process, which is conventionally applied to the protective coating of vulnerable automobile parts, oxidation and phase transformation make it impossible to preserve the original properties of the feedstock materials. Additionally, thermally induced stress and residual stress are very deteriorating to automotive components. However, in some cases, cold spray can provide a more advanced protective coating layer than thermal spraying, and, accordingly, there have recently been some investigations into protective coating using cold spray.

In this chapter, the application of cold spray to the automotive industry field is discussed, with special attention to the aforementioned three applications: additive manufacturing, fabrication methods, and protective coatings. Recent studies on the automotive application of cold spray are reviewed. Also, the background and purpose of each application are presented, and practical cases are discussed. All of the applications described in this chapter specifically involve high-pressure cold spray.

8.1 Additive Manufacturing for the Automotive Industry Using Cold Gas Dynamic Spraying

Until recently, the needs for the manufacturing of brittle material components in the industrial field and the development of metal powders and processes have expanded the application of powder metallurgy (PM) to the manufacturing process. The automobile corporations have especially driven the development of fabrication processes for lightweight components (Ref 8.24). However, the PM and sintering processes are not appropriate for the fabrication of thermally sensitive material. Also, in most cases, sintered components need additional bonding processes, which makes the manufacturing process more complicated.

On the other hand, AM technology is greatly innovative, producing components via successive layer-by-layer deposition of feedstock mate-

rial in accordance with the morphological and spatial information of partitioned cross sections of the component obtained by design programs such as computer-aided design. Accordingly, AM technology cuts the time and cost for the components manufacturing process and increases the freedom of production in shape complexity and production environment. Today (2015), various manufacturing industries, including the automotive industry, show high interest in AM technology as a component-fabrication method because of its convenience and economic feasibility (Ref 8.13–8.15).

In the global automotive field, not only original equipment manufacturers (OEMs) but also small businesses have much interest in AM technology. This is because AM technology is expected to drive rapid progress and to bring innovation in the manufacturing process throughout the automotive industry, which can help minor companies overcome the market-entry barrier resulting from the technological and financial gap between OEMs and small companies. This expectation can be attributed to the following two factors (Ref 8.15).

Product Innovation. Additive manufacturing technology has almost no restriction on the design of components, so diverse and complex shapes can be freely produced. Accordingly, breaking out from the conventionally standardized design, custom design, and manufacturing of automotive components will be possible through AM technology. Moreover, integrated multimaterial printed components whose parts have distinct and individual properties can be fabricated by suitable control of the materials.

Supply Chain Transformation. With regard to automotive components production, AM technology does not require additional tooling and needs only feedstock materials with AM equipment. Also, low- to medium-scale automotive components can be produced anytime and anywhere, if the AM equipment is in place. Thus, automotive component fabrication using AM technology exhibits high accessibility and response to the demands of the customer. These factors will change the supply chain by reducing costs, chain complexity, and dependence on extensive capital.

Under these circumstances, CGDS as an AM technology has high potential because bulk-scale deposition can be rapidly achieved with good mechanical properties. In particular, CGDS is one of the few metal and metal-ceramic composite deposition methods in bulk scale without any phase transformation and chemical/physical property change. Also, CGDS is more cost-effective than other metal-deposition AM technology, such as selective laser melting and direct metal deposition. Hence, numerous studies of the application of CGDS to AM technology have been conducted (Ref 8.16–8.19).

Figure 8.1 shows an example of a three-dimensional deposit produced by CGDS additive manufacturing (Ref 8.16). Figure 8.1(a) is the sche-

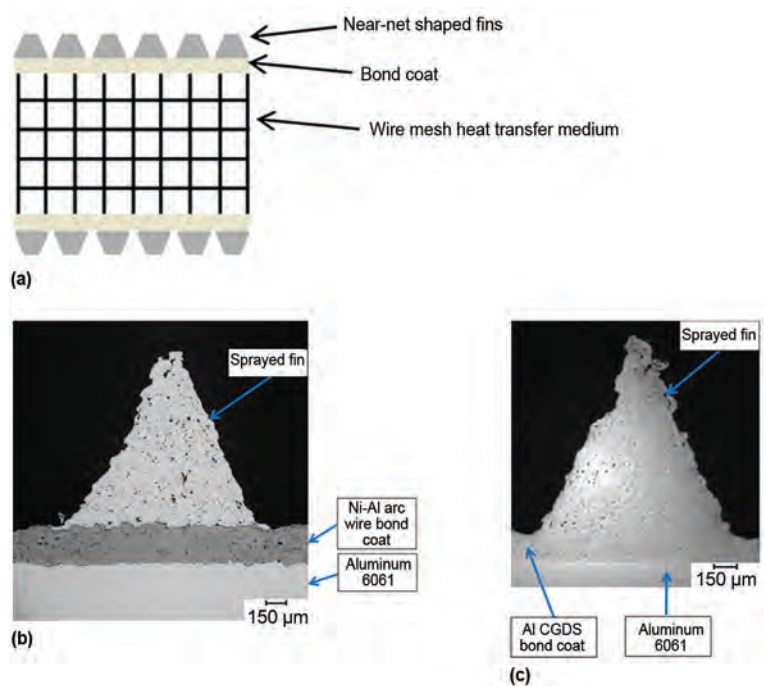


Fig. 8.1 Practical examples of three-dimensional-formed bulks using the cold gas dynamic spray (CGDS) process. (a) Schematic cross-sectional image of improved wire mesh heat exchanger. Cross-sectional images of pyramidal fins deposited on (b) nickel-aluminum and (c) aluminum bond coats. Source: Ref 8.16

matic image of aluminum near-net-shaped fins deposited on a wire mesh heat exchanger; magnified scanning electron microscope images of those fins are shown in Fig. 8.1(b and c). Sprayed fins were successfully deposited on different types of bond coats (nickel-aluminum and pure aluminum) in both cases, even though some pores existed in the deposited pyramidal fins. Other practical cases of components fabricated by CGDS additive manufacturing are shown in Fig. 8.2 (Ref 8.26, 8.27).

The automotive industry also displays an interest in CGDS additive manufacturing technology, and some automotive companies have ongoing research programs on the subject. Very few results have been released to the public, because AM of metal and metal-ceramic composite has not yet been developed to the point of commercialization. However, remarkable outcomes are expected in the near future. As shown in Fig. 8.3, General Electric has already verified that components can be manufactured with CGDS additive manufacturing by using it to restore a damaged complex shaft in 9.5 min (Ref 8.28).

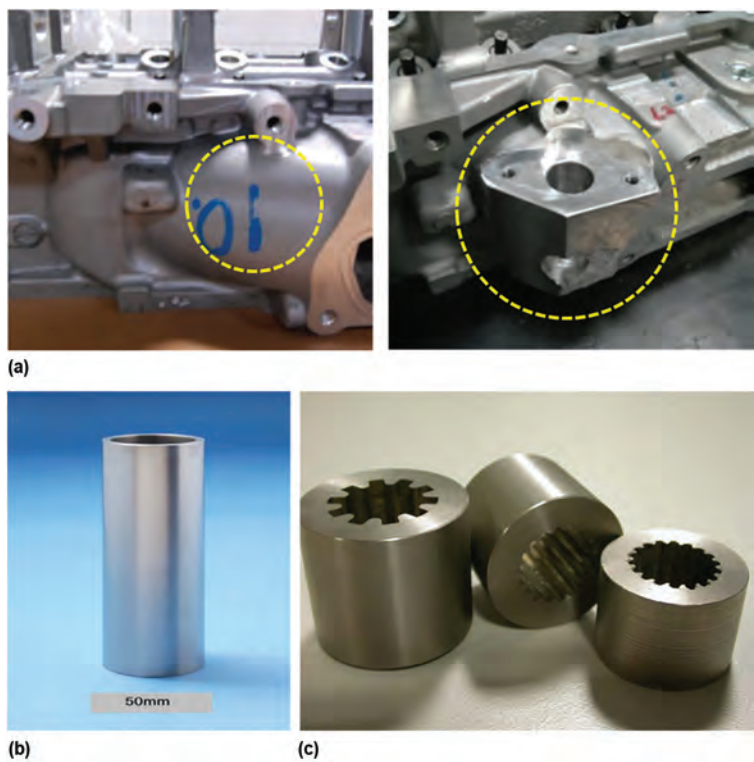


Fig. 8.2 Practical examples of three-dimensional-printed products using the cold gas dynamic spray process. (a) Prototype machine component. (b) Titanium seamless heat pipes. (c) Titanium machine components. Source: Ref 8.27, 8.28



Fig. 8.3 Practical example of shaft fabrication via cold gas dynamic spraying additive manufacturing technology, which was conducted by General Electric. Source: Ref 8.28

8.2 Product Fabrication for the Automotive Industry Using Cold Gas Dynamic Spraying

In contrast to conventional manufacturing processes, cold spray processes do not use thermal energy and so are suitable for the fabrication of thermally sensitive materials. A fairly thick layer of metal or metal-ceramic composite can be deposited on the desired substrate with advanced mechanical properties approximately similar to those of the bulk material. Also, the manufacturing process can be simplified by omitting the additional bonding process between the components of the final products. Accordingly, cold spray has been gradually applied to the automotive industry as a fabrication method for heat exchangers, torque sensors for steering shafts, and electrically conductive tracks.

Heat Exchangers. In automotive air conditioning systems, aluminum heat exchangers are essential components. Conventionally, these aluminum heat exchangers have been produced via a complex fabrication process that includes wire arc spraying, dipping, and brazing. In this process, zinc is sprayed onto aluminum brazing tubes to improve corrosion resistance using a wire arc spraying process, and the fin for broadening the surface area is then cladded by dip painting. Then, the bond-assisting flux is spread on the aluminum tube and the fin to facilitate assembly before brazing.

However, with the cold spray process, the coating materials can be sprayed on at once without any complicated midprocesses, and a dense, thick coating layer of zinc and flux can be deposited without microstructure change, oxidation, or decomposition. Figure 8.4 schematically shows the process of manufacturing an aluminum heat exchanger using the cold spray process (Ref 8.20).

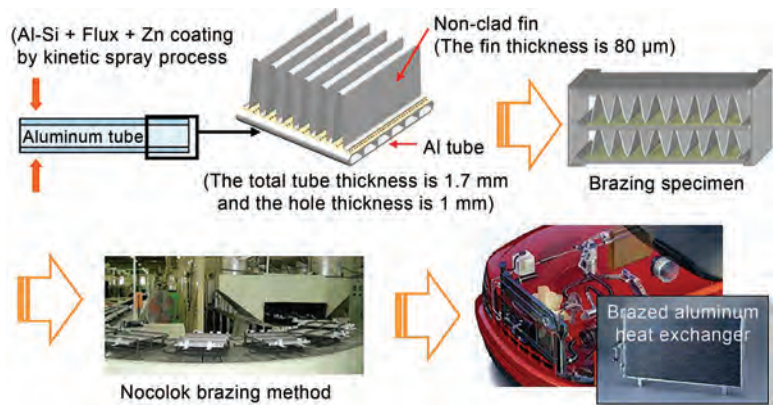


Fig. 8.4 Schematic manufacturing process of an automotive aluminum heat exchanger using the cold spray process. Source: Ref 8.20

Yoon et al. investigated the possibility of using the cold spray process as a fabrication method for aluminum heat exchangers (Ref 8.20). Figure 8.5 shows the bonding state between the cold-sprayed aluminum tube and fin after the brazing process.

All of the cold-sprayed aluminum tube-fin assemblies exhibited a good bonding state after the brazing process. There was no degradation of bonding relative to the conventionally produced aluminum heat exchanger. Moreover, this method presents the possibility of no-flux brazing, because the bonding state was not affected by the fraction of flux in the coating layer. The cold-sprayed aluminum heat exchanger also shows no leak after a 500 h corrosion test, as shown in Fig. 8.6.

Shafts. Magnetostriction is the induction of significant strain in a material on exposure to a magnetic field. The development of strain in a magnetostrictive material can change its magnetization state. In the automotive industry, magnetostrictive material is used for torque sensors of steering shafts. Torque in the shaft generates strain in a magnetostrictive

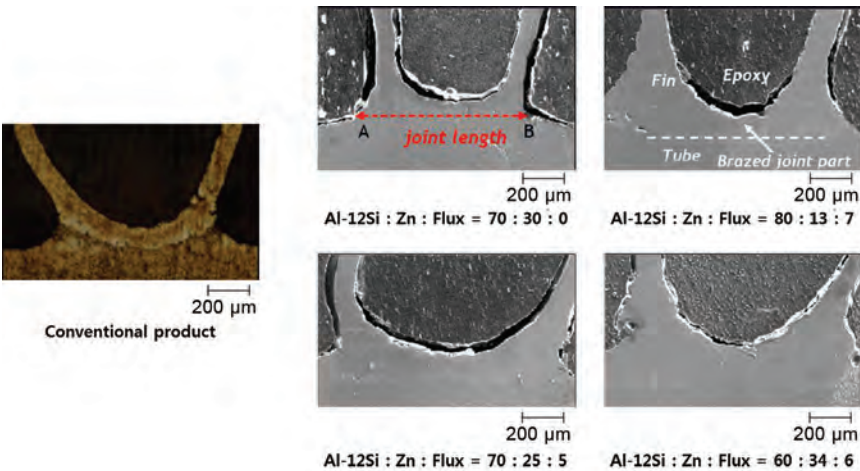


Fig. 8.5 Bonding state of aluminum tube and fin coated by cold spray after the brazing process. Source: Ref 8.20

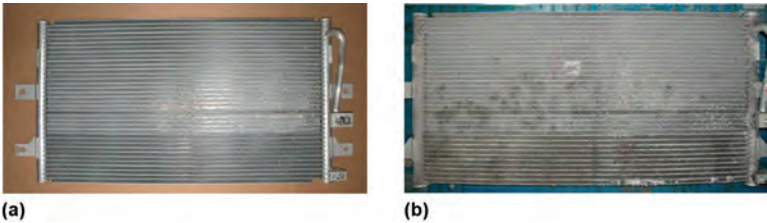


Fig. 8.6 Leak test of cold-spray-assisted fabrication of aluminum heat exchanger. (a) Before and (b) after the 500 h corrosion test. Source: Ref 8.20

ring mounted on the shaft, and the magnetization of the ring is changed, which gives information about the torque state of the steering shaft.

It has been difficult to manufacture high-quality torque sensors because the high-magnetostrictive materials, rare earth/iron compounds, are insufficiently machinable for use as automotive components, whereas materials with good mechanical properties, such as steels, have highly limited magnetostriction and low adhesion to the steering shaft. However, high-magnetostrictive rare earth/iron composite materials can be successfully deposited on the desired substrate by using a cold spray process, allowing such coatings to serve as a portion of the torque sensors on automotive aluminum or steel steering shafts. The U.S. patent 6,465,039 B1 describes a method for depositing a magnetostrictive ReFe_2 mixture onto a substrate using cold spraying (Ref 8.25). Figure 8.7 shows the constitution of a magnetostrictive-composite-coated steering shaft.

Formation of Electrically Conductive Tracks on Plastic Mold Components. In manufacturing hybrid plastic-metal products, the main fabricating processes are of two types: postmold assembly and in-mold assembly. Postmold assembly is used to bond metal and plastic parts after the individual production of each metal and plastic part. Here, welding, gluing, or screwing is used as a bonding process. In in-mold assembly, the prefabricated metal parts are overmolded with the plastic components. However, such hybrid plastic-metal components manufacturing methods are very complex and highly time-consuming.

The manufacture of hybrid plastic-metal components can be simplified by cold spraying. Metal parts produced on plastic components can also exhibit high electrical conductivity because, generally, cold-sprayed deposits show 50 to 200% higher electrical conductivity than coatings deposited by arc, plasma, or high-velocity oxyfuel (HVOF) spraying because of the low degree of defects, such as pores and oxides, detrimental to mechanical, thermal, and electrical properties.

Bobzin et al. studied a hybrid cold spray/injection molding manufacturing process for metal-plastic components (Ref 8.22). In this process, a copper layer is first deposited on the open mold. Then, the mold is closed

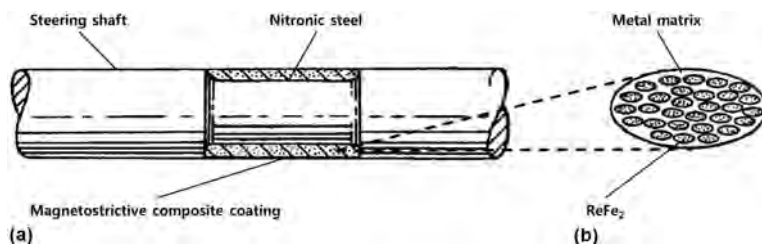


Fig. 8.7 Schematic constitution of steering shaft with cold-sprayed magnetostrictive composite deposit. (a) Whole steering shaft. (b) Detail composition of magnetostrictive composite coating. Source: Ref 8.25

and injection molding is performed. Finally, the mold is stripped off, and the hybrid copper/plastic components are obtained by transferring the copper layer to the molded plastic part. The manufacturing process is shown in Fig. 8.8.

8.3 Protective Coatings for Automotive Applications Using the Cold Gas Dynamic Spray Process

Generally, numerous automotive components are exposed to harsh environments during operation. Thermal spraying has been applied as a protective coating fabrication method in the automotive industry (Ref 8.29–8.38). However, thermal spraying has some disadvantages resulting from the use of a heat source, including oxidation or phase transformation of the feedstock material and thermally induced residual stress. In contrast, cold spraying can provide coating layers with improved mechanical and chemical properties without any oxidation or phase transformation. Recently, there have been some studies of the application of cold spray to the deposition of protective layers on automotive components. These layers can be broadly divided into two types: corrosion-resistant coatings and wear-resistant coatings.

Corrosion-Resistant Coatings by Cold Spray. Lightweight materials are frequently used in automotive components to reduce the weight of automobiles and improve fuel efficiency (Ref 8.39–8.42). However, unlike aluminum alloys, magnesium alloys are highly vulnerable to corrosion, such as galvanic, pitting, and intergranular corrosion (Ref 8.43). Figure 8.9 shows automotive parts damaged by corrosion (Ref 8.44).

Magnesium alloys easily react in the presence of oxygen and water, and the reaction produces magnesium hydroxide on the surface of such alloys. However, unlike other metals, the passivation film on magnesium easily becomes very unstable under various environments. As a result, magne-

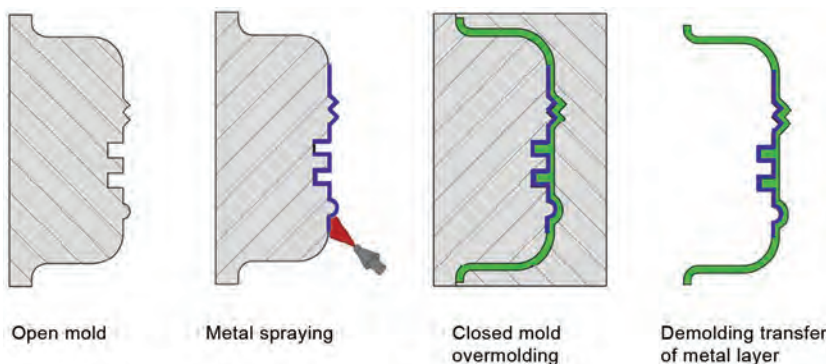


Fig. 8.8 Schematic sequence of cold spraying/injection molding hybrid process for metal-plastic components production. Source: Ref 8.22

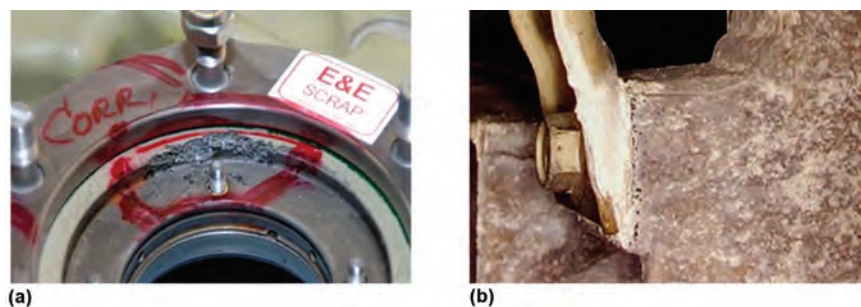


Fig. 8.9 Automobile parts damaged by corrosion. (a) Magnesium alloy used in rotorcraft. (b) Magnesium alloy fastened to a steel bracket by a coated steel bolt. Source: Ref 8.45

sium alloys are extremely sensitive to galvanic corrosion, which usually decreases their mechanical stability, as shown in Fig. 8.9(b). Such galvanic corrosion occurs when magnesium alloys are connected to other metallic materials in the presence of an electrolyte (Ref 8.45).

Currently, there are many protective coating technologies, such as thermal spray coating, electrochemical plating, conversion coating, anodizing, hydride coating, organic coating, and vapor-phase coating (Ref 8.36). For automotive components, thermal spray (especially plasma spray and HVOF spray) technologies have been used to form protective layers on magnesium alloys. However, thermal-sprayed protective coating layers sometimes provide insufficient protection as a result of oxidation or phase transformation of the feedstock materials, high porosity of the coating layer, or crack formation caused by a difference in thermal expansion coefficients or thermally induced residual stress. However, with cold spraying, high-density coating layers with advanced mechanical properties can be deposited without any phase transformations or thermally induced residual stress.

Figure 8.10 shows the improved corrosion resistance of magnesium alloy AZ31 after cold spraying of aluminum compared to other magnesium alloys (AZ91D and AM60B). This advanced corrosion resistance resulted from the reduction of the electrochemical potential differences, which provided localized protection of the magnesium alloy for general and galvanic corrosion by cold spraying on pure aluminum.

Also, according to the research of Maeva et al., a Ni-Zn/Ni-Zn- Al_2O_3 composite was deposited on magnesium alloy AZ31 (Ref 8.46). Results for cold-sprayed Ni-Zn/Ni-Zn- Al_2O_3 composite show promise in protecting magnesium alloys; the corrosion rate was highly reduced compared to the bare magnesium alloy, as shown in Fig. 8.11. This result may be induced by the decrease of the electrochemical potential differences that would otherwise usually trigger galvanic corrosion.

Ducos et al. studied zinc deposition on iron substrates to produce corrosion-resistant automotive bodies, and Renault S.A. (Boulogne-Billan-

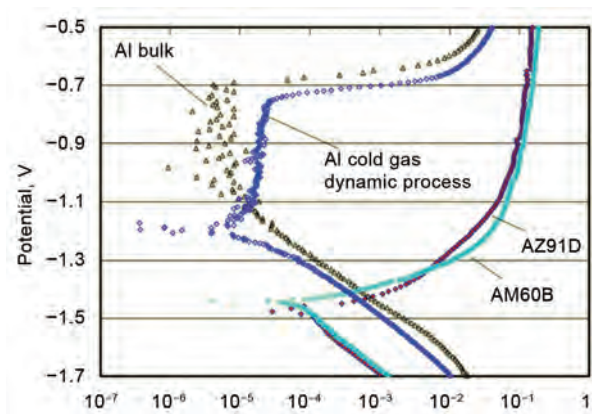


Fig. 8.10 Enhanced corrosion resistance of cold-sprayed magnesium alloy AZ31 using aluminum compared to AZ91D and AM60B alloys in 3.5% NaCl. Source: Ref 8.44

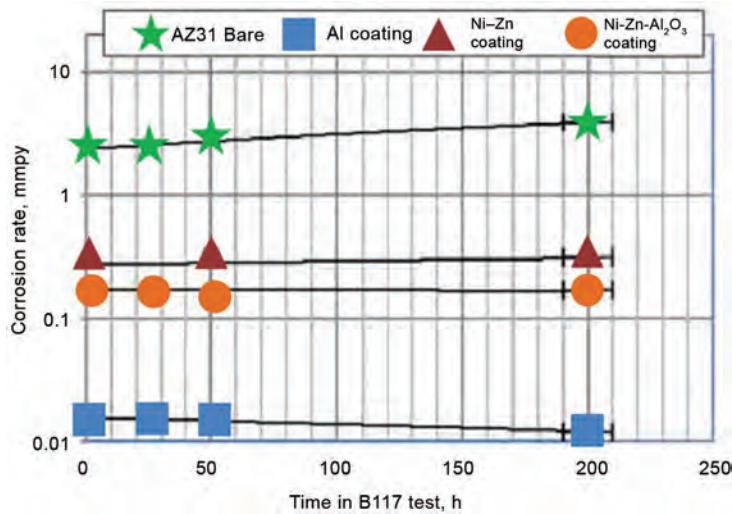


Fig. 8.11 Evolution of corrosion rate (in millimeters per year, or mmpy) as a function (linear regression) of accelerated salt fog corrosion test environment. Source: Ref 8.46

court, France) studied nongalvanized sheet steels by forming a zinc coating layer on portions of an automotive body exposed to corrosion (Ref 8.47). Additionally, many primary automotive companies have been continuously investigating the deposition of a corrosion-resistant layer using the cold spray process.

Wear-Resistant Coatings by Cold Spray. Recently, automobile manufacturers have found ways to decrease frictional loss to increase fuel effi-

ciency. One representative way is to replace a high-weight cast iron engine block with one made of a lighter-weight material. Aluminum alloys are prospective candidates for this application, not only because of their light weight but also because of their machinability and recyclability (Ref 8.42). However, in general, unprotected aluminum alloys have high wear rates, and the engine operating environment is too harsh for them. Their tribological characteristics must be enhanced if they are to be used in engine blocks (Ref 8.30).

To solve this problem, liners made of hard materials (e.g., cast iron) have been inserted into the aluminum alloy engine block to offer improved wear-resistant surfaces. Such liners have generally been produced by high-temperature techniques such as laser cladding or thermal spraying, as shown in Fig. 8.12 (Ref 8.48, 8.49).

However, these processes have been found to be undesirable because they induce residual thermal stress in the base aluminum engine block. Such thermally induced residual stress can cause distortion or cracks in the fabricated aluminum engine block at any time. It is much better to find a way to form a liner without any thermally induced stress (Ref 8.50).

Because cold spraying deposits particles in their solid state by using kinetic rather than thermal energy, the detrimental effects, particularly thermally induced stress, can be minimized. This process also has the benefit that bond strength and hardness increase after deposition.

Vo examined the enhancement of engine block wear resistance by cold spraying 316L stainless steel (Ref 8.51). Here, the 316L stainless steel was post-heat treated under 1100 °C (2010 °F) for 1 h after deposition on a 1020 steel substrate. As a result, the bonding states of the particle-particle and particle-substrate interfaces were improved, and the volume loss was decreased relative to the bare 1020 steel substrate (Fig. 8.13).

Gojon et al. studied the effect of ball-milled SiC particle size on an Al5056/SiC composite coating layer deposited by cold spray (Ref 8.52). As in the preceding case, wear testing revealed that the wear rate of Al5056/SiC composite layer decreased when the SiC particle size was increased (Fig. 8.14).

8.4 Summary

As a novel technology, cold spray can fabricate various products with more desirable properties than those of products fabricated by high-temperature processes, especially thermal spray processes. Accordingly, the capabilities of cold spray have found increasing application in the automotive industry. As research continues into the application of CGDS additive manufacturing to automotive components, this technology is expected to assume a critical position. Cold spray is particularly advantageous in producing thick protective coating layers on thermally vulnerable automotive components without any oxidation, chemical reaction, or de-

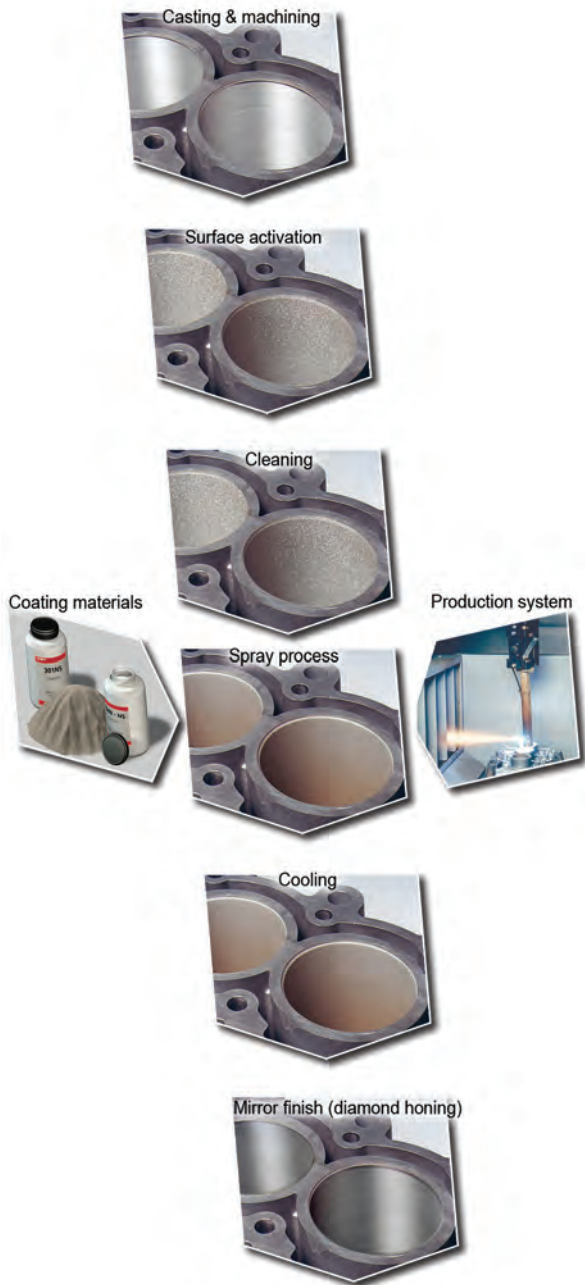


Fig. 8.12 Sequence of wear-resistant coating on aluminum alloy engine block. Reproduced by permission of Oerlikon Metco. Source: Ref 8.49

composition of the feedstock materials. This being the case, cold spray technology is sure to hold an important position in the future of the automotive industry.

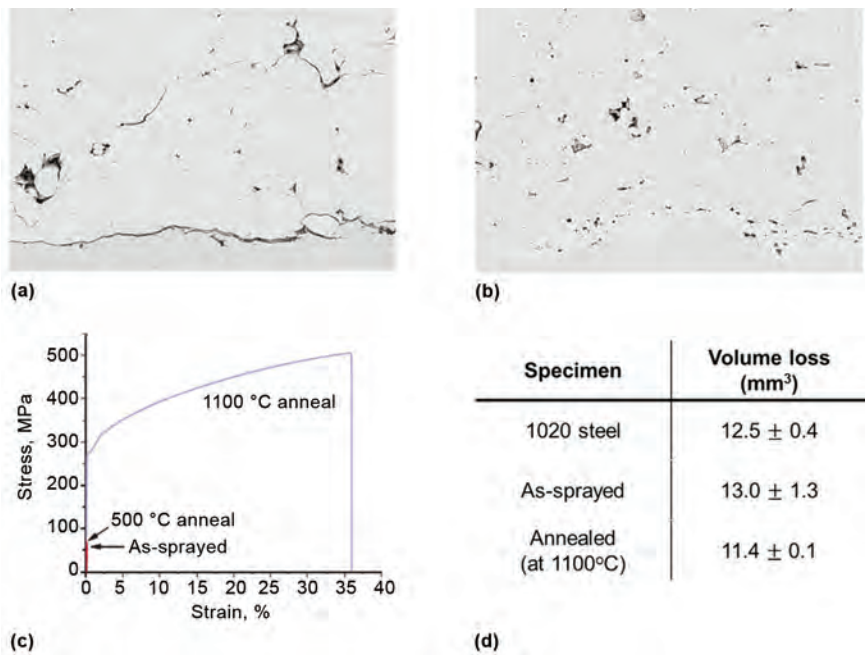


Fig. 8.13 Cross-sectional images of (a) as-sprayed and (b) heat treated 316L stainless steel coating layers. Results of their (c) tensile strength measurement and (d) wear test. Source: Ref 8.51

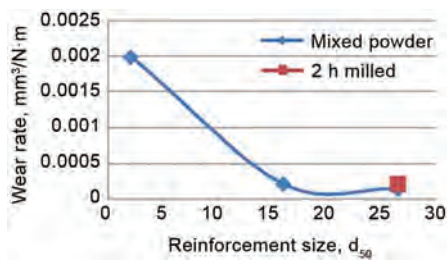


Fig. 8.14 Effect of ball-milled SiC particle size in prepared feedstock powders on the wear rate of cold-sprayed Al5056/SiC composite layer. Source: Ref 8.52

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CHAPTER 9

Cold Spray Applications in the Defense Industry

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HIGH-PRESSURE COLD SPRAY (HPCS) technology has undergone a tremendous technological evolution in the past ten years (Ref 9.1–9.3). New systems continue to be developed that operate at higher pressures and temperatures. The increased capabilities of these systems, combined with improvements in powder processing, have greatly increased the number of materials that can be deposited and the quality of those depositions. These improvements have greatly expanded the number of potential applications. High-pressure cold spraying has enjoyed a great deal of success in dimensional repair of magnesium and aluminum components for aerospace components (Ref 9.2, 9.4–9.6). Recent advancements have made it possible to repair other materials as well (Ref 9.7–9.9). Development efforts have resulted in high adhesion and tensile strengths and improved ductility, paving the way for structural repairs and additive manufacturing applications (Ref 9.4, 9.8, 9.10).

The applications presented here are for cold spray systems that have operating pressures greater than 2.4 MPa (350 psi) and operating temperatures greater than 500 °C (930 °F). Almost all of the high-pressure systems are designed to be used with a stationary robot. These systems typically have spray guns (nozzles and prechamber) that are too heavy to be held by hand. The maximum operating pressure for an HPCS system is 6.9 MPa (1000 psi) and the maximum operating temperature is 1200 °C (2190 °F). The higher gas pressure and temperatures make it possible to

deposit thick, dense layers of several different materials, such as aluminum and its alloys, copper, nickel, and tantalum.

The HPCS systems have been used to repair and restore a number of different components made from magnesium and aluminum alloys. Cast magnesium and aluminum alloys are used in aircraft components such as gear boxes and transmission housings because of their light weight, high strength-to-weight ratios, and lower manufacturing costs. The gear boxes and transmission housings suffer from corrosion, wear, and/or impact damage. When the damage reaches a critical level, the damaged components are removed from service and discarded or put in long-term storage. The cost for replacing these components is in the millions of dollars (Ref 9.11). The 2009 Sikorsky trade study reported an annual cost for H-60 main gearbox corrosion of \$10.8 million to the Navy and \$6.7 million to the Army, for a total of approximately \$17.5 million for 600 helicopters.

Conventional repair processes such as welding, plating, or patching with composite material often either impart additional damage to the component or are inadequate for permanent repairs. The high thermal input from a welding process results in unacceptable changes to the substrate material and can create large residual stresses. Vapor-deposition processes deposit thin layers of material, must be performed in a chamber, and are difficult to use on selected areas. High-temperature thermal spray processes can also create high residual stresses and can result in coatings with poor adhesion strength. The cold spray process, with its low deposition temperatures and high adhesion strengths, is an ideal method for repairing aluminum and magnesium alloys (Ref 9.4–9.6). Several examples of cold spray repairs are presented in this chapter, some of which are also described in the “Aerospace Industry” section of Chapter 11, “Cold Spray Applications in Repair and Refurbishment for the Aerospace, Oil and Gas, and Power-Generation Industries,” in this book.

9.1 Cold Spray Application Examples

Cast Magnesium Transmission and Gearbox Housings. Magnesium alloys have been developed that have good mechanical properties and low densities and can be cast into complex shapes. These alloys also have good machining characteristics. These characteristics make them ideal for use in weight-critical applications, especially in helicopters (Ref 9.4, 9.10, 9.12). A disadvantage of magnesium alloys is that they have a very high anodic index, which means they are electrochemically active and very susceptible to galvanic corrosion when coupled to another metal. The magnesium alloys used in transmission and gearbox housings have very poor resistance in wet, salt-laden environments (Ref 9.5, 9.12, 9.13). Care must be taken to apply coatings that isolate the magnesium alloys from other metals and to create an environmental barrier to prevent corrosion. Once the coating is damaged, corrosion is initiated and quickly propagates.

Magnesium alloy components are subject to severe corrosion, especially at flanges, sealing faces, and other occluded regions where moisture accumulates. An example is a helicopter transmission gearbox, which can undergo corrosion at mechanically critical joining flanges (Ref 9.13–9.15). Such occluded areas are likely locations for crevice corrosion. An example of the corrosion damage to the pads of a magnesium alloy gearbox is shown in Fig. 9.1. The water accumulates in the pad where the gearbox is mounted to the helicopter. Installing the mount bolts can damage the coating, or the coating may become damaged over time. The resulting corrosion leads to material loss.

In this example, the gearbox pads were repaired by applying a coating of commercially pure aluminum. The corrosion damage was removed from the surfaces and the surfaces were prepared for coating application. Several different aluminum alloy powders were available for the repairs. These included commercially pure aluminum (CP-Al), high-purity aluminum, Al-6061, Al-4047, and Al-5056 (Ref 9.4, 9.17, 9.18). For this repair CP-Al was selected. A coating was applied to the damaged areas and machined to the original dimensions (Fig. 9.2). Generally, the final thickness of the coating is typically greater than 0.4 mm (0.02 in.) to ensure a continuous environmental barrier. For repairs that require great hardness and high adhesion strength, Al-6061 is used, typically applied with helium as the main process gas.

The repair of magnesium gearbox housings for military helicopters is presented in detail by Champagne (Ref 9.4–9.6, 9.11). Groups from government, original equipment manufacturers, industry, and academia developed requirements for coatings and validation tests that must be performed to qualify cold spray repairs. The requirements and specifications were presented in the Materials Joint Test Protocol (JTP) (Ref 9.11, 9.14–9.16). The JTP comprises mechanical, physical, and chemical tests designed specifically for the repair of the magnesium transmission housings. The cold spray process is outlined in MIL-STD-3021, “Materials Deposition, Cold Spray,” which serves as the primary specification for industry as well as the Department of Defense. The aluminum powders used for cold spray are specified in MIL-DTL-32495, “Aluminum-Based Powders for Cold Spray Deposition.”

The critical areas and key parameters of the JTP cold spray process (that can also be used on a wide variety of applications) include:

- *Return on investment (ROI)*: Key factors in determining the ROI are the amount of money that the repair will save compared to the purchase of new components, the improvement in performance, the availability of new components, the number of damaged components that can be repaired, and the cost and time for completing the repairs.

- *Key performance parameters:* The minimum values for adhesion, hardness, and corrosion resistance are specified. In addition, the effects of the deposition on the tensile and fatigue strengths are determined.
- *Powder-selection process development:* Several powders are typically evaluated. The commercial availability; the particle size, size distribution, and morphology; and the compatibility are used to select the powders for evaluation.
- *Process parameter development:* Based on past experience and predictive modeling, initial process parameters are selected. The process parameters include the type, temperature, and pressure of the main process gas, the powder mass flow rate, and the powder characteristics.
- *Coating deposition:* The effects of surface preparation on adhesion strength and coating characteristics are determined. Methods include grit and bed blasting, sanding, and cleaning. Process parameters for each powder are developed, and test articles are produced.
- *Coating evaluation:* Characterization tests are performed to evaluate specific areas, including:
 - a. *Microstructure:* This is determined by sectioning and mounting the different coating/substrate systems and performing optical microscopy (OM), scanning electron microscopy, and hardness. Porosity is determined by OM. The coating/substrate is examined for embedded grit and adhesion characteristics.
 - b. *Adhesion strength:* Adhesion tests are performed following ASTM C633-13, “Standard Test Method for Adhesion or Cohesion of Thermal Spray Coatings.” Bend tests and triple-lug shear tests can also be performed to test coating quality.
 - c. *Tensile and fatigue strength:* Tensile tests are performed following ASTM E8, “Standard Test Methods for Tension Testing of Metallic Materials,” and fatigue tests are done by R.R. Moore testing.
 - d. *Corrosion resistance:* The corrosion tests include ASTM B117, “Salt Spray and Salt Fog Testing;” ASTM G85, “SO₂ Salt Fog Testing;” ASTM G5, “Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements;” ASTM G59, “Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Polarization Resistance Measurements;” and ASTM G78, “Standard Guide for Crevice Corrosion Testing.”
- *Process optimization:* The results of the coating characterization are used to select the powders for additional development. The process parameters are optimized for the selected powders, and the characterization process is repeated.

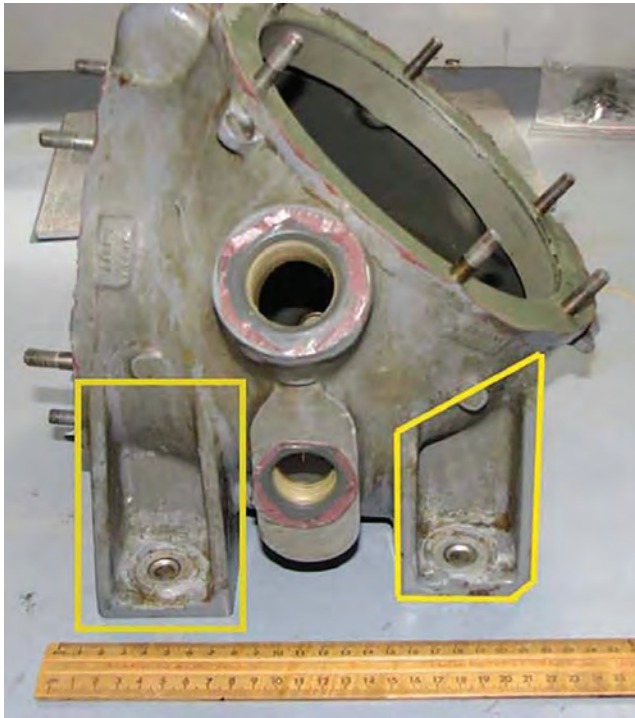


Fig. 9.1 Magnesium gear box housing showing damage to the pads. Courtesy of the Army Research Laboratory

- *Process procedure documentation:* A detailed process procedure that included the specification for equipment, powder, process parameters, and qualification test is developed.
- *Field and simulated environment testing:* Repaired components or representative hardware are tested in the actual operating environment or on test fixtures that represent operating conditions.
- *Process approval:* Test results and data, along with the process procedures, are presented to the groups responsible for approving the procedure.

Fretting Damage on an A357 Transmission Housing. Many gear boxes and transmission housings used on aircraft are made from A356 or A357. These aluminum-silicon alloys were developed as casting alloys (Ref 9.19). Their combination of strength, hardness, density, and ability to be cast into complex shapes makes them ideal for aerospace applications. During operation, the alloys can be damaged by wear, impact, and corrosion. For example, on a fighter jet aircraft, the surface of the mounting pad for a hydraulic pump on an externally mounted auxiliary transmission housing is subject to fretting, which occurs when two metal surfaces re-

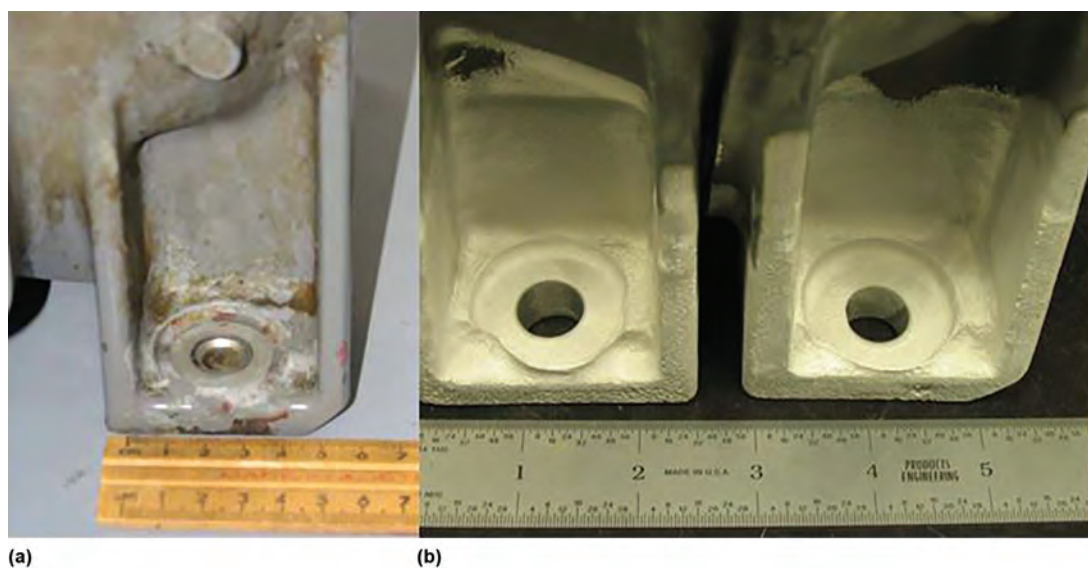


Fig. 9.2 (a) Damaged pad. (b) Pads coated with commercially pure aluminum. Courtesy of the Army Research Laboratory

peatedly contact each other and degrade through oxidation and mechanical wear (Ref 9.12, 9.20). The damage creates rough surfaces that can prevent proper sealing and can lead to cracking of the substrate material. A transmission housing with fretting damage to the hydraulic pad is shown in Fig. 9.3. Attempts to repair the damage with conventional thermal spray processes were unsuccessful: the thermal spray coatings suffered damage during the final machining process intended to create a smooth surface.

A cold spray process was then developed to repair the fretting damage to the hydraulic pump pad. The requirements for the repair were excellent adhesion strength, a hardness equal to or greater than the A357, a similar coefficient of thermal expansion (CTE), and good machinability. Several different commercially available alloys were considered. The two alloys that offered the best combination of properties were Al-4047 and Al-6061. The Al-4047 is an Al-12Si binary alloy with CTE and hardness similar to those of the A357 base alloy. The Al-6061 was selected for its high hardness and adhesion strength. The morphologies of the powders were imaged using a scanning electron microscope, and a particle size distribution analysis was performed. Both the Al-4047 and Al-6061 powders were spherical and had a mean particle diameter of 36 μm .

Small coupons of A357 were coated with Al-4047 and Al-6061 using helium and nitrogen (N_2) as the main process gas in an HPCS system. The surfaces of the coupons were bead-blasted prior to the application of the coatings. The coupons were examined for hardness and microstructure. Once the cold spray parameters were set, adhesion specimens were prepared and tested following ASTM C633 (Ref 9.21). Galvanic corrosion

was evaluated following ASTM G71-81. This gives an estimated material loss in millimeters per year. The Al-4047 coatings applied using nitrogen were 99.8% dense (0.2% porosity), with adhesion strength between 62 and 75 MPa (9 and 11 ksi) and hardness of 134 Vickers hardness number (VHN). The Al-4047 coatings applied using helium were 99.8% dense (0.2% porosity), with adhesion strength of 75 MPa and hardness of 122 VHN. The Al-6061 coatings applied using nitrogen were 99.8% dense (0.2% porosity), with adhesion strength of 62 and 75 MPa (9 and 11 ksi) and hardness of 117 VHN. The Al-6061/4047 coatings applied using helium were 99.8% dense (0.2% porosity), with adhesion strength of 75 MPa and hardness of 122 VHN. The process parameters and the results of the coating evaluation are summarized in Table 9.1. The failures during ASTM C633 were glue failures, indicating that the actual adhesion strength was higher than those reported in the table. The galvanic couplings were very small between the Al-4047 and the A357 and between the Al-6061 and the A357. The coatings were machined with an end mill to ensure that they had the required machining characteristics.

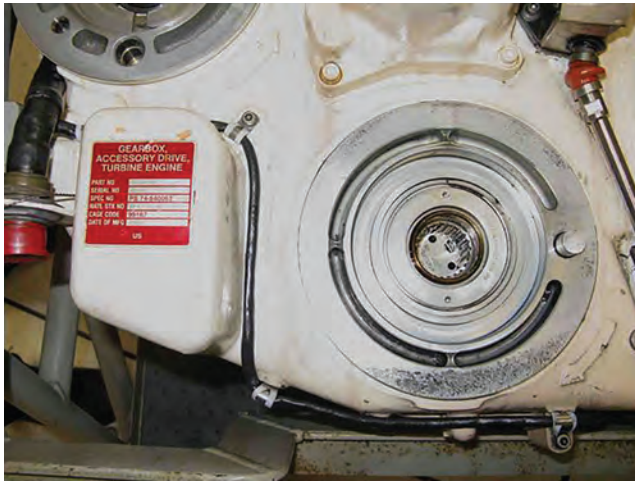


Fig. 9.3 Fretting damage on the hydraulic pump pad on an A357 cast aluminum transmission housing. Courtesy of the Applied Research Laboratory, The Pennsylvania State University

Table 9.1 Process parameters and test results for deposition of Al-4047 and Al-6061

Coating/substrate	Main process gas	Pressure		Temperature		Density, %	Hardness, VHN	Adhesion strength		Galvanic loss	
		MPa	psi	°C	°F			MPa	ksi	mm/yr	in./yr
Al-4047 on A357	N ₂	3.4	500	400	750	99.8	134	62–75	9–11	0.005	0.000
	He	2	290	400	750	99.9	122	75	11	0.009	0.000
Al-6061 on A357	N ₂	2.7	390	300	570	99.7	117	62–75	9–11	0.009	0.000
	He	4	580	400	750	99.8	122	75	11	...	...

Based on the results of the process parameter development and the testing, it was determined that the repair should be performed by applying Al-4047 using helium as the main process gas. The areas of the housing and the areas of the hydraulic pad that were not going to be coated were masked using a combination of metal and tape. The masked part is shown in Fig. 9.4. The metal masks must be designed to prevent the coating from bridging the gap between the area to be coated and the mask, so that the coating is not damaged when the mask is removed. The surface of the hydraulic pump pad that was to be coated was bead-blasted and cleaned. A coating of Al-4047 was applied using helium as the main process gas and using the parameters given in Table 9.1. The hydraulic pad with the Al-4047 coating is shown in Fig. 9.5. The coating was machined to the final dimensions, as shown in Fig. 9.6. The transmission housing was tested on an engine test stand to evaluate the coating, and the transmission housing was returned to service.

B-1 Forward Equipment Bay Panel. A common problem on military aircraft is wear due to chafing around fastener holes in skin panels. This chafing results in skin panels that exceed fit tolerances at the fastener locations. A B-1 bomber left upper aft forward equipment bay (FEB) panel suffered from chafing damage to the fastener holes that resulted in an out-of-tolerance fit for the panel. The FEB panel and its location on the B-1 are shown in Fig. 9.7 (Ref 9.22). The FEB panel is secured to the airframe with 100° tapered flat-head steel Tridair fasteners. The fasteners are designed to be installed flush with the panel for laminar airflow over the skin surface. The panel is removed during maintenance of the aircraft. The re-



Fig. 9.4 Hydraulic mounting pad on the A357 transmission housing. Courtesy of the Applied Research Laboratory, The Pennsylvania State University

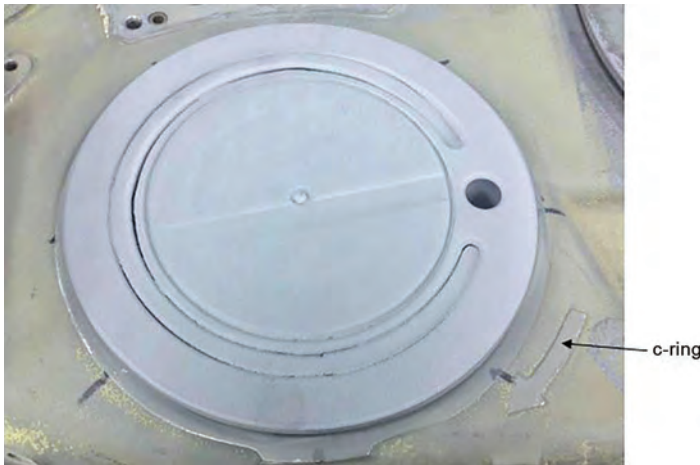


Fig. 9.5 Hydraulic pump pad in the as-sprayed condition showing the Al-4047 coating. Courtesy of the Applied Research Laboratory, The Pennsylvania State University

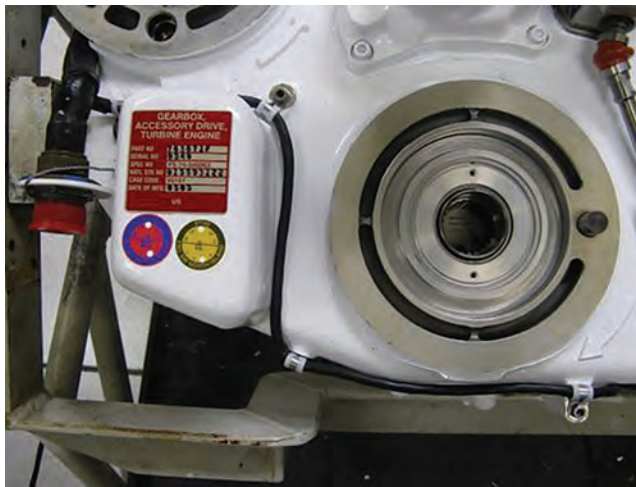


Fig. 9.6 Hydraulic pump pad after the high-pressure cold spray repair has been machined. The transmission has been assembled and is in the engine test stand. Courtesy of the Applied Research Laboratory, The Pennsylvania State University

peated removal and installation of the fasteners wears and elongates the holes in the panel. As the wear increases, the fasteners sit farther and farther below the panel surface, resulting in turbulent flow over the panel, vibration of the panel, and eventually pull-through and loss of the fastener during flight. The panels cost as much as \$225,000 and have a long lead time for replacement.

The FEB panel is an internally stiffened, bonded composite-metal hybrid structure. The skin is Al-2024-T6. To prevent damage to the hybrid

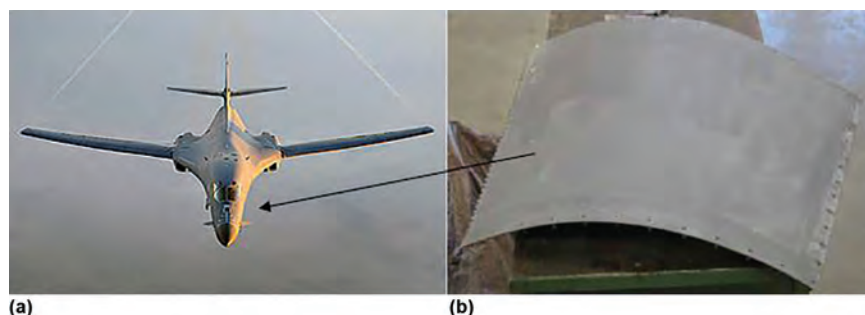


Fig. 9.7 (a) B-1B bomber. Source: Ref 9.22. (b) Forward equipment bay panel. The arrow indicates the location of the panel on the aircraft. Courtesy of South Dakota School of Mines and Technology

composite structure, the temperature of the panel must not exceed 100 °C (210 °F) during repair. Prior to cold spray, there was no approved method to repair the damage to the Al-2024-T6 skin. Because of the low-temperature input, cold spray was selected as a possible repair process (Ref 9.23). Typical damage to the fastener holes is shown in Fig. 9.8.

The development of the process began by selecting powders and developing process parameters on laboratory-scale specimens and test coupons. The powder that was selected for development was Al-6061 –325 mesh + 10 µm from Valimet (Ref 9.22). The powders were applied using a hand-held cold spray system developed at the U.S. Army Research Laboratory. Helium was the main process gas, and the powders were applied using a pressure of 2.4 MPa (350 psi) and a temperature of 350 °C (660 °F). Several tests were performed to validate the process before the FEB panels were repaired. The microstructures of the cold-sprayed Al-6061 on Al-2024-T6 substrates were examined using optical microscopy. A triple-lug shear test was performed to measure the shear strength of the cold-sprayed interface. Test articles were prepared that had damage similar to that in the FEB panels. The damaged areas were repaired and fasteners were installed following the specifications used for installation on the B-1B. These specimens were tested in a guided lap-shear test to demonstrate that the repaired area would support the full loads that the fasteners encounter in service. Fatigue tests were performed on the Al-6061 cold-sprayed specimens to demonstrate that the repaired panels would have a useful service life after repair. After completion of the test coupon and subscale test articles, the FEB panels were repaired. A damage section of the panel with the HPCS coating is shown in Fig. 9.9. The temperature of the panel was monitored during the repair process and was well below the 100 °C maximum allowable temperature. A grinding process was used to restore the outer mold line profile of the external skin surface and to remove excess cold spray material to achieve the required thickness. After grinding, the area was polished with fine abrasive discs. A microstop tool was used

to cut the proper chamfer. The cold-spray-repaired and machined fastener hole is shown in Fig. 9.10.

The final steps in the repair process are to precoat the surface, apply a primer, and then apply the top coat. A repaired panel is shown in Fig. 9.11.

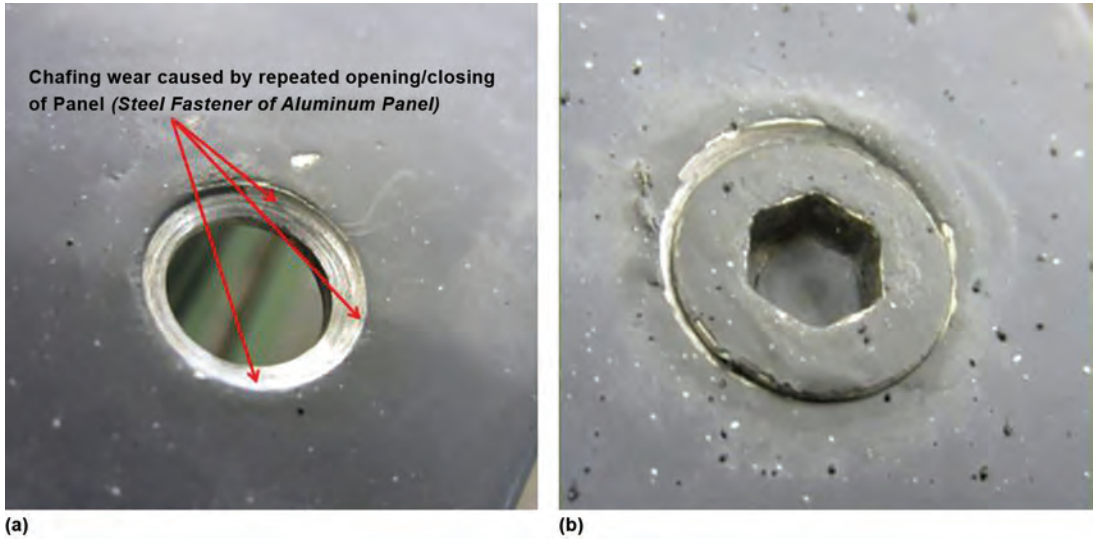


Fig. 9.8 (a) Wear damage to the fastener holes in the panel. (b) Installed fastener that is below the panel surface. The uneven surface generates undesirable turbulent flow. Courtesy of South Dakota School of Mines and Technology

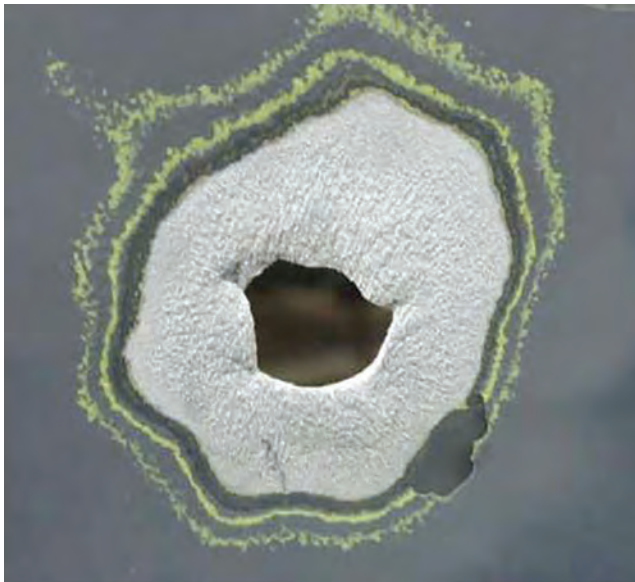


Fig. 9.9 Fastener hole in a forward equipment bay panel with a high-pressure cold-sprayed coating. Courtesy of South Dakota School of Mines and Technology

This repair demonstrated the ability of HPCS to restore the panel to full form, fit, and function. The repaired panel has been in service since August 2012. The repair process was documented, and an improved cold spray process specification for a wide range of repair applications is under development for future repairs.

TD-63 Hydraulic Actuator Body. The internal bore of an Al-6061-T6 hydraulic actuator body suffered from both exfoliation and pitting corrosion damage that resulted from exposure to seawater. The corrosion damage, shown in Fig. 9.12, led to a loss of material that prevented the actuator from working correctly. The actuator bodies have a long lead time, making a viable repair process essential. Traditional repair processes, such as tungsten inert gas welding, metal inert gas welding, and laser cladding, were possible repair options. These methods are able to produce strengths and porosities that would meet or exceed the repair requirements for the aluminum actuator in coupon test samples (Ref 9.24). However, limited space, tight tolerances, and finished part features in the bore precluded the use of these techniques. The diameter of the bore is less than 100 mm (4 in.). After reviewing the dimensions and the repair requirements, it was decided that cold spray was a viable repair option.

This challenging repair required development of spray parameters for applying coatings at a 45° deposition angle and manipulation of the actuator body during deposition to produce the coatings with the desired properties. The coating selected for the repair was the commercially available



Fig. 9.10 High-pressure cold-spray-repaired and machined fastener hole in a forward equipment bay panel. Courtesy of South Dakota School of Mines and Technology



Fig. 9.11 Fully repaired forward equipment bay panel ready to be put back into service. Courtesy of South Dakota School of Mines and Technology

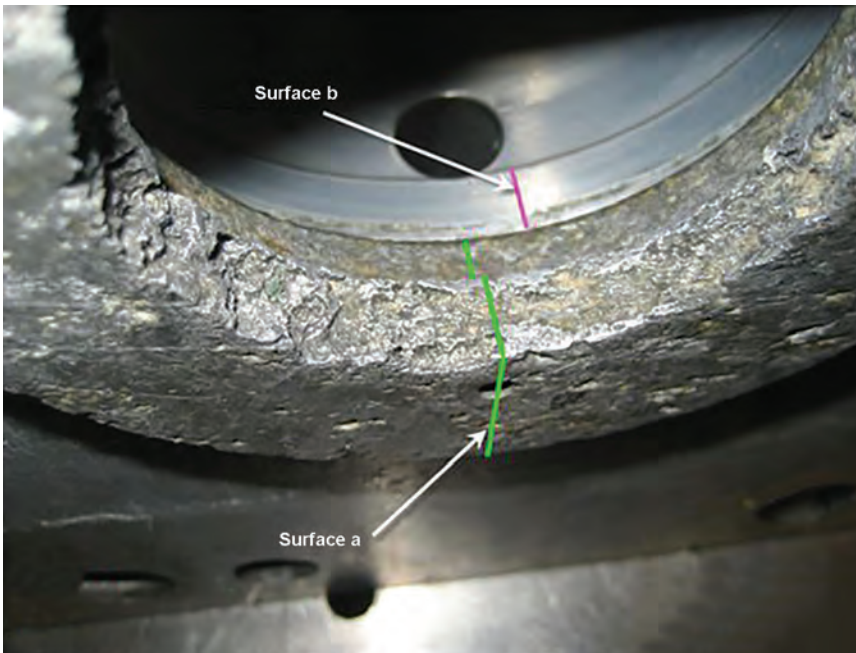


Fig. 9.12 Seawater corrosion damage on the outboard portion (a) and sealing surfaces (b) on the valve actuator internal bore. Courtesy of Puget Sound Naval Ship Yard

Al-6061 supplied by Valimet (Stockton, CA). The -325 -mesh Al-6061 powder was gas atomized. Helium was used as the main process gas to achieve high impact velocities between incident particles. The pressure and temperature of helium were maintained at 3.45 MPa (500 psi) and 500

°C (930 °F), respectively. The nozzle stand-off distance was 20 mm (0.8 in.), the angle of deposition was 45°, the powder feed rate was approximately 10 g/min (0.35 oz/min), and the nozzle traveling speed was 250 mm/s (10 in./s) (Ref 9.23). Finally, total deposition thicknesses ranged from 2 to 8 mm (0.08 to 0.3 in.). A picture of the setup is shown in Fig. 9.13.

The process parameters were developed on test coupons and on a test article or mockup that had the geometry and dimensions of the actuator body. The tests that had to be complete before the actuator body could be repaired were porosity, adhesion, and tensile strength. The cold spray coating had to be deposited at the same angle as would be used in the repair of the actuator body. Because of the stringent performance requirements, minimum coating properties had to be demonstrated before the repair of the aluminum actuator would be authorized.

The levels of porosity and bonding between the powder particles and the substrate were examined using optical microscopy and Buehler Omnimet software. After the process parameters were developed to produce the desired microstructures, adhesion and tensile tests were performed. The adhesion testing followed ASTM C633, “Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings,” and the tensile tests followed ASTM E8, “Metal Tensile Strength Testing.”

The results of the ASTM C633 tests showed that the average adhesion strength was 71 MPa (10 ksi). All the failures were glue failures. Tensile testing was the second requirement for approval to repair the aluminum actuator. For the tensile testing, a solid block of Al-6061 was produced using the same incident angle between the cold spray gun and the substrate as would be used during deposition on the critical surfaces. A set of

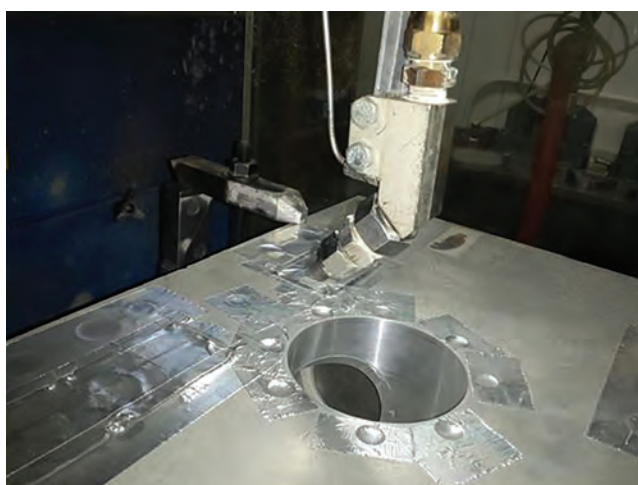


Fig. 9.13 Experimental setup for repair of the actuator valve body. Courtesy of South Dakota School of Mines and Technology

four reduced-sized ASTM E8 tensile specimens were removed using wire electrical discharge machining. Tensile specimens were tested in two different groups. The average tensile strength and elongation for the two groups were 199 MPa (28.9 ksi) and 1.92% and 203 MPa (29.4 ksi) and 2.01%. These results showed that the strength of the cold-sprayed material far exceeded the minimum requirement of 71 MPa (10 ksi) for ASTM C633 bond strength. However, there were no minimum tensile values in the qualification requirements.

The results of the porosity, adhesion, and tensile testing demonstrated that the cold spray process could produce deposits that met the required performance parameters. The next step in the development process was to perform the repair on the mockup. A mockup and a cross section of a mockup showing the internal surfaces of the bore are shown in Fig. 9.14. The maximum allowable porosity in the deposited material was 5%. The porosity in the deposited materials in the initial mockup exceeded the allowable acceptable porosity. The approach angle and speed had to be adjusted to minimize the porosity and defects in the inside bottom corner of the internal bore. A second mockup was repaired and sectioned to examine the porosity. Optical porosity measurements were performed on the final mockup cold spray repair. Measurements were made using an area fraction analysis with Buehler Omnimet software. The cold-spray-deposited material had an average of 3% porosity based on a total of 14 measurements. This result compares well with previously reported results, which produced cold spray coatings of Al-6061 using high pressure in the range of 2 to 3% porosity (Ref 9.11).

The process parameters developed for repairing the actuator were then used to repair the hydraulic actuator body. A stringent process control document was prepared and followed to ensure that the repair process was implemented correctly. The actuator body was prepared for repair by re-

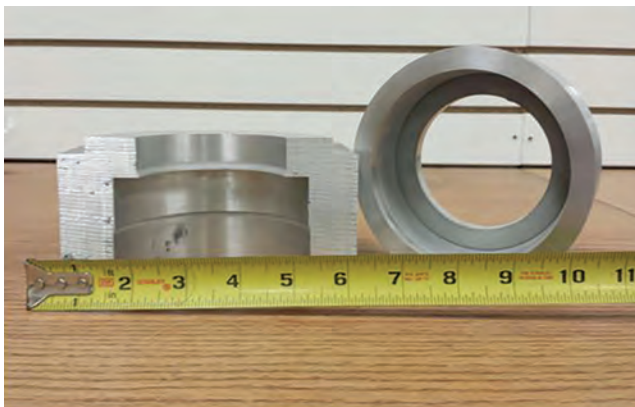


Fig. 9.14 Cross section of a repaired mockup showing the microstructure. Courtesy of South Dakota School of Mines and Technology

moving the corrosion damage and adding a small radius to the bottom surface of the internal bore. The machined actuator body is shown in Fig. 9.15. The actuator body with the cold spray deposition prior to final machining is shown in Fig. 9.16. Test articles were sprayed at the time the actuator was repaired, using the same process parameters. The porosity, adhesion, and tensile tests were performed on the test articles to ensure that the property requirements were met or exceeded. The average porosity in the final mockup was less than 1%.

A photograph of the final machined actuator internal bore is shown in Fig. 9.17. After machining, the valve body was functionally tested, and the repaired actuator was cleared for installation.

This repair demonstrated the ability of the cold spray process to repair the complex geometry of a component with a relatively deep small-diameter bore. In addition to the standard process parameters such as gas pres-

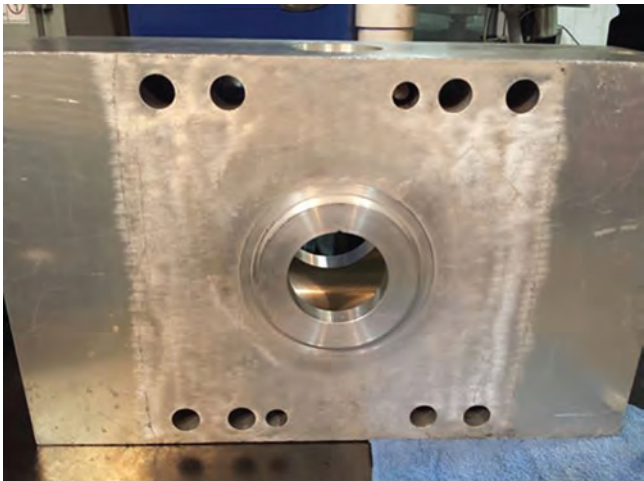


Fig. 9.15 Hydraulic actuator body that has been machined and is ready for high-pressure cold spray repair. Courtesy of South Dakota School of Mines and Technology

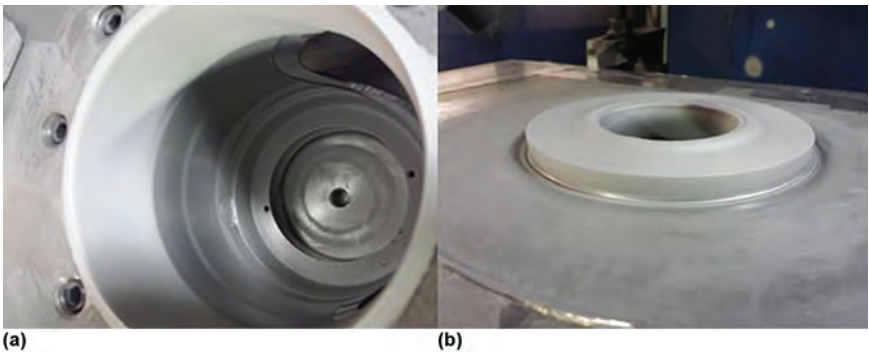


Fig. 9.16 (a) Inner bore and (b) top surface of the bore after deposition and prior to final machining. Courtesy of South Dakota School of Mines and Technology

sure and temperature, stand-off distance, and nozzle traverse rate, other parameters such as approach angle and speed had to be optimized to produce depositions with high adhesion strength and low porosity. The repair process development has shown the potential for even more challenging future applications because the strength of the cold-spray-deposited material was found to be in excess of 200 MPa (30 ksi) as deposited.

Al-2024 and Al-7075 Aircraft Components. Because of their high strength-to-weight ratios, Al-2024 and Al-7075 aluminum alloys are commonly used in aerospace applications (Ref 9.18, 9.25). These alloys are typically heat treated to obtain the desired combination of strength, ductility, and corrosion resistance. Exposure to high temperatures during conventional repair processes such as welding or cladding can change the temper and result in decreased mechanical properties. Extensive repair may require that the component be heat treated again, which can cause other problems. The low heat input from the cold spray process makes it possible to repair tempered aluminum alloys without adversely changing the properties.

B-1 Nose Landing Gear False Axle. The nose landing gear false axle attaches complete wheel assemblies to the main landing gear axle, essentially creating a quick-change tire. The component has two locations where bearings ride. As the airframe undergoes extended service, the bearings wear away the false axle to a point at which it must be replaced. The worn areas of the false axle are shown in Fig. 9.18. The axle is made of Al-2024. To increase the wear performance of the component, nickel-blended powders were selected as the candidate materials for deposition. Coatings of the candidate powders were deposited on Al-2024 samples measuring 25.4 by 76.2 by 3.12 mm (1 by 3 by 0.125 in.). The microstructure, hardness,



Fig. 9.17 Final machining performed on the repaired actuator. Courtesy of Puget Sound Naval Ship Yard

and adhesion strength of the deposited materials were evaluated. A design of experiments was developed to optimize the process parameters and to select the powder that would be used in the repair of the false axle on the B-1.

Pure nickel powder was selected because of its excellent deposition characteristics, specifically the work hardening that occurs during deposition and machinability (Ref 9.7, 9.8). It has been shown that the hardness of nickel deposited by cold spray can be up to 60% higher than conventionally cold-worked nickel. The hardness values of pure nickel in the wrought (annealed), wrought (fully), and wrought (cold-sprayed) conditions are 100, 245, and 375 VHN (Ref 9.26). Al-2024 has a VHN of 137 (Ref 9.19). A 1 mm (0.04 in.) thick layer of nickel was applied to two areas of the false axle. The coating was machined to a thickness of 0.64 mm (0.03 in.). A false axle with the nickel deposits is shown in Fig. 9.19.

LAU-128 Missile Rail. The LAU-128 is a guided missile launcher commonly used on fighter aircraft; it mounts to a standard rail launcher. The launchers are attached to each of the aircraft underwing pylons, carrying one payload per rail. The aircraft carries the missiles throughout take-off and flight; during landing it also carries any missiles that have not been used during the flight. Vibration and loading during takeoff and especially landing subject the rail tracks to chafing and wear. The primary location at which the rail tracks wear is where the missile is locked in place on the rail guides, as shown in Fig. 9.20.

A series of cold spray samples were made with Valimet –325-mesh Al-7075 powder using 3.5 MPa (500 psi) nitrogen at 500 °C (930 °F) to set the process parameters and develop the methods for performing the repair. The experimental setup is shown in Fig. 9.21. The nozzle was 75 mm (3 in.) long, with a 1.5 mm (0.06 in.) throat and a 2.25 expansion ratio. This part had the added complication that the repair zone was not easily acces-

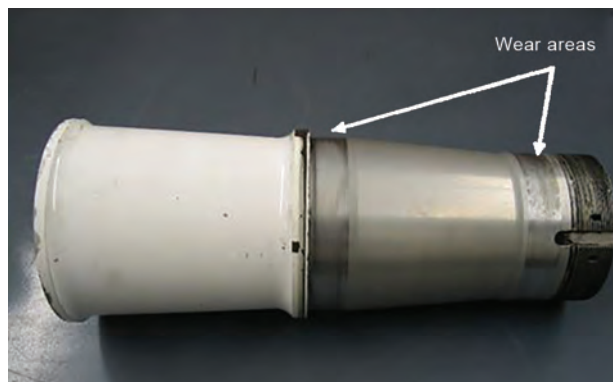


Fig. 9.18 B-1 nose landing gear false axle showing the wear damage that occurs during operation. Courtesy of South Dakota School of Mines and Technology

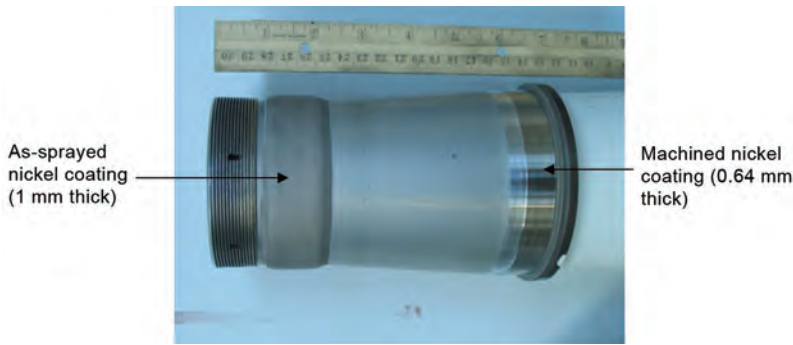


Fig. 9.19 High-pressure cold-spray-repaired false axle showing both as-deposited and machined state. Courtesy of South Dakota School of Mines and Technology

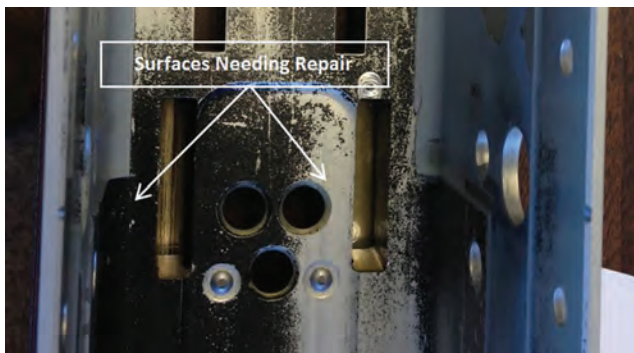


Fig. 9.20 Repair locations on the missile rail. Courtesy of South Dakota School of Mines and Technology

sible for a line-of-sight repair, which necessitated using a long working distance. The stand-off distance was over 30 mm (1.2 in.) in order to spray through a slot in the part to the wear surface on the rail below. The resulting shear strength of 46 MPa (6.7 ksi) and an adhesion/cohesion strength of 55 MPa (8 ksi) were obtained in the HPCS layer for this application.

A photograph of the repair area on the rail launcher in the as-sprayed condition is shown in Fig. 9.22. After deposition, the rail launcher is machined to the original dimensions.

Aging Aircraft Hinge Fitting. Hinge fittings used on the cargo bay door of a military transport aircraft are made from Al-7075-T6. The cargo bay door is shown in Fig. 9.23 (Ref 9.27). These hinge fittings suffer from wear and corrosion damage during operation of the bay door and during flight. The process of removing and repairing the damaged hinge fittings requires over 100 man-hours. A cold spray process was developed for depositing Al-7075 powder to repair the damage to the hinge fittings without

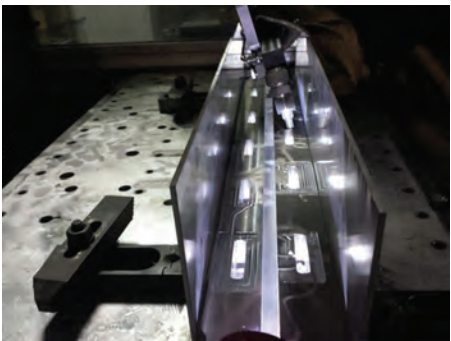


Fig. 9.21 Experimental setup for developing and validating the missile rail repair. Courtesy of South Dakota School of Mines and Technology



Fig. 9.22 Slot in Al-7075 missile rail in the as-sprayed condition. Courtesy of South Dakota School of Mines and Technology

removing them from the aircraft. The damaged hinge fittings are shown in Fig. 9.24. The light-colored areas are the areas that can be repaired by cold spray.

B-1B Chafing. A major emphasis in the Department of Defense (DoD), Federal Aviation Administration (FAA), and National Aeronautics and Space Administration (NASA) is to extend the useful life of aircraft that are currently in service. Repair processes are needed to address maintenance issues and repair damaged parts. Chafing of hydraulic tubing is a chronic problem on nearly all U.S. Air Force, Army, and Navy aircraft and results in significant cost in maintenance man-hours and reduction in operational readiness rates. Chafing of titanium hydraulic lines is one of the most significant and chronic maintenance problems on the B-1 aircraft.



Fig. 9.23 Cargo bay door where the hinge fittings are located. Source: Ref 9.27



Fig. 9.24 Hinge fittings made from Al-7075-T6 that can be repaired without being removed from the aircraft. Courtesy of South Dakota School of Mines and Technology

The titanium tubes are difficult to cut and bend into the configuration needed for each individual aircraft. Failures in the tubing cause cavitation in the hydraulic system, which can lead to failures in other components. The repairs are difficult to perform when the aircraft is deployed or stationed in remote locations. A hydraulic tube and the location of the chafing are shown in Fig. 9.25.

A cold spray repair was developed to repair tubing with chafing damage and to apply additional coating to mitigate the chafing on new tubing. The process can be performed during programmed depot maintenance or dur-

ing the processes to prevent or reduce occurrences of hydraulic tube chafing in the field.

Two different commercially pure titanium (CP-Ti) powders were selected for evaluation. The first powder was supplied by AP&C (Albany, OR), and the second powder was supplied by Accushape (Quebec, Canada). Both powders were deposited using helium as the main process gas at a temperature of 500 °C (930 °F) and a pressure of between 2.8 and 3.4 MPa (400 and 500 psi). The powders and the carrier gas were heated to temperatures ranging from 200 to 500 °C (390 to 930 °F) prior to entering the nozzle. Using these parameters, deposits were produced that had densities greater than 99.0% of theoretical density, hardness between 211 and 225 VHN, and adhesion strengths greater than 70 MPa (10 ksi). The hardness of the deposited CP-Ti was twice the hardness of the tubing. Figure 9.26 shows the application of CP-Ti on a section of Haynes AMS 4994 (Ti-3Al-2.5V) hydraulic tubing.

A section of tubing with the CP-Ti deposit that was installed on an aircraft is shown in Fig. 9.27. The tubing with the deposition in the as-sprayed condition is shown in Fig. 9.27(a). The tubing in Fig. 9.27(b) shows the deposition after the surface has been finished. This application demonstrated the ability of cold spray to produce high-quality CP-Ti depositions.

Several sections of hydraulic tubing have been repaired and have been flying on the B-1B for the past two years. The cold spray process provided a fast, economic repair to a critical problem that results in millions of dollars of savings.

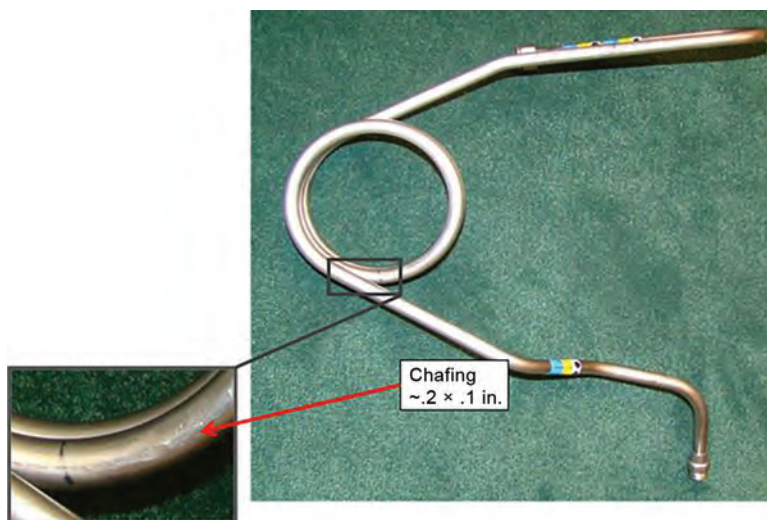


Fig. 9.25 Example of hydraulic tube chafing from the landing gear line on the U.S. Air Force B-1B. Courtesy of South Dakota School of Mines and Technology



Fig. 9.26 Application of commercially pure titanium on 9.5 mm (0.4 in.) Haynes AMS 4944 (Ti-3Al-2.5V) hydraulic tubing. Courtesy of South Dakota School of Mines and Technology

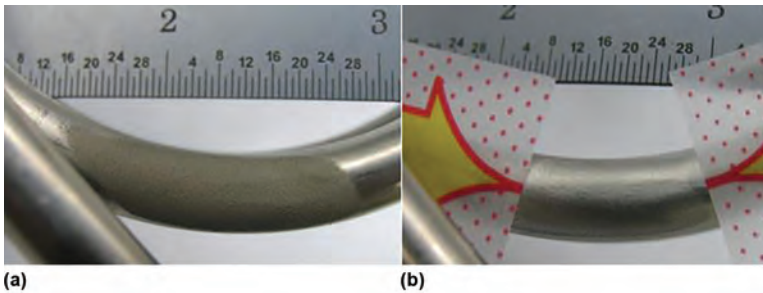


Fig. 9.27 Hydraulic tubing with commercially pure titanium powder deposited to prevent chafing. (a) Tube in the as-sprayed condition. (b) Same area after a surface finish. Courtesy of South Dakota School of Mines and Technology

9.2 Summary

The HPCS repair process has been used on a number of different applications in the defense industry. Several repairs have been developed for aluminum and magnesium alloys. New repairs are being developed for higher-strength materials such as steel, nickel-base superalloys, and brass/bronze alloys. There is also an effort to develop additive manufacturing applications that can be used to exploit the unique properties of HPCS.

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CHAPTER 10

Application of Copper Coatings onto Used-Fuel Canisters for the Canadian Nuclear Industry

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National Research Council, Canada
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THE NUCLEAR WASTE MANAGEMENT ORGANIZATION (NWMO) was established in 2002 under the Nuclear Fuel Waste Act to investigate approaches for managing Canada's used nuclear fuel. Currently, nuclear power plants are operating or undergoing decommissioning in Ontario, Quebec, and New Brunswick. Canada's CANDU (CANada Deuterium Uranium) reactors generate used fuel with small amounts of fissile nuclides compared to other types of nuclear reactors, due to the use of unenriched uranium as a fuel source; used nuclear fuel is currently planned for disposal without reuse/reprocessing. The present approach, shown in Fig. 10.1, envisions the long-term storage of radioactive fuel bundles in specially designed canisters. The canisters would be emplaced in the rock of a suitable geological formation at a minimum depth of 500 m (1650 ft) for an intended lifespan of more than 100,000 years (i.e., indefinite storage). The Canadian spent-fuel canister consists of an inner

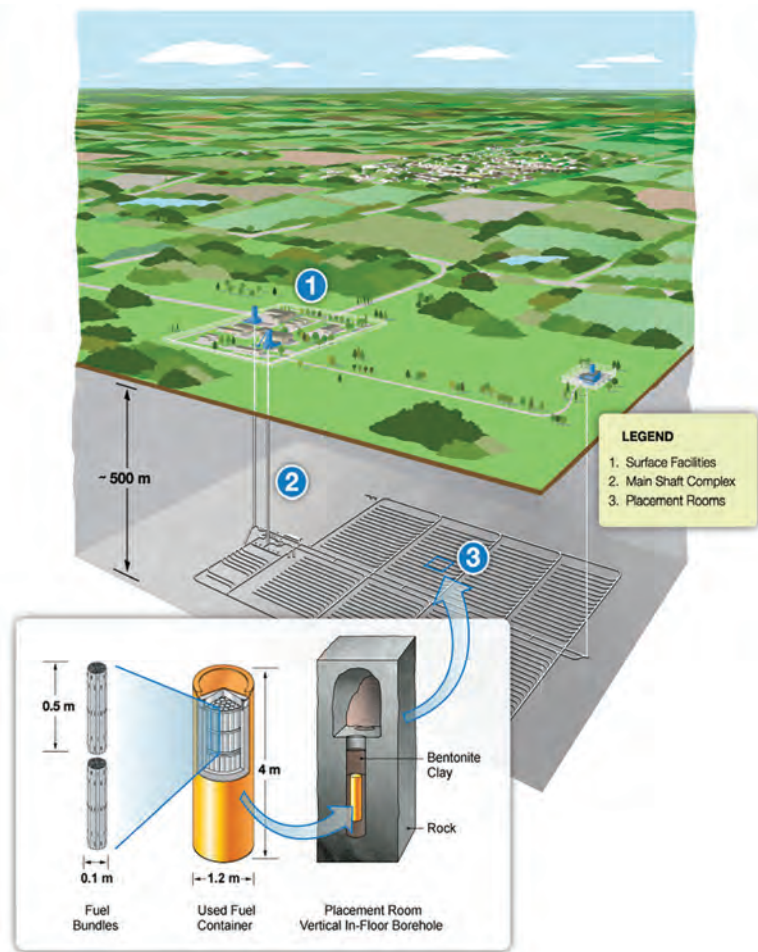


Fig. 10.1 Deep geological repository concept

container of steel strong enough to withstand geological pressures, including glaciation, and an outer shell of copper for corrosion resistance.

One reference container (1.2 m in diameter by 4 m in length, or 4 by 13 ft) features a copper shell that is up to 50 mm (2 in.) thick; this is predominantly a manufacturing necessity rather than a performance requirement. For corrosion purposes, a much thinner layer of copper is required; a 100,000 year container life can be achieved with less than 0.4 mm (0.016 in.) of copper. Under low-salinity groundwater conditions, the corrosion allowance is 0.27 mm (0.01 in.) (fixed) for oxygen-related corrosion and 0.1 nm/year for sulfide corrosion (Ref 10.1). However, the use of conven-

tional pierce/draw or extrusion methodologies to fabricate large copper shells from the extremely large copper ingots requires parts to retain significant strength to avoid collapse during manufacturing; this leads to large thickness dimensions. As a further manufacturing challenge, the requirement of a 1 mm (0.04 in.) nominal gap between the copper shell and inner steel container for assembly of the two-piece container must also be met; this requirement is due to copper creep considerations. If the gap is too large, creep occurring under geological load can induce fracture of the copper; phosphorus doping helps to minimize creep-related fracture (Ref 10.2). As an alternative, copper coatings directly deposited onto the steel canister offer the opportunity to produce a gap-free corrosion barrier, with no structural requirements. Copper cold spray is a promising methodology to provide sufficient corrosion protection to the steel canister while avoiding the handling and manufacturing issues associated with the wrought copper shell of the reference design described previously.

Copper is one of the most common cold-sprayed materials, and an extensive knowledge base on myriad aspects is available in the literature. Indeed, early developmental work into cold spray technology by a number of researchers was performed using copper (Ref 10.3–10.8). The effects of various spray parameters were recently reviewed by Assadi et al. (Ref 10.9) in their development of parameter selection maps for cold spraying, which show the relative influence, and relatively wide-ranging possibilities, of gas temperature and gas pressure for copper cold spray. The characterization of microstructures and mechanical properties for copper coatings has shown that bulk-equivalent material can be obtained, provided appropriate spray conditions and postspray heat treatments are employed (Ref 10.10–10.12). Initial feasibility work for the specific application of cold spray copper on used-fuel canisters has also been performed on small-dimension samples by researchers at the Korea Atomic Energy Research Institute (Ref 10.13–10.15).

As part of a larger program investigating concepts of copper coatings, NWMO has recently begun exploring copper cold spray in collaboration with the National Research Council (NRC). Within the coating program, a large variety of copper coating sizes have been investigated, from small corrosion coupons to full-scale used-fuel containers/canisters (UFCs). Electrodeposition and various weld claddings are also coating technologies of interest; corrosion and mechanical performance programs are designed to support the use of copper coatings for UFCs. While it suffers from relatively small industrial usage in comparison to the electrodeposition and cladding options, the versatility of cold spray has led NWMO to select it as a primary candidate for UFC coating; the extensive research and development (R&D) of the method are summarized as follows. Although the summary is comprehensive to date, the NWMO and NRC recognize that extensive validation work will be required prior to implementation of cold spray coatings for UFCs.

10.1 Methodology

The preliminary development methodology consisted of four general stages: powder selection, general coating development, UFC coating optimization, and prototyping activities. Future activities will include an extensive validation study of the resultant methodology within a series of settings, including the R&D environment, a pilot-scale plant, and eventually a manufacturing plant, prior to the final selection of cold spray process inputs. During powder selection, a range of commercial powders were screened via powder and as-sprayed coating properties to determine two likely candidates. The two most promising powders were then employed for general coating development to obtain an initial reference set of spray parameters and annealing conditions. In the third stage, reference parameters were optimized for UFC-specific materials and geometry. The prototyping stage involved final process adjustments and the production of mock-up assemblies in the R&D setting.

Photos of the various types of spray setups, with fixtures for smaller flat test substrates and larger spherical/cylindrical mock-up assemblies, employed in the different development stages are shown in Fig. 10.2. The cold spray systems employed at various stages in the development process included the Kinetiks 4000 (CGT Technologies, Germany) and the PCS-

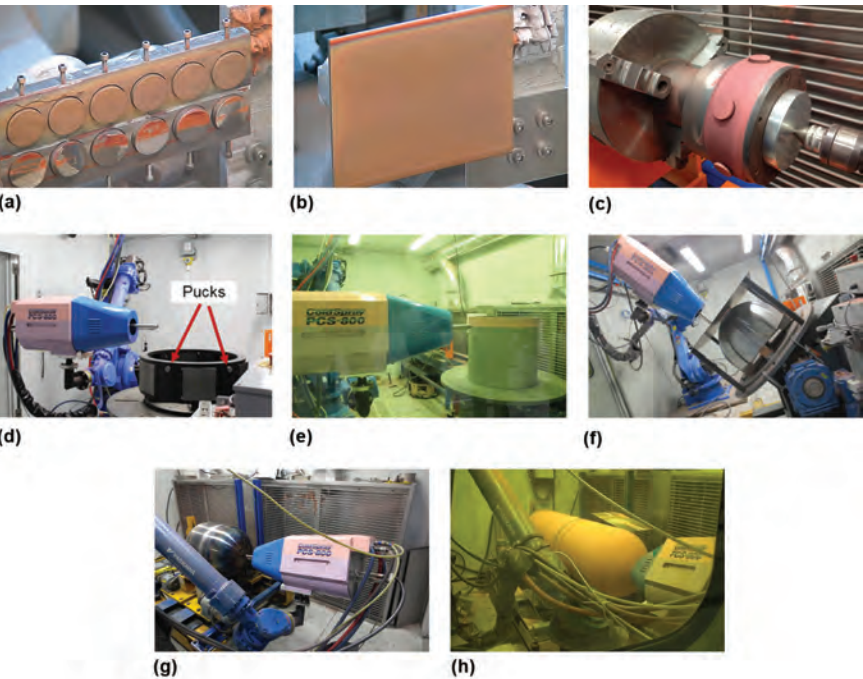


Fig. 10.2 Coating setups for (a and b) general coating development, (c and d) used-fuel container coating optimization, and (e–h) prototyping

800 and PCS-1000 (Plasma Giken Co., Ltd., Toshima-ku, Tokyo), using helium and/or nitrogen as the accelerating gas. Heat treatments were performed using a tube furnace with an argon atmosphere. A wide range of characterization methods was employed, including, among others, powder size as measured by laser diffraction; powder flowability by Metal Powder Industries Federation standard 03; chemical analysis by inert gas fusion; particle velocity by time-of-flight optical particle diagnostics (cold spray meter); Vickers microhardness; surface roughness by stylus profilometer; surface topography by confocal microscopy; porosity measurement by image analysis; bond strength by ASTM C633 (Ref 10.16) and/or modified ASTM E8; tensile testing by ASTM E8 (Ref 10.17); bend testing by ASTM E290 (Ref 10.18); and microstructural analysis by scanning electron microscopy (SEM) and/or optical microscopy.

10.2 Powder Selection

Initial Screening via Powder Properties. For initial screening, eight commercially available copper powders were selected and acquired from five different suppliers. Powders are referred to hereafter by powder size (d_{50} value) and/or supplier (suppliers 1 to 5), where appropriate. Initial screening of the powders was performed through a characterization of the powder composition as well as powder size, morphology, and flowability. In general, the ideal powder size distribution features average and maximum sizes as small as reasonably possible, because of the mass dependence of particle speed, and a minimum size greater than 8 μm , which is the critical particle diameter required for adiabatic shear instability with copper particles (Ref 10.19). Unimodal particle size distributions are also favored because they tend to produce more homogeneous coatings. The flowability, which can be affected by powder size and morphology, is a practical consideration in powder feeding.

Table 10.1 compares the chemical composition of the various feedstock powders with C10100 specifications. The C10100 reference was initially established by the NWMO because it is one material that is extensively used in corrosion testing for its high purity of copper (>99.99%). A second reference copper within NWMO and other nuclear waste organizational work is oxygen-free phosphorus-doped copper, a form of copper with similar corrosion properties in deep geological repositories but with improved creep ductility properties due to the 30 to 100 ppm phosphorus doping (Ref 10.20). All feedstock powders exceeded the allowable phosphorus level for C10100; this was not deemed to be detrimental to the subsequent corrosion test program. Most powders also exceeded C10100 limits for tin, iron, and zinc, while excess silver, bismuth, manganese, nickel, lead, antimony, and selenium were found in some; this may indicate a need for emphasizing powder procurement or manufacturing in future NWMO programs, should highly pure coatings be desirable. Overall,

Table 10.1 Selected characterization data for feedstock powders

Supplier	Powder (d_{50}), μm	Chemical analysis							Powder size distribution			Flowability, s/50 g
		Cu, %	O, %	Ag, ppm	S, ppm	Fe, ppm	Ni, ppm	Other(a), ppm	d_{10} , μm	d_{50} , μm	d_{90} , μm	
1	20	99.89	0.08	18	12	28	5	5P, 5Sn, 29Zn	9	20	34	5.2(b)
	42	99.92	0.054	27	11	3	7	4P, 2.2Sn	17	42	62	10.7
2	23	99.85	0.107	21	11	3	2	212P	14	23	35	22.4
	29	99.83	0.113	11	12	71	11	198P, 92Sn, 12Zn, 20Bi, 4Mn	12	29	52	5.4(b)
3	26	99.84	0.106	54	11	25	93	51Pb, 75Sb, 29P, 198Sn, 20Zn, 4Se	12	26	36	33.2
	49	99.86	0.022	54	11	22	46	49Pb, 11Sb, 26P, 8Se, 810Sn, 12Zn, 1.6Bi	37	49	70	12.2
4	N/A	N/A	1.13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Failed
5	31	N/A	0.211	N/A	N/A	N/A	N/A	N/A	14	31	43	11.9
C10100(c)	...	99.99	0.005	25	15	10	10	4Pb, 4Sb, 3P, 3Se, 1Sn, 1Zn, 1Bi, 0.5Mn	N/A	N/A	N/A	N/A

N/A, not applicable. (a) Only nonconforming values to C10100 listed for powders; maximum values for C10100. (b) No flow through Metal Powder Industries Federation 3 standard funnel with 50 g of powder (i.e., method used for other measurements). Value obtained from flow of 100 g of powder through a 5 mm (0.2 in.) diameter funnel. (c) ASTM B 152-09: minimum limit for copper; maximum limit for all other elements

supplier 1 powders displayed the highest purity, and the analysis suggests that C10100 specifications could be met, if required, with the proper manufacturing method and raw material composition.

Among the examined powders, spherical powders were produced using gas or plasma atomization, while the irregular powder was produced using water atomization. Powders from suppliers 4 and 5 displayed relatively high oxygen content with values of 1.130 and 0.211%, respectively. The latter value was somewhat surprisingly high because the plasma atomization manufacturing process was performed in vacuum, although one possible explanation is that the powder may have been from an old lot. The oxygen content varied from 0.022 to 0.113% for other powders, with higher values for the smaller powders because of their higher specific surface. Feedstock powders were kept in a glove box under an inert nitrogen atmosphere between spraying sessions to prevent oxidation. Should it be determined that the final application requires ultralow-oxygen-level coatings, emphasis must be placed on the proper handling of the feedstock powders, because this can result in a higher gain in oxygen content than the cold spraying process itself.

A summary of powder size and flowability is also shown in Table 10.1. Powder d_{50} values ranged from 20 to 49 μm , with suppliers 1, 2, and 3 each providing two size distributions. Particles with larger average particle size from the same supplier displayed a better flowability value than their smaller counterparts. In addition to the differences in size distribution, the surface appearance and morphology of powder particles from

suppliers 1, 2, and 3, shown in Fig. 10.3, can also be broadly described, respectively, as follows: spherical and satellite free (Fig. 10.3a, b); irregular and satellite free (Fig. 10.3c, d); and spherical with fine satellites (Fig. 10.3e, f).

Initial screening via powder properties eliminated powders from suppliers 4 and 5 because of very high oxygen contents ($>0.2\%$) and/or poor flowability (e.g., leading to a failed test for supplier 4 powder). However, regardless of deviations from the C10100 specification, the remaining six candidates were deemed acceptable in composition, size, and flowability. Consequently, powder selection between these six powders was performed via characterization of coating properties.

Powder Selection via Coating Properties. The six candidate powders from suppliers 1 to 3 were N_2 sprayed using three gas temperature/pressure combinations ($400\text{ }^\circ\text{C}/2\text{ MPa}$, $600\text{ }^\circ\text{C}/3\text{ MPa}$, and $800\text{ }^\circ\text{C}/4\text{ MPa}$, or $750\text{ }^\circ\text{F}/290\text{ psi}$, $1110\text{ }^\circ\text{F}/435\text{ psi}$, and $1470\text{ }^\circ\text{F}/580\text{ psi}$), with other spray conditions summarized in Table 10.2. Coatings of 0.3 to 1.0 mm (0.01 to 0.04 in.) thickness were produced on 3.2 mm (0.13 in.) thick plates and $>50\text{ mm}$ (2 in.) thick cylinders of low-carbon steel, with the latter used for bond strength testing. The powder particle velocities were measured and coatings screened by bond strength, porosity, and microstructure.

The highest particle velocities were obtained with the irregular powder from supplier 2, because of the higher drag force in that case. However, particle velocities of all powders measured at these conditions, ranging from ~ 480 to 820 m/s (1570 to 2700 ft/s), appeared to be within the deposition window between the erosion and critical velocities needed to provide high-quality coatings with good deposition efficiencies (~ 400 to 1100

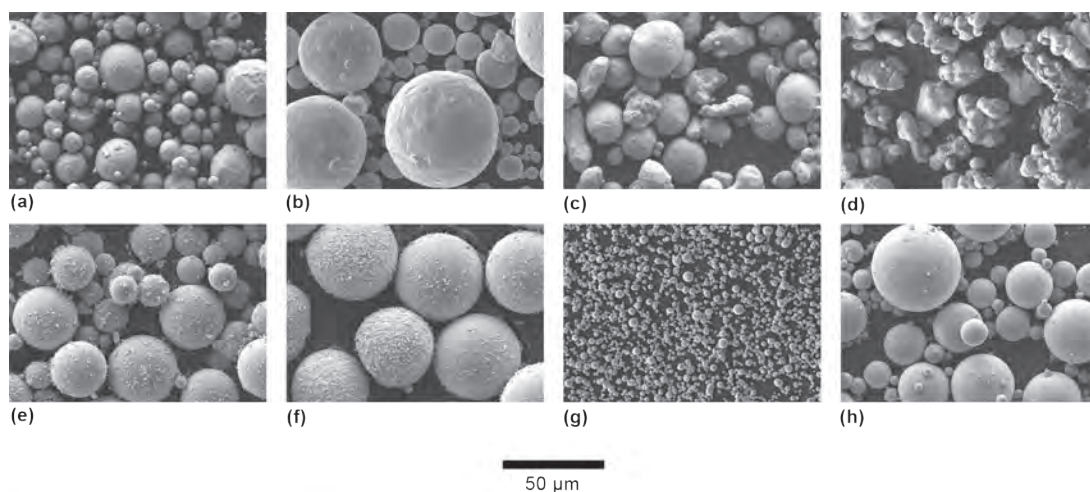


Fig. 10.3 Feedstock powder morphologies. (a) Supplier 1, $d_{50} = 20\text{ }\mu\text{m}$. (b) Supplier 1, $d_{50} = 42\text{ }\mu\text{m}$. (c) Supplier 2, $d_{50} = 23\text{ }\mu\text{m}$. (d) Supplier 2, $d_{50} = 29\text{ }\mu\text{m}$. (e) Supplier 3, $d_{50} = 26\text{ }\mu\text{m}$. (f) Supplier 3, $d_{50} = 49\text{ }\mu\text{m}$. (g) Supplier 4, $d_{50} = \text{not applicable}$. (h) Supplier 5, $d_{50} = 30\text{ }\mu\text{m}$

Table 10.2 Spray conditions employed in various development stages

Parameter	Powder selection	General coating development		Used-fuel container optimization and prototyping
	N ₂ spray	N ₂ spray	He spray	N ₂ and He spray
System	PCS-1000	PCS-1000	Kinetiks 4000	PCS-800, PCS-1000
Powder (<i>d</i> ₅₀), μm	20, 23, 26, 29, 42, 49	23, 42	42	42
Gas temperature (<i>T</i> _g), °C (°F)	400, 600, 800 (750, 1110, 1470)	400, 500, 600, 700, 800 (750, 930, 1110, 1290, 1470)	350 (660)	600, 800 (1110, 1470)
Gas pressure (<i>P</i> _g), MPa (psi)	2, 3, 4 (290, 435, 580)	3, 5 (435, 725)	3.5 (510)	5 (725)
Traverse speed, mm/s (in./s)	300 (12)	60, 100, 1000 (2.4, 4.0, 40)	100 (4.0)	Various
Step size, mm (in.)	1 (0.04)	1 (0.04)	1.25 (0.05)	Various
Standoff distance, mm (in.)	25 (1.0)	25, 100, 200 (1.0, 4.0, 8.0)	40 (1.6)	30 (1.2)

m/s, or 1300 to 3600 ft/s) (Ref 10.21). Here, the critical and erosion velocity lines correspond to the simulated values for 25 μm cold particles, although both velocities depend not only on the particle size but also on the temperature, oxygen content, and substrate surface temperature.

The ASTM C633 bond strength values were as high as 41 ± 5 MPa (6000 ±725 psi) for 350 to 630 μm thick coatings. While higher particle velocity somewhat favored coating adhesion, the investigation of the relationship between specific powders, spray conditions, and bond strength was inconclusive. All powders allowed for the production of relatively dense coatings at the highest gas condition (800 °C/4 MPa, or 1470 °F/580 psi). Some porosity was observed at lower (temperature/pressure) gas conditions, and porosity measurements of coatings produced at 600 °C/3 MPa (1110 °F/435 psi) indicated that particle velocities above ~600 to 650 m/s (1970 to 2130 ft/s) resulted in less than ~0.5% porosity. Smaller powders (and associated higher velocity) typically yielded lower-porosity coatings than larger powders, although both *d*₅₀ = 26 μm and *d*₅₀ = 49 μm powders from supplier 3 yielded relatively high-porosity coatings. This result was assumed to be due to low associated particle velocities, although the fine surface satellites may also play a role.

Based on the aforementioned coating characterization, no single powder proved to be significantly better than other powders. However, additional testing with the *d*₅₀ = 26 μm powder from supplier 3 revealed clogging of the powder injector, and, as a result, supplier 3 powders were eliminated. As is very often the case, no specific powder characteristics were identified as more significant than the others in causing clogging of this powder. Clogging is a general issue that limits the number of powders available for practical use in cold spray. The powder/nozzle material couple as well as the nozzle and powder injector design are important aspects to consider for nozzle clogging. Spraying parameters, such as a high process gas temperature, can also trigger nozzle or injector clogging, although

this was minimized with the use of the PCS-1000 gun that integrates nozzle cooling. Clogging also increases at higher feed rates, such as the very high rates that will be eventually targeted for production, because the charge effect changes the structure of the gas flow. In general, powders in the coarser range are recommended because they offer better flowability, which is an important aspect in cold spraying. However, dense coatings were produced from most powders studied, regardless of their different attributes, which suggests that powder supply will be easy to obtain and that suitable powders will be available from multiple sources.

10.3 General Coating Development

A comprehensive program was performed to investigate the effects of spray conditions and postspray heat treatment conditions on copper coatings produced using a typical cold spray setup (i.e., an *XY* spray pattern on a generic substrate). The objective of this stage was to develop a set of reference process parameters that would be optimized in subsequent UFC coating development and prototyping stages (described later). For the sake of brevity, only selected results are discussed in this section. Extensive literature is available concerning the general and fundamental aspects of cold spraying copper coatings (Ref 10.3–10.12).

Selection of Coating Parameters. For the selection of general copper coating spray parameters, an 18-run design of experiment (DOE) was performed, varying powder, gas type, gas temperature, gas pressure, gun traverse speed, step size, and/or standoff distance. The values employed for each parameter are shown in Table 10.2. The $d_{50} = 42 \mu\text{m}$ and $d_{50} = 23 \mu\text{m}$ powders from suppliers 1 and 2, respectively (Fig. 10.3b and c, respectively), were employed, with the former powder displaying relatively low oxygen content, high flowability, and high coating bond strength, while the latter powder offered an alternative (irregular) morphology and smaller size distribution. Coatings were produced on low-carbon steel puck substrates (25.4 mm diameter by 6.35 mm thick, or 1 in. by 0.25 in.), shown in Fig. 10.2(a), that were grit blasted with grit 24 ($\sim 975 \mu\text{m}$) alumina.

A chemical analysis of selected coatings showed that oxidation due to the cold spray process was limited. Coatings sprayed at 800 °C (1470 °F) with N_2 gas using $d_{50} = 42 \mu\text{m}$ displayed values of 0.066% compared to as-received values of 0.054%. The similarity of oxygen content in powders and coatings was also observed during testing for the powder selection (not shown). Switching to helium gas spray at 350 °C (660 °F) in an enclosed helium atmosphere did not significantly change the oxygen pickup, with 0.018% measured for a coating with $d_{50} = 42 \mu\text{m}$ powder.

The ASTM C 633 bond strength of coatings sprayed onto the 6.35 mm (0.25 in.) thick steel pucks ranged up to $29 \pm 10 \text{ MPa}$ ($4206 \pm 1450 \text{ psi}$), although the majority of coatings displayed bond strength values below 10 MPa (1450 psi). Aside from the helium-sprayed coating, bond strengths

greater than or equal to ~20 MPa (2900 psi) were only obtained using gas temperatures of 800 °C. The variation in bond strength obtained for coatings produced during the DOE runs as well as during the powder selection tests illustrates the difficulty in developing optimal spray parameters for coating adhesion; in principle, bond strength is a very important coating parameter for the program of producing UFCs. Bond strength may be influenced by specimen preparation, coating parameters, substrate condition, residual stresses, and other factors.

Overall, the capability of cold spray to produce fully dense copper coatings using a wide range of spray parameters was demonstrated by the DOE runs: measured porosity was less than or equal to $0.4 \pm 0.6\%$ for all coatings. For a relatively low-strength, ductile metal such as copper, the window of deposition of ~400 to 1100 m/s (1300 to 3600 ft/s) (Ref 10.21) is well within the capability of cold spray equipment. The average particle velocity measured for 13 different spraying conditions (powder with $d_{50} = 42 \mu\text{m}$) ranged from 570 to 750 m/s (1870 to 2460 ft/s), as shown in Fig. 10.4, with optimized conditions at the upper end of the measured range. In comparison, average particle velocities measured for the various powders during the powder selection stage ranged from 480 to 820 m/s (1570 to 2700 ft/s). The effects of the spray parameters are typically linked to impact particle velocity, particle temperature, and substrate temperature because of the influence of these parameters on particle deformation. Coatings with greater degrees of particle deformation are typically associated with minimal porosity, high amounts of bonded area, and relatively high values of cohesive strength (Ref 10.9).

Selection of Annealing Conditions. For initial investigation of post-spray annealing, 3 mm (0.1 in.) thick coatings were produced on low-car-

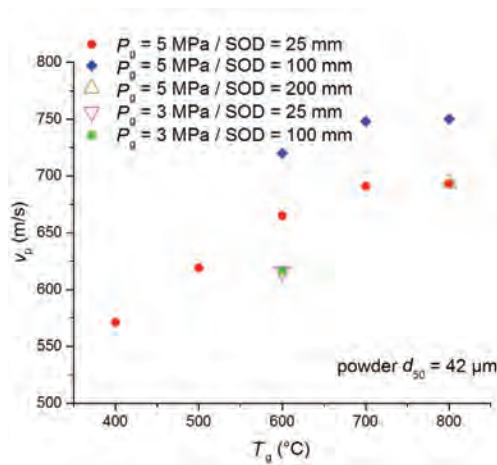


Fig. 10.4 Particle velocity (V_p) for $d_{50} = 42 \mu\text{m}$ powder versus gas temperature (T_g) at various gas pressures (P_g) and standoff distances (SODs)

bon steel plate substrates (165 by 140 by 3 mm, or 6.5 by 5.5 by 0.1 in.), shown in Fig. 10.2(b), using helium spray and N₂ spray. For brevity, only results with N₂-sprayed, $d_{50} = 23 \mu\text{m}$ powder coatings are presented in this section. A range of annealing conditions based on the temperatures of stress relieving and annealing of pure wrought copper was screened through microhardness and microstructure characterization. Annealing temperatures of 200, 300, 400, 500, and 600 °C (390, 570, 750, 930, and 1110 °F) for 1 and 10 h were investigated, as was one long-term/low-temperature anneal at 200 °C for 100 h. Two optimized conditions were then selected for subsequent characterization by ASTM E8 tensile testing, ASTM C633 bond testing, and ASTM E290 bend testing. Coatings were machined to eliminate surface irregularities for bend and bond testing (0.8 to 1.1 mm, or 0.03 to 0.04 in., removed) and to produce 1 mm (0.04 in.) thick coating-only specimens for tensile testing.

Based on the hardness measurements and microstructure analysis of the micrograph coupons in screening tests, the following two optimized annealing conditions were identified: 1 h at 300 °C and 1 h at 600 °C. The first condition featured a relatively low temperature that produced a significant decrease in hardness from the as-sprayed condition as well as no apparent increase in porosity, as shown in Fig. 10.5(a) and Fig. 10.6(b), respectively. The second condition employed a relatively high temperature that produced microstructural restoration (i.e., recrystallization) in the annealed coating (Fig. 10.6c). The 1 h anneal time was selected because of the minimal hardness difference obtained between 1 and 10 h.

Bond strength was high for coatings in both as-sprayed and annealed conditions. Samples generally failed in the epoxy (used to attach the pull test studs in ASTM C633), which indicated bond strength was, at minimum, equal to the epoxy strength of 60 to 70 MPa (8700 to 10,150 psi). Representative stress-strain curves for coatings in the as-sprayed and annealed conditions, shown in Fig. 10.5(b), revealed that annealing decreased coating strength and increased ductility, with a greater effect obtained at higher temperature. Tensile strength and strain at failure values of $370 \pm 33 \text{ MPa}$ ($54,000 \pm 4800 \text{ psi}$) and $0.5 \pm 0.2\%$, $245 \pm 4 \text{ MPa}$ ($35,500 \pm 580 \text{ psi}$) and $16 \pm 3\%$, and $180 \pm 2 \text{ MPa}$ ($26,000 \pm 290 \text{ psi}$) and $34 \pm 3\%$ were obtained for as-sprayed, 300 °C annealed, and 600 °C annealed conditions, respectively. These results are consistent with reported values in the literature for cold spray copper coatings (Ref 10.10, 10.11). For comparison, the ASTM B152 (Ref 10.22) minimum tensile strength is 205 MPa (30,000 psi) for hot rolled tempers and 220 to 360 MPa (31,900 to 52,200 psi) for cold rolled tempers, with a minimum 40% elongation for C11000 and C12200 plate with hot rolled tempers; it is worth noting that such a large minimum requirement is unlikely to be used for UFCs. Typical bend-test specimens, shown in Fig. 10.5(c), produced a crack through the entire coating within a $5 \pm 1^\circ$ bend for the as-sprayed condition; a first edge crack after a $52 \pm 14^\circ$ bend and 90° bend without a crack

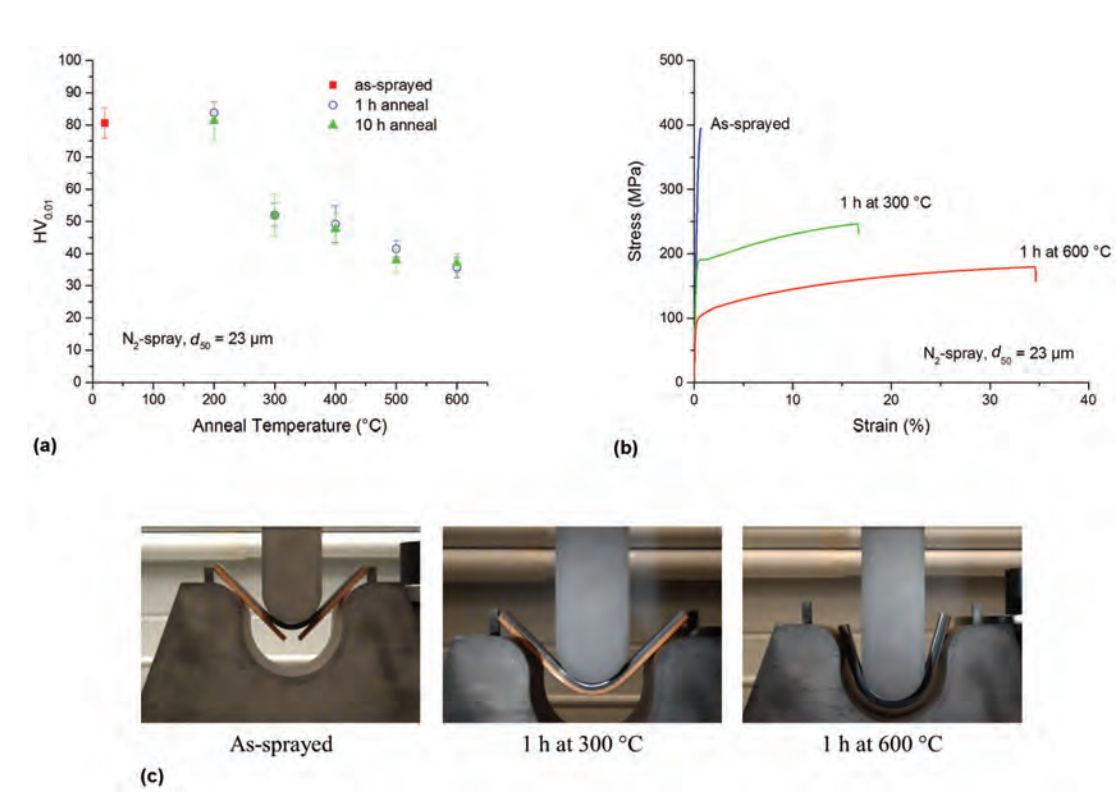


Fig. 10.5 Selected mechanical test results for N₂-sprayed coatings ($d_{50} = 23\text{ }\mu\text{m}$ powder) after annealing at various temperatures. (a) Microhardness as a function of anneal temperature. (b) Stress-strain curves. (c) Photos of bend-test specimens

propagating through the entire coating thickness after heat treatment at 300 °C; and no visible cracks after a full bend (146°) in samples annealed at 600 °C.

The coatings in the as-sprayed condition displayed a relatively smooth fracture surface and clearly delineated particle boundaries (Fig. 10.6d). In contrast, a dimpled fracture surface without discernible particle boundaries was observed in coatings annealed at 600 °C (Fig. 10.6f). From these results, it may be interpreted that fracture was associated with particle debonding (e.g., the as-sprayed condition), and the improvement in ductility after annealing was potentially due to better interparticle bonding (e.g., the 600 °C heat treatment) (Ref 10.10, 10.11). Heat treatment at 300 °C represented a transition between these conditions (Fig. 10.6e), so only moderate ductility improvements were observed.

In this work, the effect of the increase in porosity observed in coatings annealed at 600 °C (Fig. 10.6c) was not evaluated. Calla et al. (Ref 10.10) also obtained an increase in apparent porosity located at interparticle boundaries in cold-sprayed coatings annealed at 600 °C for 1 h. This increase was cited as a potential source of the lower ductility obtained for

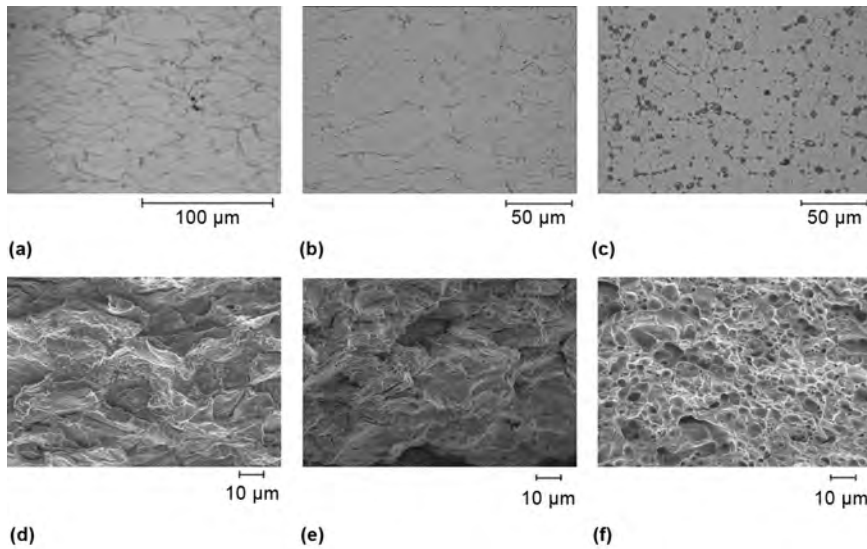


Fig. 10.6 Selected metallographic results for N_2 -sprayed coatings ($d_{50} = 23 \mu m$ powder) after annealing at various temperatures. Etched microstructures obtained (a) as-sprayed, (b) after annealing at 300 °C (570 °F) for 1 h, and (c) after annealing at 600 °C (1110 °F) for 1 h. Fracture surfaces of tensile specimens (d) as-sprayed, (e) after annealing at 300 °C for 1 h, and (f) after annealing at 600 °C for 1 h

annealed coatings relative to annealed bulk sheet and was attributed to a possible relaxation of compressive residual stresses or the expansion and spheroidization of driving gas entrapped within the cold spray structure. Stoltenhoff et al. (Ref 10.12) observed the development of spheroidized oxides in coatings annealed at 600 °C for 1 h, which were located at former interparticle boundaries in N_2 -sprayed coatings and randomly distributed in helium-sprayed coatings. Another possible cause of the increase in observed porosity is the spheroidization of pores through a mechanism analogous to sintering, which has been reported for other cold-sprayed material (Ref 10.23). In that case, the increase in apparent porosity would result from a reorganization of the initial planar defects (interparticle boundaries) into spherical and thus more visible pores and not from an actual/real increase in porosity. In general, the effects of porosity are dependent on the amount, size, and morphology of the pores. Pores can act as defects that raise stress concentrations, and although no porosity-strength relationships are available for cold-sprayed copper, Hyun et al. (Ref 10.24) showed that tensile strengths of ~150 MPa (21,750 psi) can still be obtained with as much as 2 to 3% porosity for copper castings. To date, no specification on allowable porosity has been defined for the UFC application.

10.4 Used-Fuel Container Coating Optimization

Based on the aforementioned general coating development, parallel coating feasibility studies (not shown), and UFC requirements, an initial reference cold spray coating system was defined. To maximize coating adhesion, a bond coat sprayed with helium was selected, followed by a N_2 -sprayed top coat to build the required thickness. However, such a process was not sufficiently validated to implement on mock-up containers. In addition, postdeposition heat treatment was only roughly defined at this point in the study; results from parallel modeling in-repository container performance, conducted concurrently with cold spray feasibility studies, were able to better define copper coating ductility requirements. Finally, only planar coupons of various steel grades were cold spray coated within the feasibility studies indicated previously. To be considered for UFCs, it was necessary to demonstrate that cold spray coating can be achieved on materials such as the steel grade of the UFC body, welded steel substrates, larger-dimension steel coupons, and cast iron substrates, prior to implementing a program dedicated to UFC fabrication.

Validation of Reference Coating on Planar Substrates. The initial reference cold spray coating system was defined with the following parameters:

- 10 to 70 μm spherical low-oxygen copper powder
- 25.4 mm (1 in.) minimum thick A516 grade 70 steel, grit blasted with 24 grit to remove mill scale
- 100 μm bond coat, applied with helium spray at 5 MPa (725 psi) and 800 °C (1470 °F)
- 3 mm (0.1 in.) top coat, applied with N_2 spray at 5 MPa and 800 °C

Based on powder availability and reference powder criteria, the $d_{50} = 42 \mu m$ powder from supplier 1 used previously for general coating development was selected for validation testing, and two new powder lots were obtained. To maintain continuity and avoid confusion, the powder is hereafter generically referred to as $d_{50} = 42 \mu m$ powder (with lots A, B, or C, when applicable). The original lot (A) and two new lots (B and C) were similar in size distribution ($d_{50} = 42, 48,$ and $43 \mu m$, respectively), and all three lots displayed a dense, spherical morphology with particle surfaces free of satellites.

Initial validation trials were performed using the Plasma Giken PCS-1000 unit and powder lot B and involved coatings produced on the flat surface of cylinders (25.4 mm diameter by 38.1 mm, or 1 by 1.5 in.) held in a rotating substrate holder (15 cm, or 6 in., diameter), shown in Fig. 10.2(c). The A36 steel substrates, which are compositionally similar to the reference A516 grade 70, did not significantly affect the coating density or bond strength. The first spray trial using initial reference parameters pro-

duced a visually uniform coating surface, and ASTM C633 bond strength testing resulted in epoxy failure (i.e., minimum 60 to 70 MPa, or 8700 to 10,150 psi). The coating microstructure, shown in Fig. 10.7(a), displayed a dense, $\sim 340\text{ }\mu\text{m}$ thick bond coat produced by helium spray, and an additional $\sim 3\text{ mm}$ (0.1 in.) was subsequently deposited by N_2 spray with coating porosity measured at $0.1 \pm 0.1\%$.

An attempt to spray with powder lot C using initial reference conditions showed clogging issues that did not occur with A or B powder lots. A difference in oxygen content for lot C and/or a higher amount of fines may have been significant. A change in gas temperature (from 800 to 600 °C, or 1470 to 1110 °F) and spray unit (from PCS-1000 to PCS-800) from the initial reference was employed to resolve the clogging. Coatings produced using the lower gas temperature, as well as increased substrate rotation speed to accommodate the spraying of the large-diameter UFC, were dense ($0.1 \pm 0.2\%$ in $\sim 3\text{ mm}$, or 0.1 in., top coat) and achieved comparable bond strength minima to the previous materials. Because the lower-temperature parameters were necessary to avoid clogging with one of the two powder lots used, the reference coating condition was modified to allow for a gas temperature of 600 °C for this lot.

A secondary validation through four production runs using larger-scale substrates was performed using the Plasma Giken PCS-800 unit and powder lot C. Each production run involved depositing 3 mm thick coatings on plate substrates (A516 grade 70, 150 by 150 by 38 mm, or 6 by 6 by

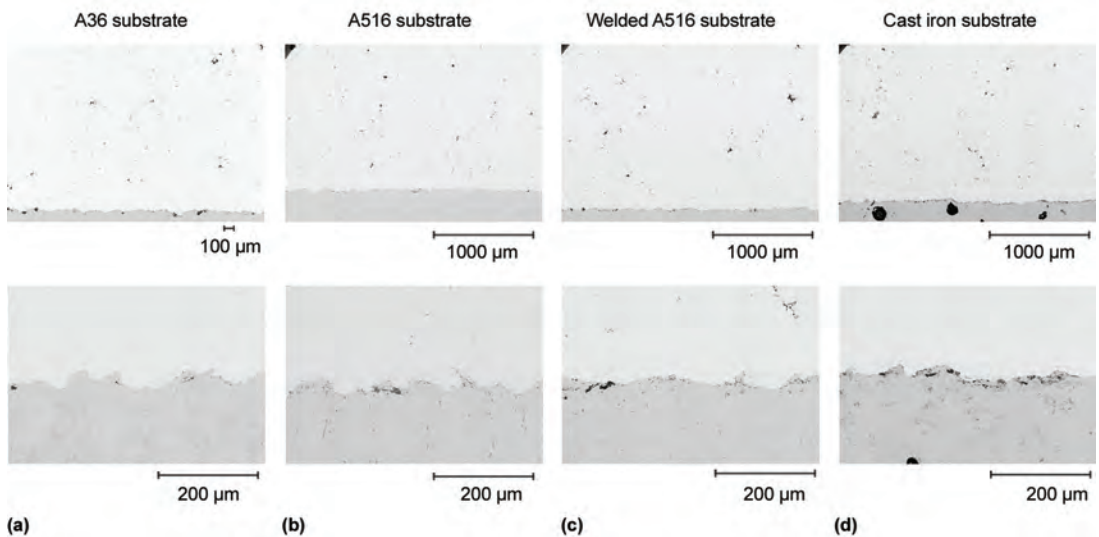


Fig. 10.7 Selected results for N_2 -sprayed coatings ($d_{50} = 42\text{ }\mu\text{m}$ powder) produced during used-fuel container optimization. As-polished coatings sprayed using initial reference parameters with gas temperature (T_g) = 800 °C (1470 °F) on (a) A36 substrate, and optimized reference parameters with $T_g = 600\text{ }^\circ\text{C}$ (1110 °F) on (b) A516 grade 70 substrate, (c) welded A516 grade 70 substrate, and (d) cast iron substrate

1.5 in.) fixed into a rotating 560 mm (22 in.) diameter sample holder, which also allowed puck substrates (25.4 mm diameter by 38.1 mm, or 1 in. by 1.5 in.) to be simultaneously coated, as shown in Fig. 10.2(d). In addition to standard 3 mm (0.1 in.) thick coatings, 5 and 10 mm (0.2 and 0.4 in.) thick coatings were also produced. Two plates with 3 mm thick coatings were arbitrarily selected as representative coatings for characterization. During one production run, A36 pucks were simultaneously coated to produce specimens for immediate analysis (i.e., avoiding machining delay) and to confirm that spraying on A36 or A516 grade 70, which have similar compositions, would not change coating properties. This latter equivalency demonstration is particularly important in that the nearest steel to A516 grade 70 plate in a rod form is A36. Coating porosity was measured at $0.5 \pm 0.4\%$ and $0.3 \pm 0.2\%$ for the plate and puck samples, respectively, from the same run, as shown in Fig. 10.7(a and b). The other coated plate specimen appeared completely dense, with porosity measured at $0.0 \pm 0.1\%$. The coating-substrate interfaces were also similar, and all bond strength tests resulted in epoxy failure (minimum 60 to 70 MPa, or 8700 to 10,150 psi) instead of the coating-substrate interface. Because of the similarity in coating density, coating interface, and bond strength results, the effect of using different substrates (A516 and A36) was considered minimal.

Bond strength measurement using a modified ASTM E8 tensile test on small-scale specimens (5.90 mm, or 0.2 in., gage length by 20 mm², or 0.03 in.², area cross section) was performed by an external contractor (Exova, Cambridge, ON) on the 10 mm thick cold spray coating on A516 plate. All failures were reported to occur at the coating-substrate interface, with no measurable elongation and a bond strength of 83 ± 15 MPa ($12,000 \pm 2200$ psi). The bond strength was consistent with the ASTM C633 results, which showed epoxy failures at >60 MPa (8700 psi) for 3 mm thick coatings on A516 plate. Because coating adhesion decreases with increasing coating thickness, the minimum bond strength of the 3 mm thick coatings can be considered, at minimum, equal to the 10 mm thick coating (i.e., minimum 83 ± 15 MPa instead of minimum 60 MPa).

Application of Reference Coating to Weld Samples. The application of reference coatings on the weld area of A516 grade 70 substrates involved the same setup as the validation using A36 cylinders (Fig. 10.2c, d). A cross section of the as-received welded steel substrate confirmed that the weld surface was much larger (~ 35 mm, or 1.4 in., wide) than the 25.4 mm (1 in.) diameter rod specimens machined from the weld area. Overall, the coatings produced on weld substrates under the conditions investigated were comparable in bond strength and coating density to the coatings produced during the reference parameter validation (e.g., epoxy failure in ASTM C633 bond strength test and $<0.3\%$ porosity at a gas temperature of 600 °C, or 1110 °F, shown in Fig. 10.7(c), using a helium-sprayed bond coat with N₂-sprayed top coat).

Application of Reference Coating to Cast Iron Substrates. Reference coatings on cast iron substrates were produced by the same procedure as the weld substrate samples. In general, coatings on cast iron displayed low porosity ($0.4 \pm 0.5\%$), shown in Fig. 10.7(d), which was similar to the reference A516 grade 70 (or A36) steel grade(s). However, bond testing produced adhesive failure at the coating-substrate interface with a measured strength of 37 ± 12 MPa (5400 ± 1750 psi), which was significantly below the epoxy failures at ~ 60 to 70 MPa (8700 to $10,150$ psi) for A516 (or A36) reference substrates. The relatively large standard deviation was due to one outlier at 14 MPa (2000 psi) failure (i.e., 41 ± 3 MPa, or 6000 ± 435 psi, for the other four replicates).

The root cause of the lower bond strength on the cast iron substrate was not clear, although differences were observed with coatings on reference substrates. The higher-magnification SEM micrographs ($250\times$) in Fig. 10.7 reveal that the coating-substrate interface was generally more uniform (i.e., flat) on the cast iron substrate. Coatings on the A36 substrate qualitatively displayed more closely spaced peaks along the interface and a higher peak-to-trough distance, which suggest that deformation of the particle and/or substrate was higher than for the coating on cast iron. A lower degree of deformation may result in lower bond strength (e.g., due to a decrease in mechanical interlocking and/or adiabatic shear instability). Spheroidal (nodular) graphite was distributed throughout the matrix (Fig. 10.7d), with partial nodules observed along machined edges. However, these relatively large nodules were not observed along the coating-substrate interface, which suggests that nodules were removed during the substrate preparation (i.e., grit blasting) and/or spray process (i.e., particle impact). The presence of graphite at the interface (e.g., crushed fragments) may reduce bond strength by decreasing the well-bonded area between the copper particles and the matrix of the cast iron.

Optimization of Annealing Conditions. Results from the initial study for general coating development showed that coatings heat treated for 1 h at 300°C (570°F) did not quite meet the preliminary ductility requirement (20% elongation prior to fracture), while coatings heat treated for 1 h at 600°C (1110°F) displayed small pores not observed in the as-sprayed condition. As a result, a brief optimization of annealing conditions was performed. Planar samples coated with the reference coating system were tested in the as-sprayed condition and after heat treatment for 1 h at 350 and 400°C (660 and 750°F).

The as-sprayed coating displayed a tensile strength of 171 ± 14 MPa ($25,000 \pm 2000$ psi) and strain to failure of $0.2 \pm 0.0\%$. Heat treatment of coatings for 1 h at 350 and 400°C produced increases in ductility values to $23.2 \pm 3.0\%$ and $25.9 \pm 6.6\%$, respectively, as well as minor increases in tensile strength to 198 ± 7 MPa ($28,700 \pm 1000$ psi) and 194 ± 11 MPa ($28,100 \pm 1600$ psi), respectively. Micrographs of the coating cross sections indicated that coating porosity (as-polished) did not increase signifi-

cantly after heat treatment at 350 to 400 °C, which was consistent with previous observations during general coating development. Instead, any differences in observed porosity were attributable to variations in the as-sprayed coating. Etched micrographs, shown in Fig. 10.8, revealed the development of equiaxed grains within deformed particles after heat treatment, presumably as a result of recrystallization. Grain boundaries were not resolved in the as-sprayed microstructure (Fig. 10.8a), and the deformed particle boundaries were heavily overetched to reveal grain boundaries in the coatings annealed at 350 and 400 °C (Fig. 10.8b and c, respectively). Overall, the mechanical and microstructural characterization demonstrated that coatings heat treated for 1 h at 350 to 400 °C displayed acceptable strength and ductility, although the 400 °C anneal may be preferable because of the development of more qualitatively uniform, equiaxed grains.

10.5 Prototyping

Process Adjustments. To scale up from 150 by 150 mm (6 by 6 in.) planar samples to mock-up assemblies of up to 2.15 m (7 ft) length, the validated coating parameters required several process adjustments. Changes for substrate handling/preparation (e.g., lift system, portable grit blast) and productivity (e.g., increased feed rate) were relatively straightforward to introduce. In comparison, significantly greater effort was needed for the development of a new procedure for reducing helium gas consumption. Although performed to accommodate facility helium gas storage capability, this modification is also a step forward in process cost optimization.

For the prototyping activities, coating of the first cylindrical pipe segment was performed with the conditions validated for the planar samples, while all subsequent coatings were produced with the adjusted conditions described here. The reference coating process for both N₂ and helium gas spray used the same nozzle, which featured a nozzle diameter designed to maximize N₂ spray productivity. Consequently, a smaller-diameter (throat

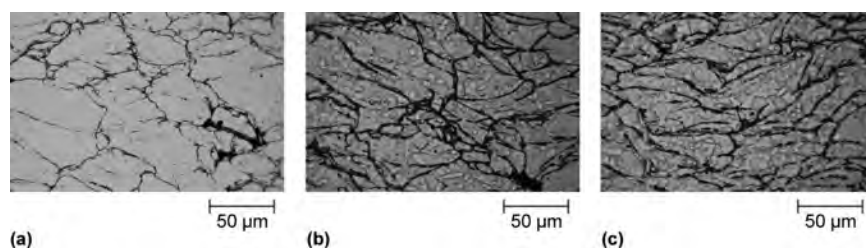


Fig. 10.8 Etched microstructures for N₂-sprayed coatings ($d_{50} = 42 \mu\text{m}$ powder). (a) As-sprayed. (b) After annealing at 350 °C (660 °F) for 1 h. (c) After annealing at 400 °C (750 °F) for 1 h

and exit) nozzle optimized for helium spray was employed to reduce flow rate (~65% lower) while still maintaining similar particle velocity (measured with N₂ gas only). A switch to the smaller-diameter nozzle (for bond and top coats), with all other conditions kept constant, to produce a 3 mm (0.1 in.) thick coating on A36 cylinders (25 mm diameter by 38 mm thick, or 1 in. by 1.5 in.) resulted in a bond strength of 42 ± 5 MPa (6100 ± 725 psi), which was lower than coatings produced with the larger-diameter nozzle (i.e., minimum 60 to 70 MPa, or 8700 to 10,150 psi).

Upon obtaining these results, this difference was attributed to a lower substrate temperature caused by less gas flow through the smaller-diameter nozzle. To investigate this hypothesis, the substrate surface temperatures were measured using an infrared camera, for simulated (i.e., powder-free) deposition runs. The small nozzle resulted in 15 to 20 °C (25 to 35 °F) lower substrate temperatures. Consequently, the substrate temperature was raised using two simulated runs (without powder) prior to actual deposition runs, and the resultant coatings met bond strength requirements with a value of 61 ± 3 MPa (8850 ± 435 psi) epoxy failure. Concurrently, it was found that the preheating could be done using a radiant lamp, for a similar bond strength result (58 ± 2 MPa, or 8400 ± 290 psi, epoxy failure). Subsequent to the nozzle switch, the powder feed rate was increased from 80 to 250 g/min (2.8 to 8.8 oz/min) to increase productivity. The increase in powder load did not adversely affect the coating porosity as measured via image analysis. However, a decrease in adhesion occurred (43 ± 7 MPa, or 6250 ± 1000 psi), principally as a result of the higher deposition rate per pass and not of the powder feed rate itself. When the rotation speed of the samples was increased to match the deposition rate per pass obtained at lower feed rate, the coating adhesion was recovered (56 ± 5 MPa, or 8100 ± 725 psi).

Coatings for prototyping were applied using the PCS-800 cold spray unit with two large volumes of powder lots of $d_{50} = 42$ µm powder (lots D and E). However, it was immediately found that the coatings produced using lot E displayed lower adhesion than the others. It was initially unclear whether the poorer performance of this lot was due to a different powder surface state and/or a higher proportion of coarse particles ($d_{90} = 62$ to 67 µm for lots A to D, and 72 µm for lot E). Both powder sieving and powder heat treatment under H₂ helped to recover adequate coating adhesion, but only powder sieving was actually performed prior to prototyping coating.

Cylindrical Body. The reference coating was applied to an ~300 mm (12 in.) length on a pipe segment of A106 schedule C steel (508 by 406 by 38 mm, or 20 by 16 by 1.5 in.) fixed on a turntable, shown in Fig. 10.2(e). The helium-sprayed bond coat, N₂-sprayed top coat, and machined surface displayed macro coating appearances similar to those obtained in the planar validation. Although not specifically measured or recorded during production, the helium-sprayed bond coat thickness was estimated to be ~100

to 150 μm based on the planar validation results, while the N_2 -sprayed top coat thickness was $3.85 \pm 0.20 \text{ mm}$ ($0.15 \pm 0.008 \text{ in.}$) as-deposited. The SEM micrographs of the coating in locations at the top, midlength, and bottom of the coated pipe revealed the coating to be completely dense at all three locations.

Hemispherical Head. Two methods were used to coat the hemispherical heads: simultaneous rotation of the heads and manipulation of the cold spray gun, and sequential masking of stationary heads with gun manipulation. Figure 10.9(a) illustrates some developmental patterns explored during the former approach, which occasionally led to incomplete or uneven coverage, while Fig. 10.9(b) illustrates the coating with masking used in the latter method. A pulled-back view of the latter method is also shown in Fig. 10.2(f). Full-sized heads were made using both approaches.

Specimens from the coating on the actual hemispherical head were machined by electrical discharge machining (Fig. 10.9c), and results showed good coating uniformity, except near the sphere apex. Coating adhesion was estimated following ASTM C633 standard guidelines, although a bias was introduced by the curved coating surface (probable change in stress distribution and difficult alignment of the pull studs with the tensile axis).

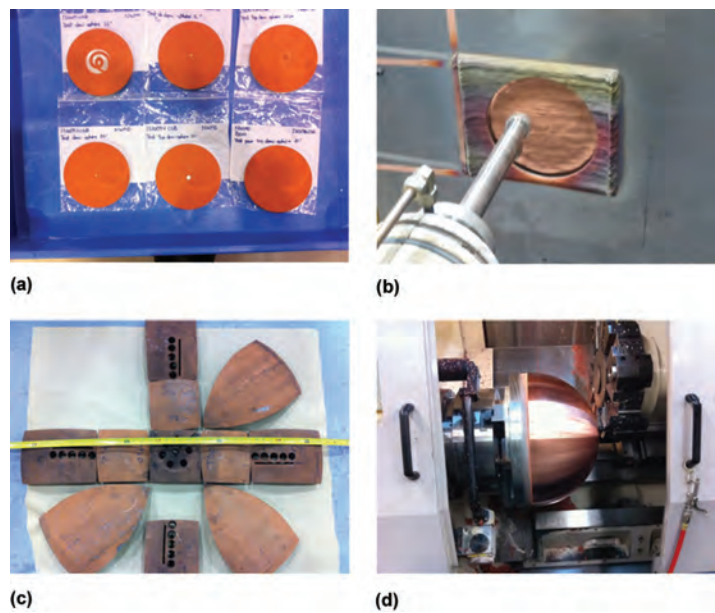


Fig. 10.9 Photos showing coating development for hemispherical head. (a) Coated dishes (with matching geometry to the apex) used in the optimization of a curved spray pattern. (b) Apex coated using an XY pattern with masking. (c) Coated hemisphere sectioned for characterization. (d) Computer-numerical-controlled machining of a coated hemisphere

Coating adhesions between 35 and 55 MPa (5100 and 8000 psi) were achieved, the highest value being obtained at the apex of the sphere. Upon fabrication, one coated hemispherical head was computer numerical control machined (Fig. 10.9d).

Mock-Up and Lower Assembly. The coating process for the UFC was first demonstrated on one mock-up assembly consisting of the cylindrical body, hemispherical head, and weld transition. This assembly represented a full-diameter lower section of the canister (i.e., full-sized hemispherical head and weld transition) with a truncated cylindrical body (560 mm diameter by 620 mm part length, or 22 by 24.5 in.). An actual lower assembly (full part length of 2270 mm, or 90 in.) was subsequently coated. The setup for coating the truncated assembly and full-sized lower assembly, shown in Fig. 10.2(g) and (h), respectively, employed a horizontal frame with motorized rollers to rotate the assemblies.

Because of the assembly sizes, the coatings were applied in sections over multiple work days. This practical issue required the development of restarting procedures to account for surface preparation and blending/joining of the coatings deposited on previous sections. In principle, previous sections may undergo slight surface oxidation, which must be removed prior to overspraying; there is also a substrate temperature necessary for achieving satisfactory coatings, as discussed earlier in this chapter in the section on nozzle selection. Accordingly, the spray pattern was modified to produce a taper at the edge of the each day's section to mitigate coating variation at the transition between sections. Prior to spraying, the overlapping copper region was grit blasted at the same time as the section to be newly covered. Postdeposition microstructural observations of companion coupons did not show any coating variation in overlap regions. Figure 10.10 shows the full-sized lower assembly after coating of two sections and the entire assembly. Similar to the hemispherical head, both assemblies were machined following deposition to remove macroscopic surface roughness, as shown in Fig. 10.9(d).

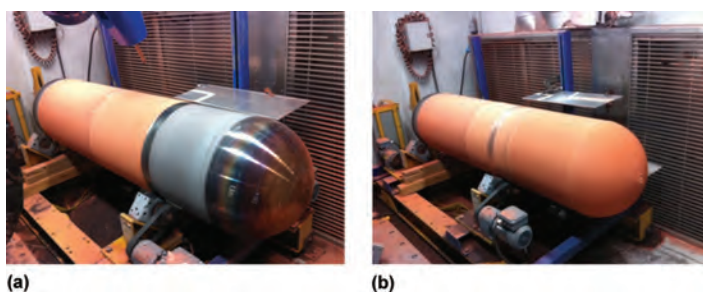


Fig. 10.10 Full-sized lower assembly after coating of (a) two sections and (b) entire assembly

10.6 Conclusions and Future Work

The successful application of cold spray coating technology to full-scale geometric representative Mark II UFC mock-up configurations (carbon steel cylinder/spherical heads and applicable weld substrates) was demonstrated through activities involving powder selection, general coating development, UFC coating optimization, and prototyping. Reference spraying and annealing conditions were established, and coating quality and properties were validated on different substrate geometries and compositions. Results also indicated that powder manufacturing and robust handling procedures are key considerations for reliability and consistency of coating properties. A clear path to manufacturing copper coatings on UFCs via cold spray deposition was developed, including details on process parameter scale-up adjustment, spray set up and pattern development, coating joining procedure, and coating machining. Ongoing development of the coating process is focused on the weld closure zone, where the process will need to be adapted to limit the rotation of filled UFCs. The establishment of a clear operating window sufficient for large-scale manufacturing of the process is also still required and will be investigated in ongoing work.

ACKNOWLEDGMENT

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CHAPTER 11

Cold Spray Applications in Repair and Refurbishment for the Aerospace, Oil and Gas, and Power-Generation Industries

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COLD SPRAY COATING TECHNOLOGY, as described in previous chapters, has the capability to provide surface enhancement over a wide range of applications across various industrial sectors. Multimaterials, nanostructured materials, composites, and multilayered functionally gradient materials that are difficult to produce by thermal spray can be deposited as thick surface embellishments via the additive manufacturing of cold spray coatings. Cold spray is a versatile process that finds use in depositing novel materials with unique properties for several niche applications.

In addition to their use in new manufacture, cold-sprayed deposits are important in repair and refurbishment of scratched, dented, worn, and/or expensive parts. The ability to form dense, oxide-free layers makes cold-

sprayed coatings an attractive alternative to more expensive bulk forms in many structural engineering applications. There can be major financial incentives to using cold spray to apply coatings of superior materials/alloys to lower-cost substrates, which is often a desirable practice because of the high prices of some alloys.

This chapter focuses on cold spray applications pertaining to repair and refurbishment in the aerospace, oil and gas, and power-generation industries, the last specifically involving repair of gas turbine components.

11.1 Advantages of Cold Spray Repair and Refurbishment

Service-returned parts in various types of structural application are in need of new technologies for repair and restoration to operation. In many cases, component repair and refurbishment pose far more challenges than new-make applications, due to the fact that parts have seen service operation and thus been exposed to temperature as well as mechanical and thermal fatigue, in some cases have been subject to time-dependent inelastic strain or creep, and have probably undergone irreversible microstructural changes. In addition, the repair procedure may induce residual stresses that must be relieved after the repair; this can pose a challenge, especially for a part needing only localized repair even though the heat treatment is applied to the entire part.

Moreover, traditional repair practices involve either replacing the part or carrying out full repair, starting with material removal and followed by rebuilding to print, which involves fairly extensive, time-consuming, and expensive steps. In many cases, the damage during service operation may not be extensive enough to warrant a replacement. In addition, not only do replacement parts incur cost, but disassembly and reassembly must be done with care so that other parts are not damaged.

In this context, cold spray technology is an ideal choice for restoring damaged metal parts, both for dimensional restoration of corroded, worn, or damaged parts and for providing a functionally upgraded material when a part comes in after service. Cold spray is able to perform repair and refurbishment with a faster turnaround time; it also provides solutions that do not require dealing with the thermal stresses that are a part of other repair processes, such as welding or thermal spray. An attractive proposition during repair would be to upgrade the component with a new functional coating using cold spray, especially considering the life extension of structural engineering components. In some cases, by the time the part comes for repair, after 2 to 4 years of service, the new-make product has undergone upgrades in design and therefore proves to be very expensive to replace. The best alternative is an overlay coating that can provide the product upgrade with superior properties and with

no major detriment to the substrate properties, via the cold spray technique. Such a coating will greatly enhance the product value to customers.

In addition to the features listed in Chapter 7, “Cold Spray Coating Applications in Protection and Manufacturing,” in this book, cold spray coating offers the following advantages specifically in the repair and refurbishment of structural engineering components:

- Ability to perform localized or patch repair
- In situ field repair, eliminating disassembly/reassembly and complete teardown
- Ease of scalability from the coupon level
- Repair production yield by salvaging parts with defects and reclaiming field-returned parts

Popular metals and alloys that have been reclaimed using this technology in dimensional restoration and repair include magnesium and its alloys, nickel and its alloys, low-alloy steels, stainless steels, cast iron, titanium and its alloys, and aluminum and its alloys. Repairs of these materials have been performed for wear, erosion, corrosion, cavitation, weld replacement, and other problems associated with service. Table 11.1 summarizes some of the industrial sectors in which cold spray coatings have been applied to date, along with some of the future applications.

To qualify a cold spray coating for repair, various statutory tests must be performed. Going from the coupon level to a prototype geometry typically takes several optimization trials. Table 11.2 lists some of the tests used in the aerospace, oil and gas, and gas turbine repair applications; first and foremost are the coating microstructure, density, phase evolution (for alloy systems), and distribution (for composite coatings). The

Table 11.1 Cold spray applications in repair and refurbishment

Application	Coating materials	Industry sector
Corrosion mitigation	Ni, Ti, Ta, Nb, Al, Mg, Zn and their alloys	Aerospace Oil and gas Petrochemical
Cavitation wear resistance	Co Alloys, Stellite6 WC-Co, Cr3C2-NiCr	Aerospace Power generation
Anti-fretting erosion resistance	Ni Alloys	Oil and gas
Bio-materials	Ti Alloys Mg Alloys	Medical
Thermal management conductive tracks	Cu Al Cu-W	Electronic Automotive
Oxidation and hot corrosion	Ni Alloys MCrAlY composites	Aerospace Power generation Oil and gas

Table 11.2 List of tests used for repair qualifications

Test	Repair qualifications
Microstructure	Coating microstructure Porosity Roughness Interface structure Residual stress Almen strips Oxygen content
Mechanical Tests	Hardness Flat tensile test – free standing coatings Tubular tensile test (TCT) Bond adhesion test ASTM C633 Fatigue – RCB Impact ASTM D5420 Erosion – ASTM Abrasive wear ASTM G65 Plastic strain bend test
Corrosion	Unscribed ASTM B117 Scribed ASTM B117 Galvanic corrosion Accelerated corrosion ASTM G61 Crevice corrosion G78 Beach corrosion

coating surface finish and residual stress play especially important roles in applications in which it is common for localized or patch repairs to be carried out. The hardness of the coating, typically expected to be at least 20% higher than that of the base material, is of importance in gaging the life of the coating, because these coatings typically tend to have little or no ductility. Due to the nature of the process, where the metal undergoes severe plastic deformation, the coatings tend to be under a compressive residual stress. Assessments of the thermal stability of the coating and of the effect of deformation on the substrate are both imperative in studying the life cycle of the coatings. Fatigue, corrosion, erosion, and the tensile adhesion strength are all integral to the coating assessment, especially for repair applications, in which, again, the coating is often applied as a partial or patch coating.

11.2 Aerospace Industry

Most of the repair applications that have recently started using cold spray as an affordable repair technology are in the aerospace sector, which makes use of aluminum, magnesium, titanium, and their alloys for reclamation of parts. Some of the examples discussed in this section are also described in Chapter 9, “Cold Spray Applications in the Defense Industry,” in this book.

One of the successful applications for cold spray is in repair of magnesium alloy parts (Ref 11.1–11.3) for U.S. Army and Navy aircraft components, such as fan blades, landing gears, transmission and gear box

housing for rotorcraft, and advanced fixed-wing aircraft parts. The UH-60, for example, has several parts that have been reclaimed using cold spray technology, resulting in enormous savings without having to replace old parts with new ones. Figure 11.1 (Ref 11.2) is an overview of the areas where magnesium housings are used (the main, intermediate, and tail gearboxes) on fairly large and expensive parts. Especially when these parts become corroded, this technology has become ubiquitous in lieu of replacing expensive parts and has thereby significantly reduced life-cycle costs.

The U.S. Air Force Research Laboratory (AFRL) has developed prototype repair capabilities and successfully implemented several cold spray repairs for large magnesium components in U.S. Air Force helicopters. Figure 11.2 shows reclamation of a magnesium transmission housing that has undergone significant corrosion in service exposure (Fig. 11.2a–c) and a dented gear box repaired using cold-sprayed Al-6061 (Fig. 11.2d, e) (Ref 11.2). Figure 11.2(f) shows a representative coating microstructure of dense aluminum on a magnesium substrate (0.8 mm, or 0.03 in.).

The efficacy of helium versus nitrogen gases was studied in optimizing the properties of the aluminum coating on a ZE41A magnesium alloy for microstructure, hardness, bond adhesion, and corrosion properties prior to implementation in the field (Fig. 11.3) (Ref 11.2). The coatings were optimized for a dense microstructure (<0.1% porosity) using helium and nitrogen process gases (Fig. 11.3a), with high hardness and tensile strength comparable to those of an Al-6061 alloy in the T6 heat treated condition (Fig. 11.3b), good adhesion strength as measured by ASTM C 633 (Fig. 11.3c) as well as a triple-lug shear test (Fig. 11.3d), and comparable corrosion properties to those of a high-velocity oxygen-fuel-

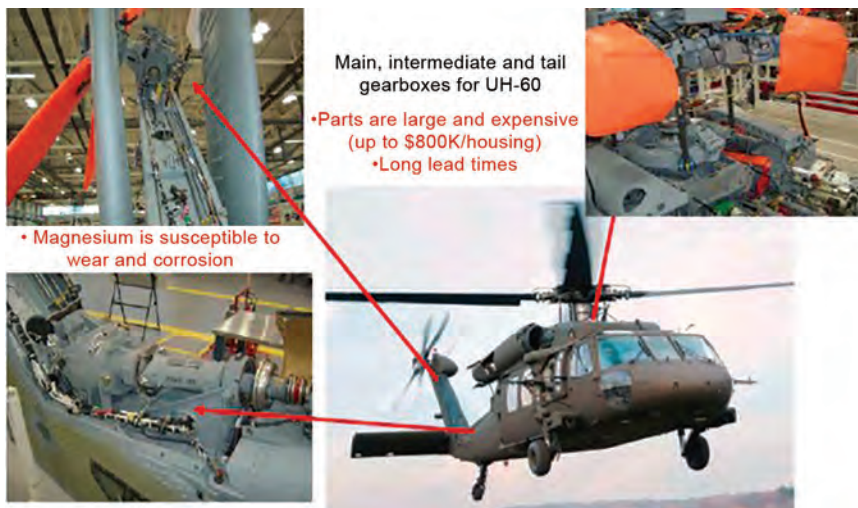


Fig. 11.1 Areas where magnesium housings are used in the UH-60. Source: Ref 11.2

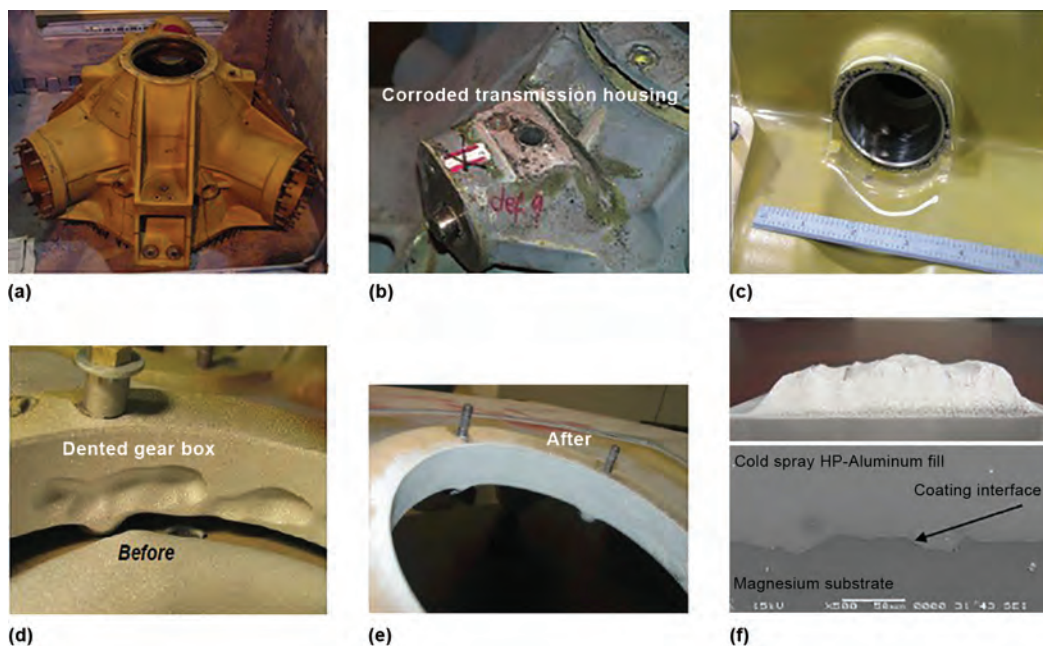


Fig. 11.2 Magnesium repair by cold spray in the UH-60 helicopter. (a and b) Corroded transmission housing that was repaired by using (c) a cold-sprayed commercial-purity aluminum/Al-6061 coating. (d) Dented gear box component before and (e) after cold spray coating. (f) Macro- and microstructure of a thick (up to 6 mm, or 0.24 in.), dense coating. Source: Ref 11.2

sprayed Al-12Si coating (Fig. 11.3e). The tensile adhesion test resulted in a glue failure on different magnesium substrates (ZE41A, Z91C-T6, EV31-T6) using helium gas, and predominantly a cohesive coating failure with nitrogen gas. However, in no instance was there any interface failure with the substrate. Similar repairs were carried out on the helicopter tail, as shown in Fig. 11.4(a), to get rid of the corrosion pits by placing a new overlay aluminum coating on top of the magnesium alloy (Ref 11.4). Figure 11.4(b) shows a dented tee-box housing made of cast aluminum that has undergone a cold spray repair (Ref 11.4). Figure 11.4(c) shows cold spray coatings used as shim replacements in a helicopter transmission housing (Ref 11.2).

Aluminum cold spray coatings have been successfully used for the restoration of aluminum propellers on military engines (Ref 11.5, 11.6) without compromising the substrate properties. The repair can be performed both in the shop with a high-pressure stationary system as well as in the field with a portable low-pressure cold spray system (Ref 11.4, 11.7–11.13), depending on the application. Figure 11.5 shows an application that has been able to employ a portable low-pressure cold spray unit to successfully repair a helicopter rotorcraft mast. Since that time, vendors have begun performing similar work using high-pressure systems.

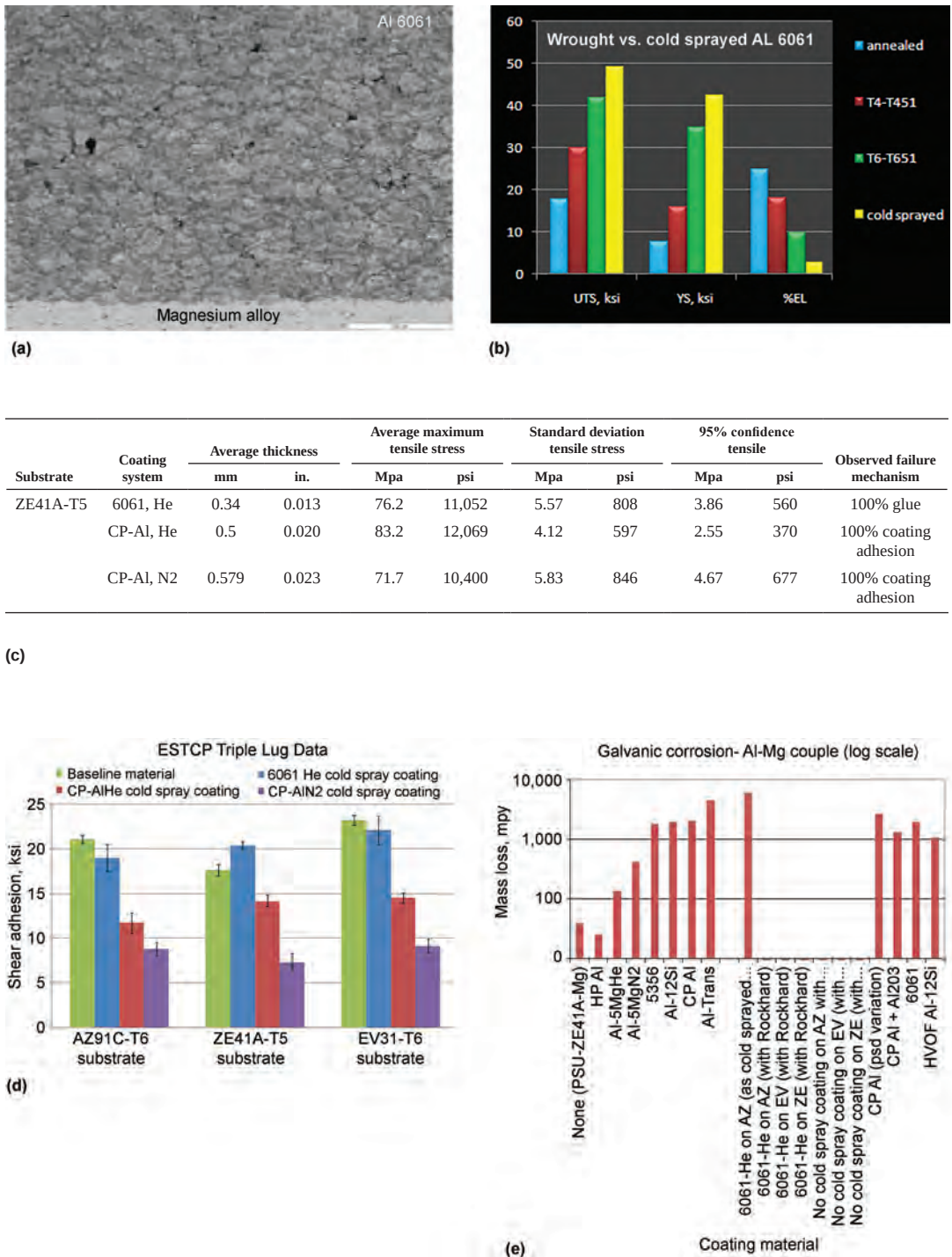


Fig. 11.3 (a) Dense (99.9%) microstructure of Al-6061 cold-sprayed coating on a magnesium substrate. (b) Comparison of wrought vs. cold-sprayed Al-6061 mechanical strength. (c) Bond adhesion test for cold-sprayed aluminum. (d) Lug shear test on different magnesium substrates. (e) Galvanic corrosion comparison for the aluminum-magnesium couple. Source: Ref 11.2

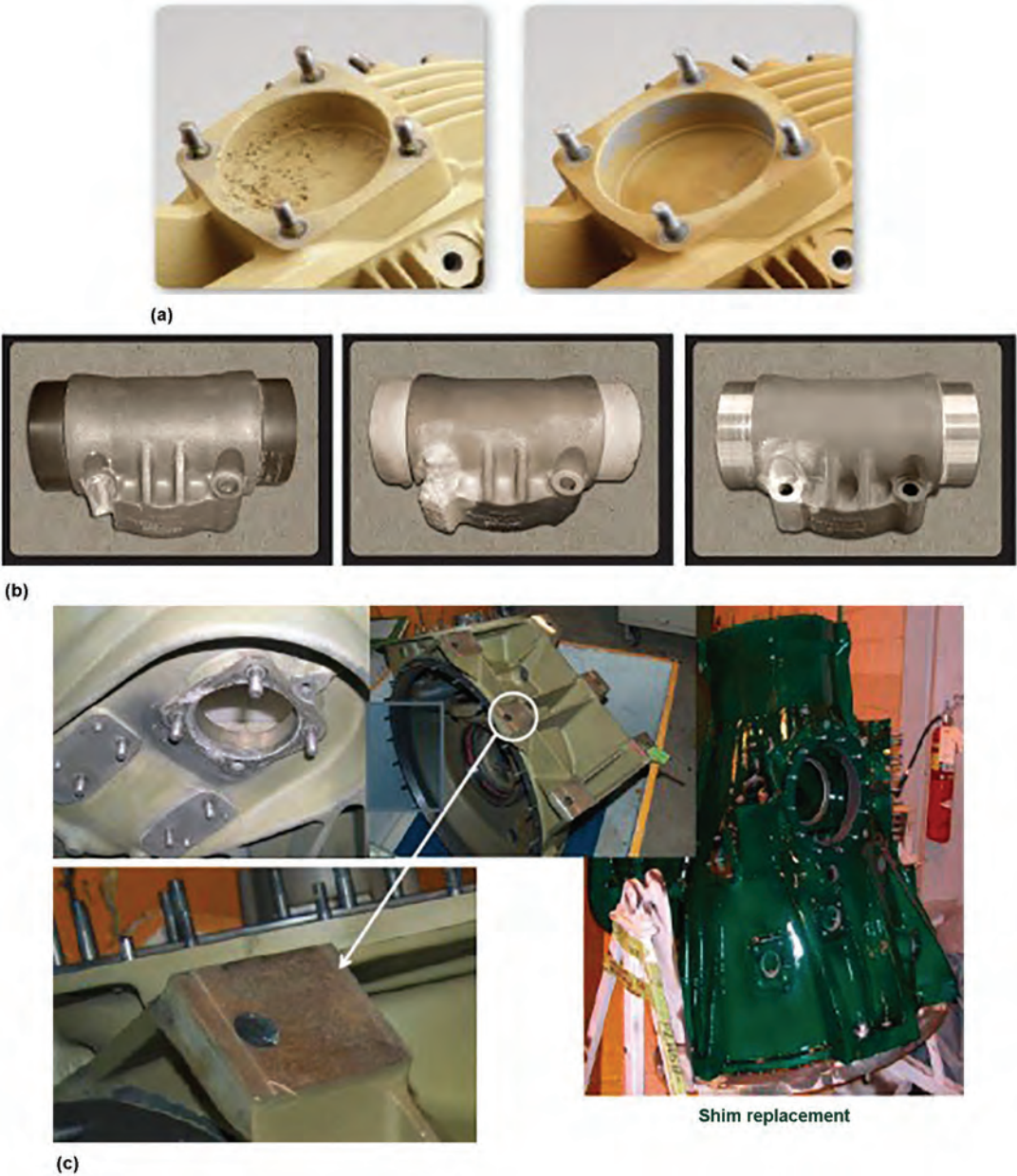


Fig. 11.4 High-pressure cold-sprayed aluminum on magnesium, using nitrogen gas. (a) Helicopter tail housing corrosion. (b) Transmission tee box. Source: Ref 11.4. (c) Shim replacement. Source: Ref 11.2

Moreover, as noted in Chapter 4, “Cold Spray Equipment,” in this book, portable high-pressure systems have been developed.

Leyman and Champagne (Ref 11.5) have reported good coating hardness and bond adhesion of commercial-purity (CP) aluminum as well as

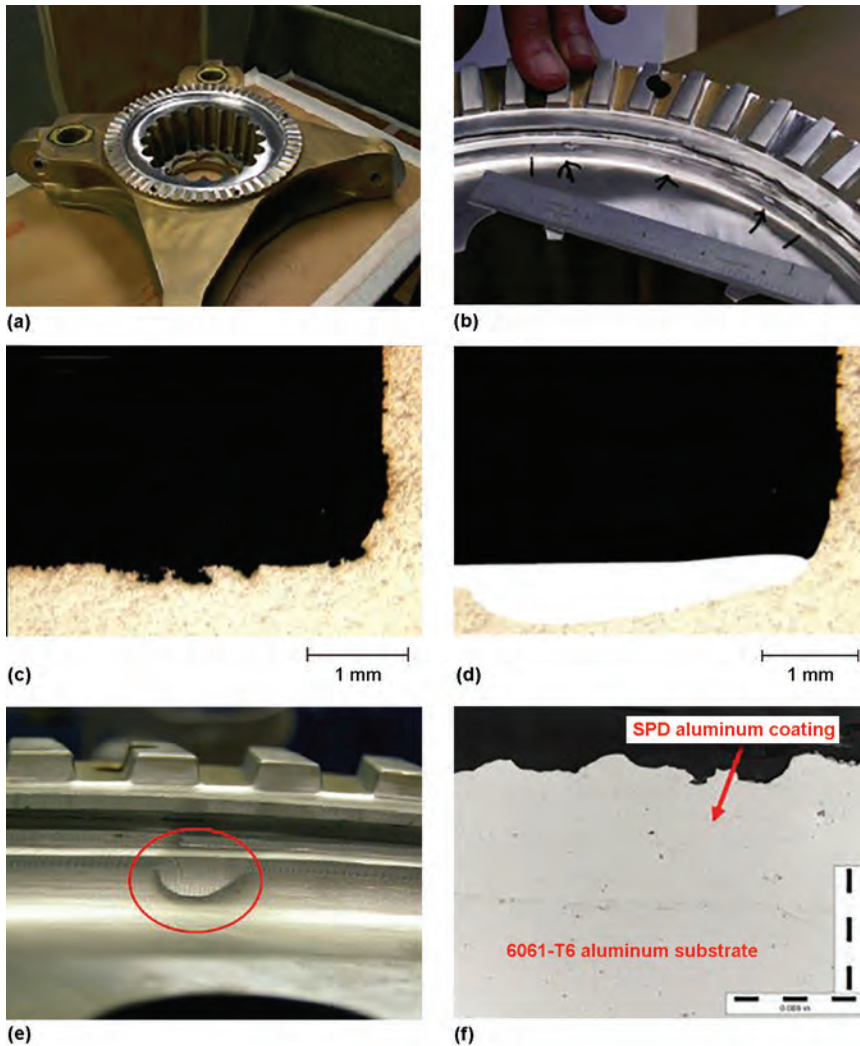
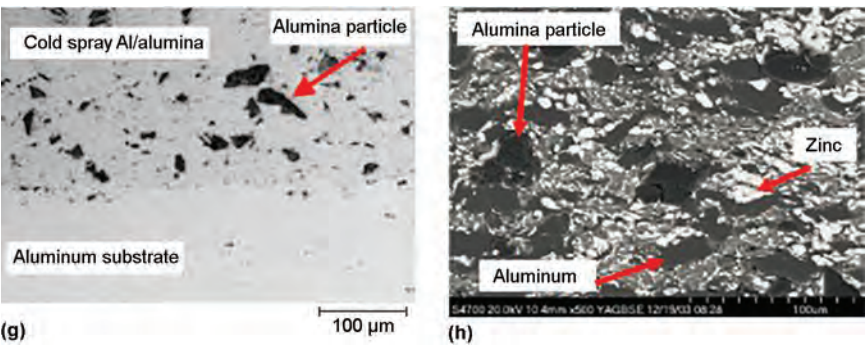


Fig. 11.5 (a–h) Low-pressure cold spray repair, using a portable unit. (a) Al-7075-T73 helicopter mast with (b) corrosion pits in the lower lip of the snap ring groove. (c) Cross section of the pitted surface. (d) Pitted surface ground and rebuilt to print using the cold-sprayed coating. (e) Macro picture of the repaired corrosion pit. (f–h) Aluminum-base cold-sprayed coating microstructures from (f) commercial-purity aluminum, (g) Al-30vol%Al₂O₃, and (h) Al-15%Zn-25%Al₂O₃. (i) Bond adhesion strength and hardness of these coatings. (j) Fatigue response of the coatings. Source: Ref 11.5

Al-Al₂O₃ and Al-Al₂O₃-Zn composite coatings (100 to 150 μm thick) onto an Al-7075-T73 alloy, with excellent mechanical properties and corrosion response. The composite coatings were used to impart better hardness than a soft CP aluminum coating could have provided. Figure 11.5(a–d) illustrate the corroded portion of the mast, which has been repaired with an aluminum coating. Figure 11.5(f–h) show representative dense microstructures taken from the three types of coatings, along with



Powder	Vickers hardness	Bond strength	
		Mpa	psi
Cp aluminum	46.2	22.75	3300
A050	60.1	56.42	8184
A027	66.9	34.12	4948

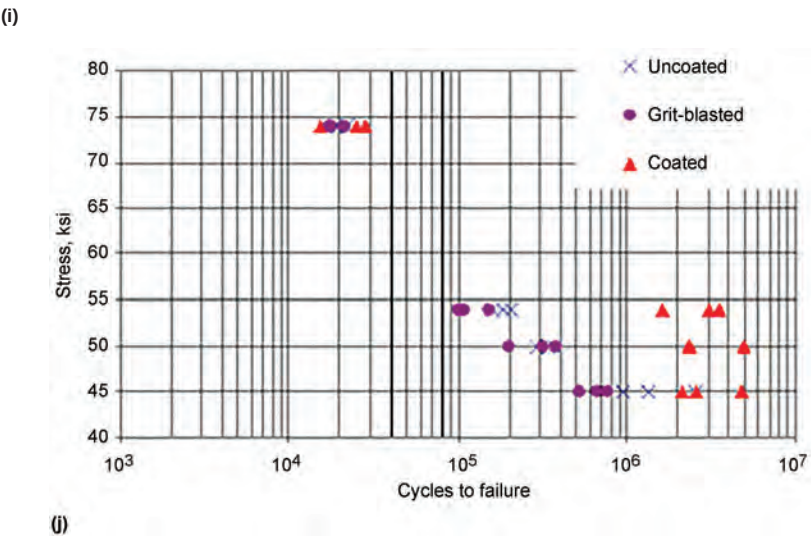


Fig. 11.5 (continued) (a–h) Low-pressure cold spray repair, using a portable unit. (a) Al-7075-T73 helicopter mast with (b) corrosion pits in the lower lip of the snap ring groove. (c) Cross section of the pitted surface. (d) Pitted surface ground and rebuilt to print using the cold-sprayed coating. (e) Macro picture of the repaired corrosion pit. (f–h) Aluminum-base cold-sprayed coating microstructures from (f) commercial-purity aluminum, (g) Al-30vol%Al₂O₃, and (h) Al-15%Zn-25%Al₂O₃. (i) Bond adhesion strength and hardness of these coatings. (j) Fatigue response of the coatings. Source: Ref 11.5

the comparative bond adhesion strengths (Fig.11.5i), and Fig. 11.5(j) shows that the cold spray coating has a marginally better fatigue life than the parent Al-7075 and the grit-blasted bare substrate. The corrosion response of the coating was also evaluated and found acceptable for repair of aluminum components. Other components, such as dam-

aged snap ring grooves (Fig. 11.6a) and dented splines (Fig. 11.6b) (Ref 11.5) belonging to a helicopter mast, have been repaired using cold-sprayed aluminum. Figure 11.6(c) shows a transmission housing dent that has been repaired (Ref 11.10).

Other components that have been repaired include the airframe-mounted accessory drive (AMAD) transmission housing cover, ion vapor deposition aluminum repair, AH-1 and UN-1N support case mount foot, and H-60 tail cone bulkhead (Ref 11.10). There are extensive applications in naval submarines, where this technology has been used for repair of seawater pumps, air compressors, motor casings, and so on, especially due to the unavailability of casting vendors with a short lead time for

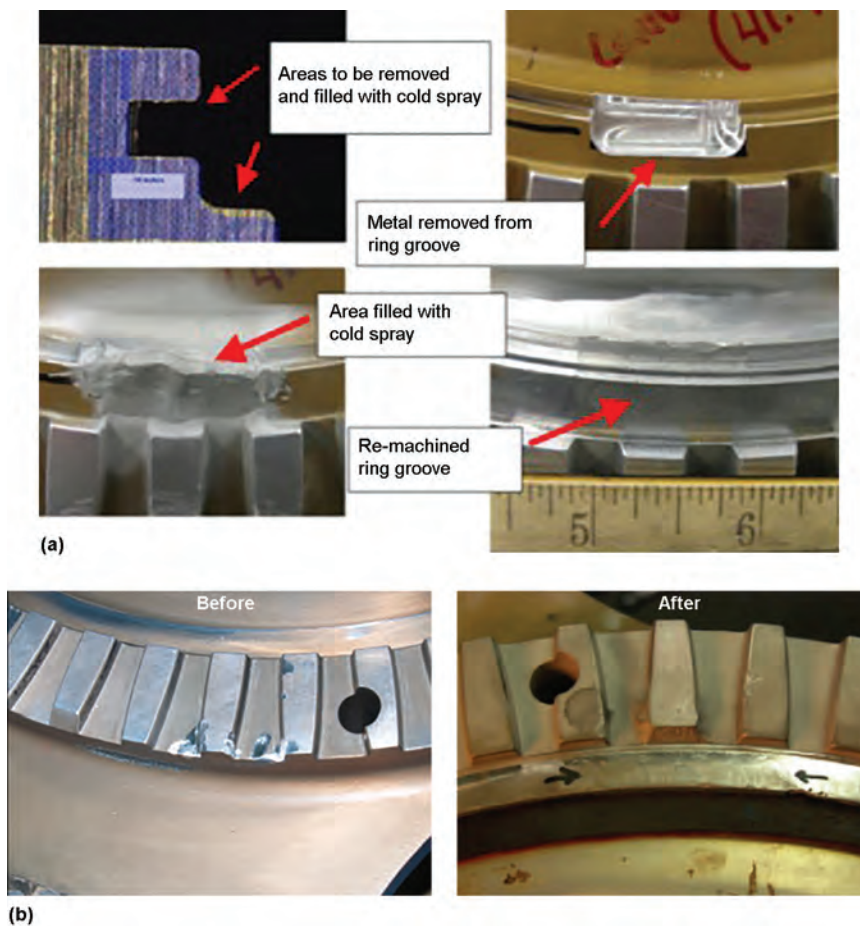


Fig. 11.6 Examples of aluminum cold-sprayed coatings to repair mechanically damaged parts on an Army helicopter mast support. (a) Snap ring groove and (b) splines filled with cold-sprayed aluminum to restore original dimensions. Source: Ref 11.5, 11.6. (c) Naval helicopter transmission housing repaired using the low-pressure cold spray system. Source: Ref 11.10

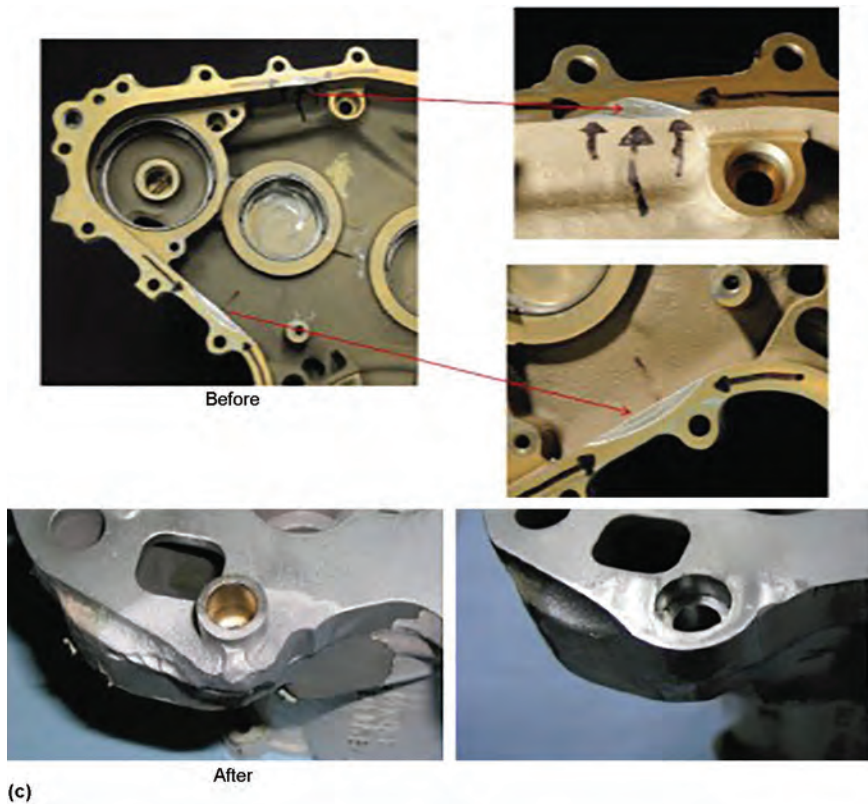


Fig. 11.6 (continued) Examples of aluminum cold-sprayed coatings to repair mechanically damaged parts on an Army helicopter mast support. (a) Snap ring groove and (b) splines filled with cold-sprayed aluminum to restore original dimensions. Source: Ref 11.5, 11.6. (c) Naval helicopter transmission housing repaired using the low-pressure cold spray system. Source: Ref 11.10

replacement of these parts (Ref 11.10). Figure 11.7(a) shows a repair application on a TD-3 valve actuator body for the U.S. Navy, with corrosion and sealing surface repair. Figure 11.7(b) shows an AMAD housing body that is about to be repaired using cold-sprayed coating. The challenges during actual repair are in masking points and inside corners. Repairing aluminum panels using cold spray, rebuilding worn regions after service, and rebuilding bolted locations that undergo wear and corrosion were successfully beta-tested and implemented, as shown in Fig. 11.8(a and b) for defense applications and in Fig. 11.8(c) for civilian aircraft repairs (Ref 11.6, 11.10). There have been attempts to cold spray brass as well as bronze for several auxiliary components related to naval applications. This was able to save over 70% of the replacement cost for the customer and provide a better solution for wear and corrosion.

There are reports of dense aluminum and composite coatings for repair of steels and cast iron repair. Kashirin et al. (Ref 11.12, 11.13) have

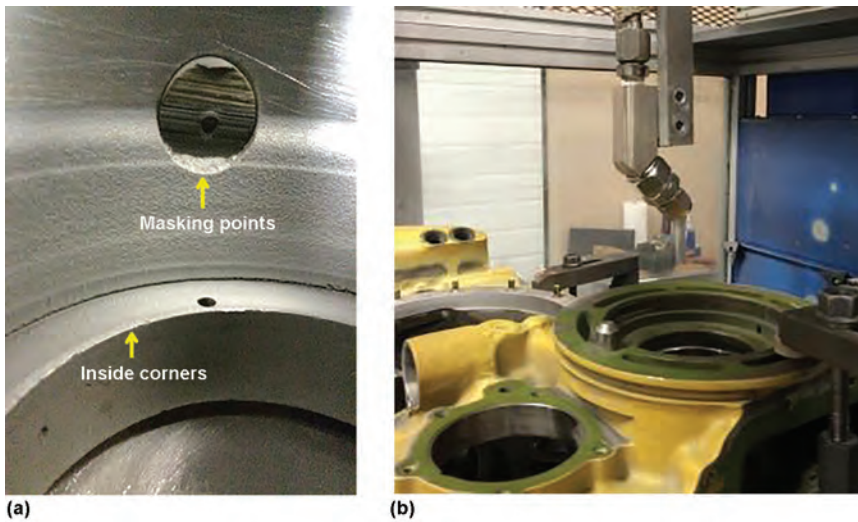


Fig. 11.7 (a) Corrosion and sealing surface valve actuator body repair application (TD-3, U.S. Navy), using cold-sprayed aluminum on steel. (b) Airframe-mounted accessory drive housing repair buildup. Source: Ref 11.14

achieved cold-sprayed coatings with good adhesion strength of these composite coatings, as shown in Fig. 11.9, which indicates the structural integrity of an Al-SiC cold-sprayed coating on a steel substrate and an Al-Al₂O₃ coating on a cast iron part, measuring up to several millimeters in thickness. The same authors have successfully produced copper and zinc coatings for similar applications using the low-pressure cold spray process, indicating that similar results can be achieved in the shop with high-pressure equipment.

In a technical breakthrough for materials and alloys that are difficult to repair by conventional means, such as welding, it is now commonplace to use the cold spray process to provide a buttering layer for crack-sensitive alloys during welding. This prevents liquation cracking during subsequent welding repair. Difficult-to-weld Al-6061 and Al-6082 have been repair-welded by using a cold spray coating of Al-4047 as a buttering layer (Ref 11.15). Figure 11.10 (a and b) are a comparison of the weld crack in an Al-6082 alloy that has been repaired using a cold-sprayed buttering layer, resulting in a crack-free weld. This has enabled enormous savings in productivity for difficult-to-repair alloys. The weld mechanical properties (hardness) and weld integrity were tested and shown to exhibit less crack sensitivity when using the cold-sprayed buttress layer. This is especially beneficial for complex geometries.

Titanium alloy components have been successfully repaired, as shown in the case study in Fig. 11.11(a), which shows a tubing repair of a hydraulic line followed by machining to the required finish (Ref 11.16). Chafing is a common issue in hydraulic tubing due to vibrations and

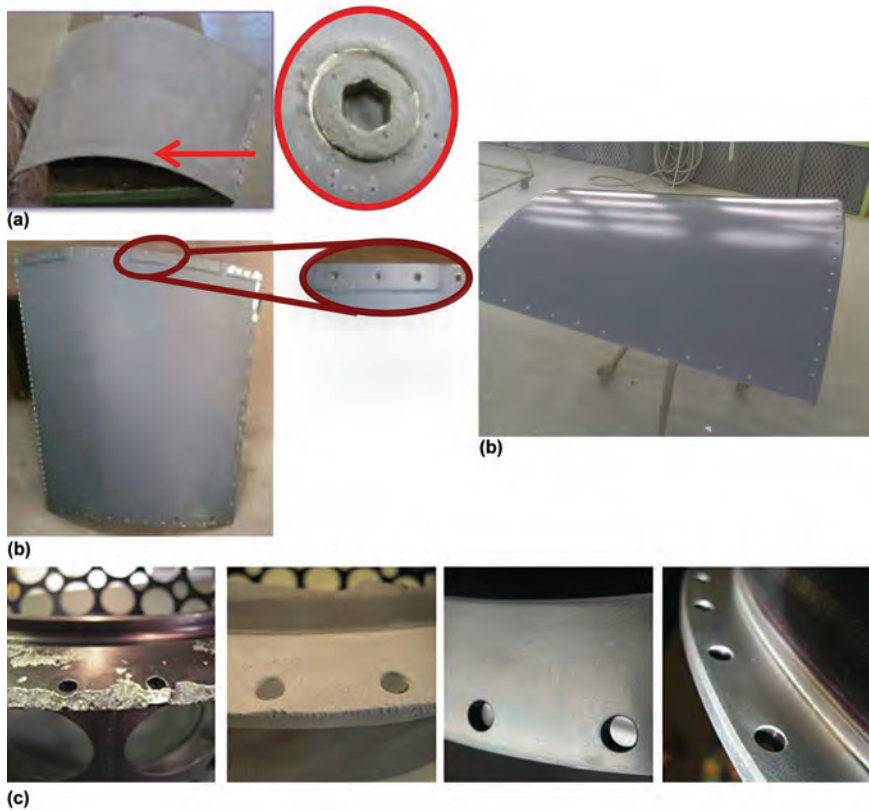


Fig. 11.8 (a and b) Repair of a B-1 bomber nonstructural component. (a) Skin panel for wear at fastener holes. (b) External doubler repair. Source: Ref 11.14. (c) Repair of an aluminum component in a commercial aircraft by the low-pressure cold spray system to protect against corrosion. Source: Ref 11.6

abrasive action. Such tubing can now be repaired by cold spray in a localized region, as shown in Fig. 11.11(b). This has resulted in significant cost reduction in maintenance man-hours as well as operational readiness for B-1 bombers and various other applications. A number of optimization studies were carried out using various cold spray systems with differences in the pressure, nozzles, and particle shape and size, as shown in Fig. 11.12 (a–d). While dense coatings with good adhesion strength have been achieved using helium gas, there is still scope for improvement using nitrogen gas. The adhesion strengths of CP-Ti on Al-6061 as well as Ti-6Al-4V are shown in the table in Fig. 11.12(b). In this case, due to the complex geometry and accessibility of the component location that must be repaired, a number of different cold spray systems, including a manual one, were tried to arrive at the optimum coating for repairing the part.

Pure nickel is used as a functional upgrade for building more corrosion-resistant materials in a nose wheel steering actuator barrel (made of IN738)

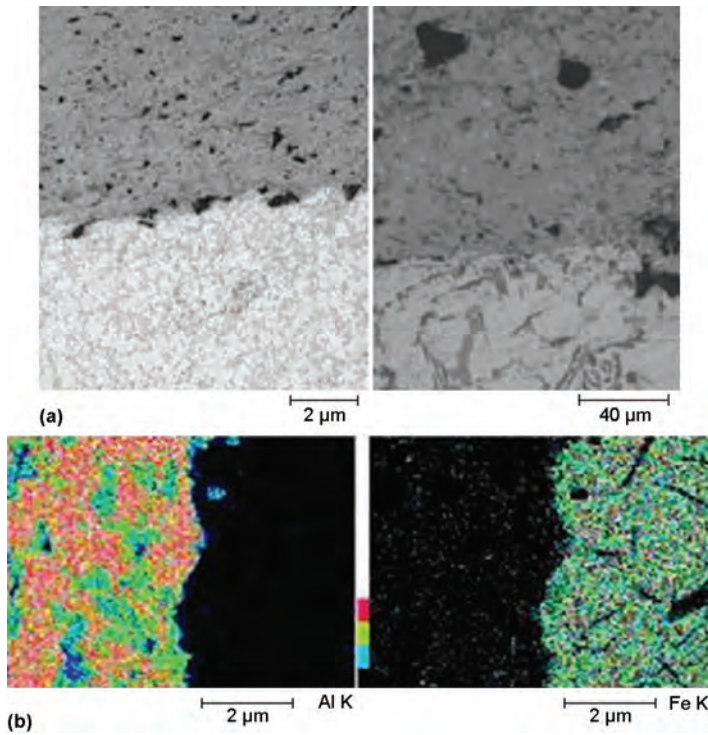


Fig. 11.9 Composite coatings using the low-pressure cold spray system for repair. (a) Al-SiC coating on steel. (b) Al-Al₂O₃ coating on cast iron. Source: Ref 11.12, 11.13

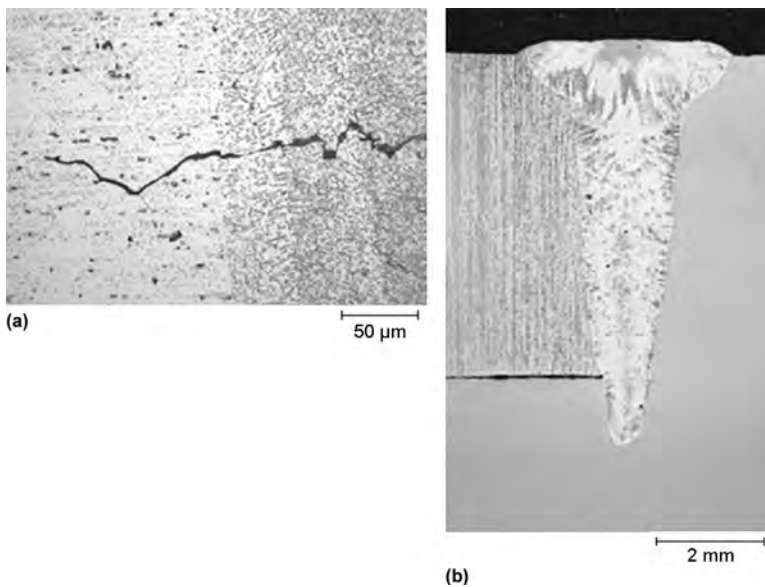


Fig. 11.10 (a) Crack in electron-beam-welded aluminum alloy Al-6061 (right: weld metal; left: parent metal). (b) Crack-free electron beam weld in Al-6082 alloy made with cold-sprayed buttering layer using Al-4041 alloy. Source: Ref 11.15. Courtesy of TWI Ltd.

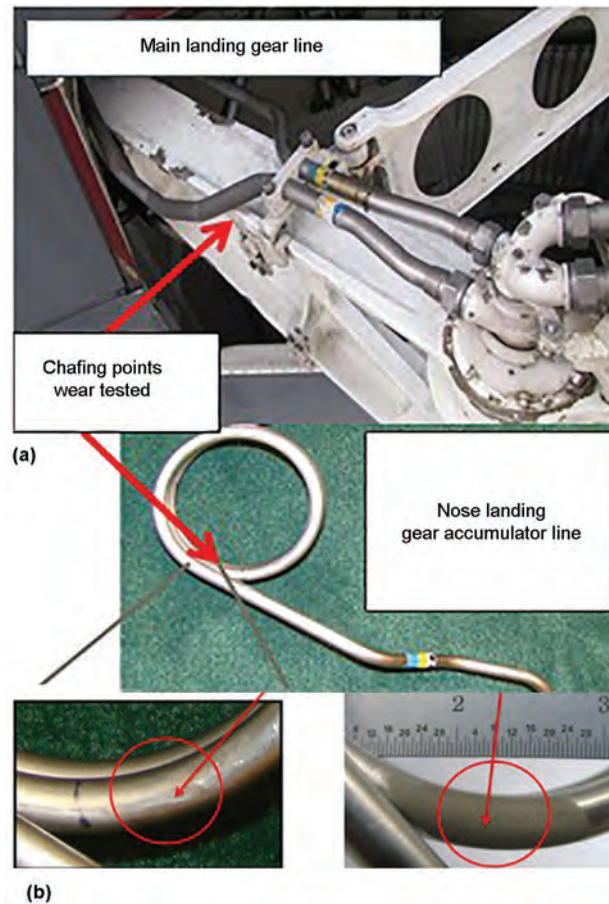


Fig. 11.11 (a) Chafing of hydraulic tubing. (b) Repair by cold-sprayed titanium. Source: Ref 11.16

of an aircraft (Ref 11.4). The part is located at the front of the aircraft, where it is exposed to moisture and dirt, which cause the gear to corrode, as shown in Fig. 11.13(a). A cold-sprayed nickel coating proved to be a very cost-effective alternative and, in addition, served to extend the component life by improving the corrosion life even beyond that of the original material. Another example is a B-1 bomber axle repair on worn aluminum bearing surfaces by means of a nickel cold spray buildup, as shown in Fig. 11.13(d) (Ref 11.10). One of the challenges faced was that the uniformity of structure and properties for layer thickness is not always easy to predict on large buildups. Figure 11.14 is a summary of the AFRL's implementation of cold spray technology for repairs of various helicopters, bombers, and fighter planes, for different types of components from the nose cone to the tail end housing, for aluminum, magnesium, and titanium materials (Ref 11.1–11.3).

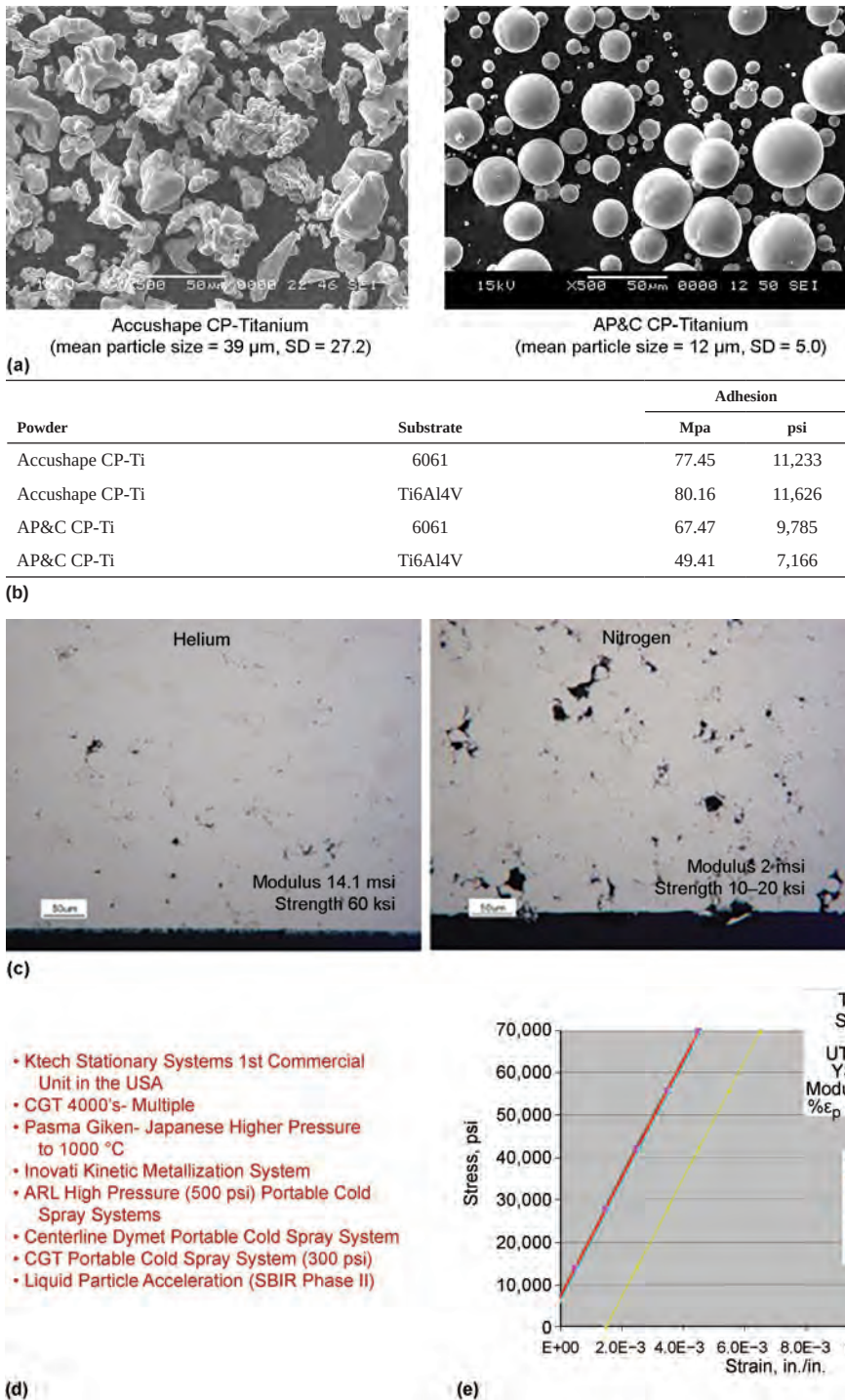


Fig. 11.12 (a and b) Optimization of cold-sprayed titanium on the Ti-6Al-4V chafing tubing repair by using different types of powders. (b) Bond adhesion strength of the different powders. (c) Coating microstructure comparison between helium and nitrogen process gas. (d) Various cold spray systems used. (e) Tensile strength of the commercial-purity titanium cold-sprayed coating. Source: Ref 11.16

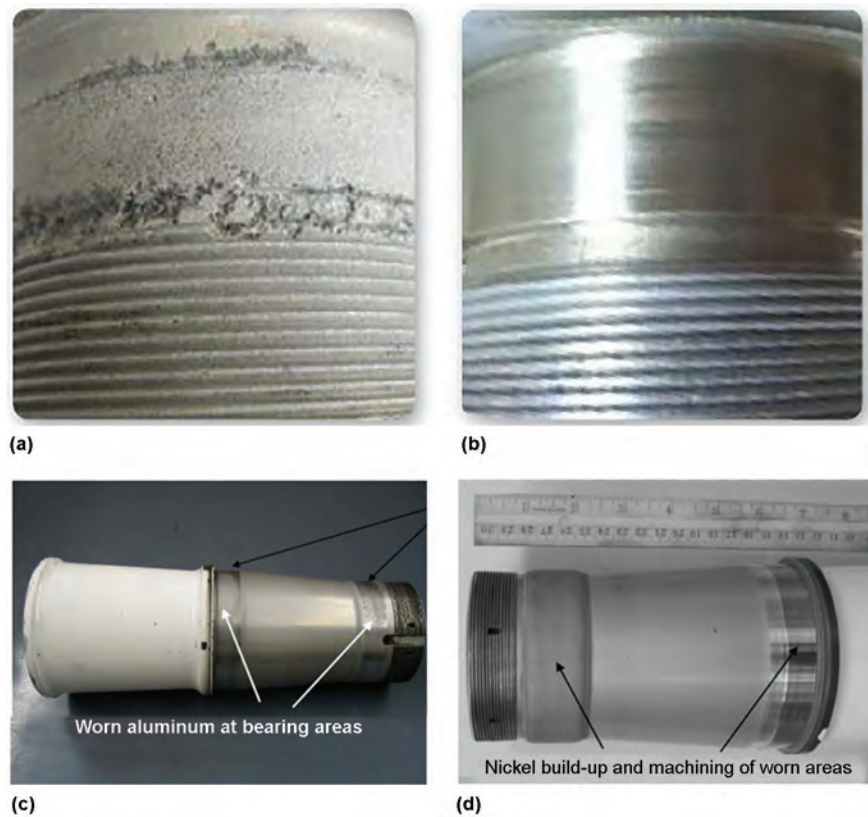


Fig. 11.13 (a) Corroded nose wheel steering actuator and (b) repair using cold-sprayed nickel onto a 737. Source: Ref 11.4. (c) Worn aluminum bearing area in a B-1 bomber and (d) nickel cold spray buildup machined to print. Source: Ref 11.2



Fig. 11.14 Cold spray repair applications, from prototype to the field. Source: Ref 11.2

11.3 Oil and Gas Industry

Subsea drilling and production components make use of workhorse alloys, including AISI 4130, 8630, and 4140 low-alloy steels. These are cathodically protected during new-make assembly, but during repair they undergo corrosion, wear, and, in some cases, erosion. The current industry practice is to weld-clad such a part with a corrosion-resistant alloy (CRA) (e.g., nickel-base Inconel 625) before returning it to service, in accordance with American Petroleum Industry norms. The repair process involves several steps: machining the entire part, cladding it with the CRA, subjecting the clad part to a postweld heat treatment, and machining to the component print dimensions. This process is time-consuming and, due to the high cost of the CRA, expensive if a significant amount of the alloy is used. Cold spray coating is an attractive alternative method for repairing these large structural components (Ref 11.17–11.25).

Figure 11.15 (Ref 11.19) illustrates some of the oil and gas components that are being considered for repair by cold spray coatings. Figure 11.15(a–c) show an example of a fluid-assist bearing with wear marks after service exposure, and Fig. 11.15(d–f) show a riser with a choke-and-kill pin that exhibits pitting corrosion. Cold spray repair of these components can avoid a number of steps, such as machining away a large amount of the steel, carrying out a patch repair, and performing a stress-relieving heat treatment after weld cladding.

A number of repair applications are being addressed by researchers at General Electric (Ref 11.17), with various types of nickel-base superalloys sprayed via the cold spray process. Dense, pore-free Inconel 625 and NiCr coatings of up to 3 mm (0.1 in.) in thickness were deposited on AISI 4130 steel substrates, as shown in Fig. 11.16(a) (Ref 11.19), using high-pressure cold spray to establish the proof-of-concept of these coatings in lieu of repair with weld cladding (Ref 11.17–11.25). The coating microstructure, the bonding mechanism, and the coating relaxation behavior were studied to establish the feasibility of the application. The hardness was approximately 500 to 550 Vickers hardness (HV) using helium as the process gas and approximately 420 to 480 HV using nitrogen as the process gas (Fig. 11.16b) (Ref 11.19). Figure 11.16(c) (Ref 11.19) is a plot of the residual stress of the coatings before and after heat treatment, revealing the complete relaxation of the compressive stress at 650 °C (1200 °F). Upon heat treatment, a hardness increase was observed in the Inconel 625 coatings up to 700 °C (1290 °F), followed by a decrease at higher temperature (Fig. 11.16b).

Srinivasan et al. (Ref 11.20–11.28) have carried out detailed microstructural characterization of the coating structure that revealed very fine grains in both the Inconel 625 and the NiCr in the as-sprayed condition, imaged via transmission electron microscopy. Upon heat treatment, the Inconel 625 alloy coating revealed a fine-grained recrystallized struc-

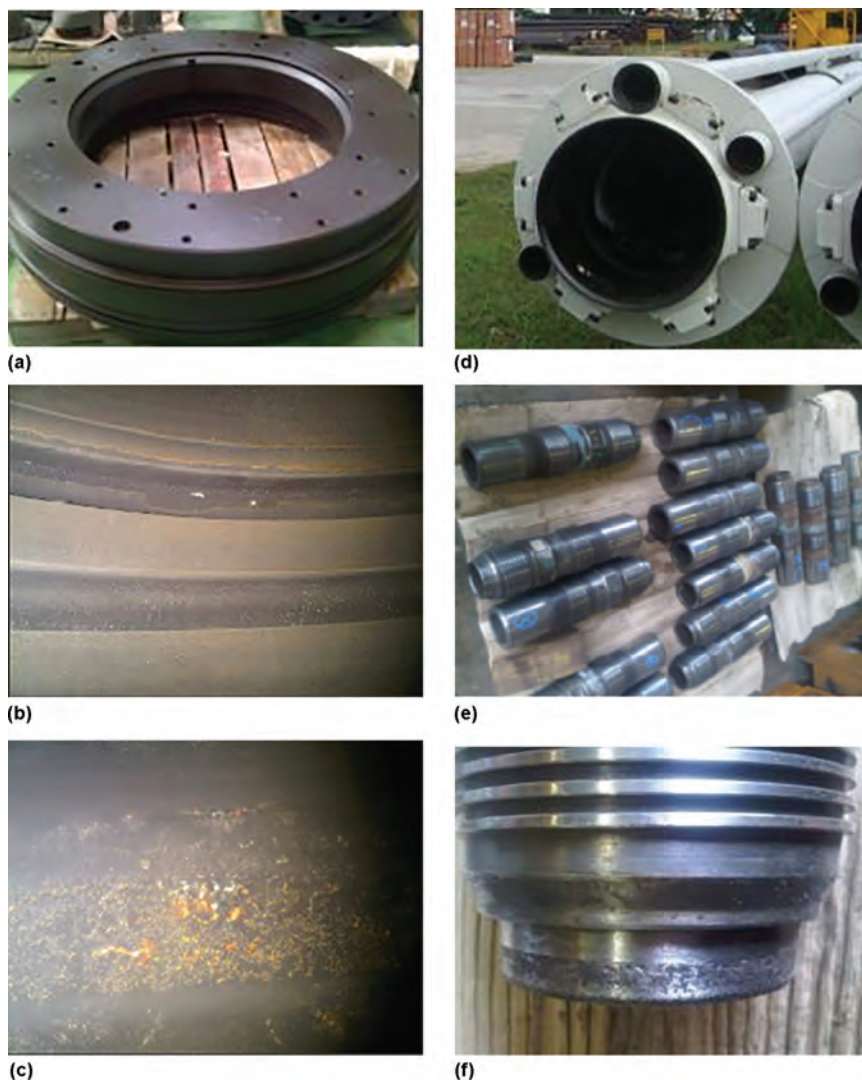


Fig. 11.15 (a–c) Oil and gas subsea drilling and production component. (b and c) Corroded and worn areas on the groove that (d) is connected using (e) the choke-and-kill pin. (f) Pitting corrosion on the choke-and-kill pin. Source: Ref 11.19

ture (<100 nm), whereas the NiCr had recrystallized into much larger grains. In addition, unlike in wrought alloys, they found a strain-induced phase transformation in Inconel 625 cold-sprayed coating, leading to a modified time-temperature-transformation diagram (Fig. 11.17) (Ref 11.21) that shows the thermal stability of the coating at elevated-temperature heat treatments.

A detailed characterization of the interface chemistry and the nature of bonding, metallurgical versus mechanical interlocking, was carried out by performing systematic heat treatments and mapping the diffusion kinetics

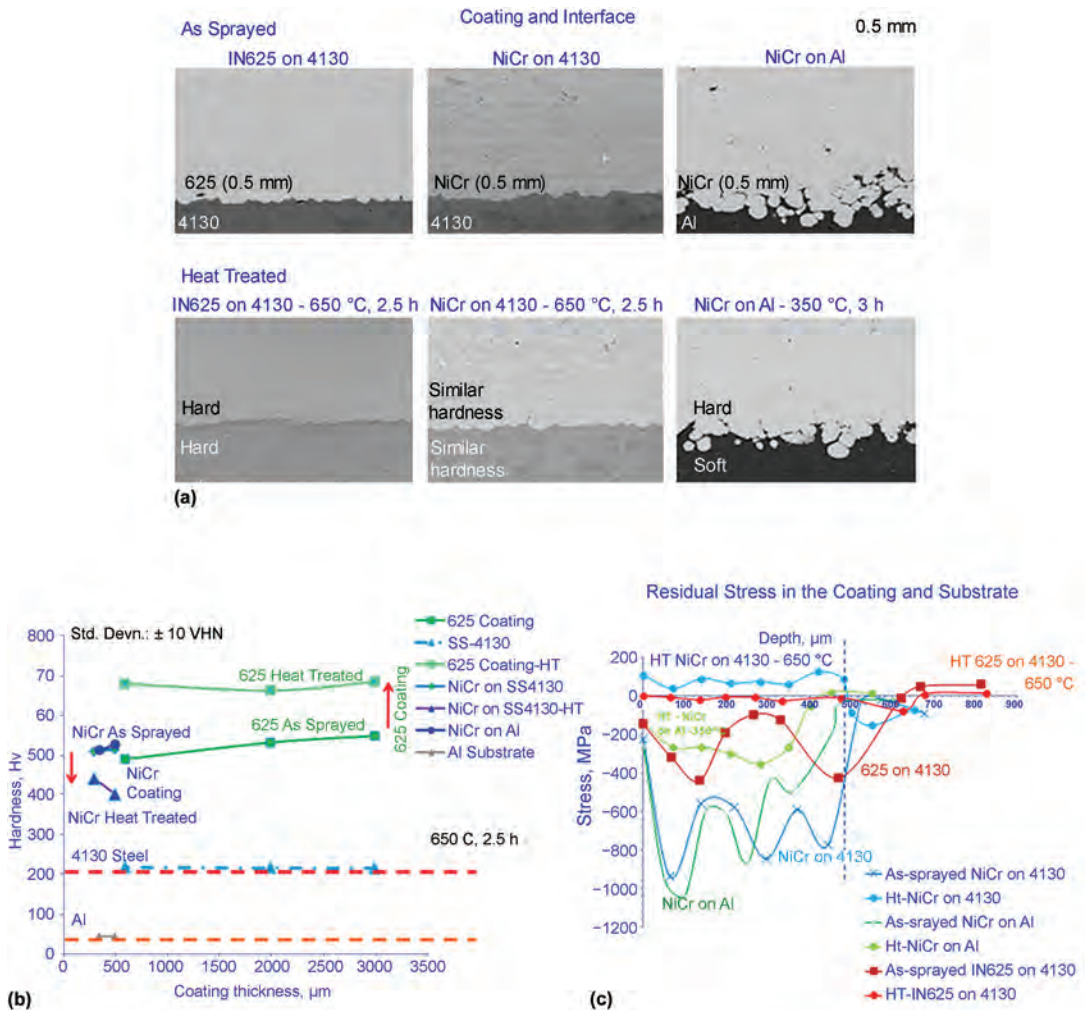


Fig. 11.16 (a) Dense coatings of Inconel 625 and NiCr on AISI 4130 steel with good bonding onto AISI 4130 and aluminum substrates. (b) Coating hardness in the as-sprayed and heat treated conditions. (c) Residual stress of the cold-sprayed coatings. Source: Ref 11.19

along the interface (Ref 11.22). The residual stresses of these coatings were studied to establish the longevity of the coating in service operation (Ref 11.25, 11.26). Correlations were made between the mechanical properties of the coatings, such as bond adhesion strength, hardness, and fatigue behavior, and their residual stresses. The corrosion response of these coatings revealed that the cold-sprayed Inconel 625 coatings, using both helium and N_2 as the process gas, gave good corrosion protection to the 4130 steel under cyclic polarization (0.5% NaCl solution) (Fig. 11.18a). In fact, a marginally better corrosion resistance was seen with the helium-sprayed coating than with bulk wrought Inconel 625. The bond adhesion strength of Inconel 625 as well as NiCr coatings demonstrated a

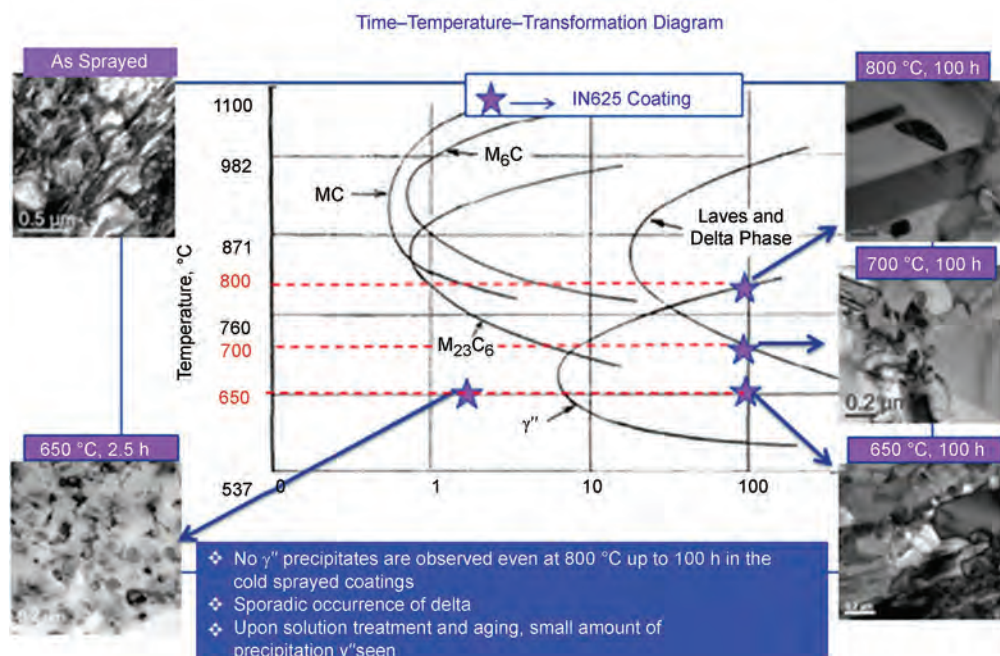


Fig. 11.17 Inconel 625 cold-sprayed coatings (helium) showing a modified time-temperature-transformation behavior as compared to bulk Inconel 625. Source: Ref 11.21

glue coating failure for helium-sprayed coatings (Fig. 11.18b). However, eight out of twelve tests showed an adhesive coating failure on the 4130 steel with nitrogen for Inconel 625, with strengths of 55 to 70 MPa (8000 to 10,000 psi), while three of them showed cohesive coating failure and only one had a glue failure. Upon heat treatment, there was an improvement in the bond strength of the coating showing glue failure (Fig. 11.18b). In the case of NiCr coatings, there was a similar behavior seen in the as-sprayed coatings using nitrogen gas, with all of them failing at bond strengths of 28 to 35 MPa (4000 to 5000 psi) (Ref 11.18, 11.19). Here again, upon heat treatment there was an improvement in the bond strength. There is still some scope for improving the parameters using nitrogen gas for Inconel 625 and NiCr coating to yield better adhesion in the as-sprayed condition. This was correlated with the residual stress of the coatings, as shown in Fig. 11.18(c and d) (Ref 11.25, 11.26).

11.4 Gas Turbines

Repair of gas turbine hot gas path components using cold spray is being tried by several original equipment manufacturers (OEMs). Many of these approaches are not published as extensively as those for new-make coat-

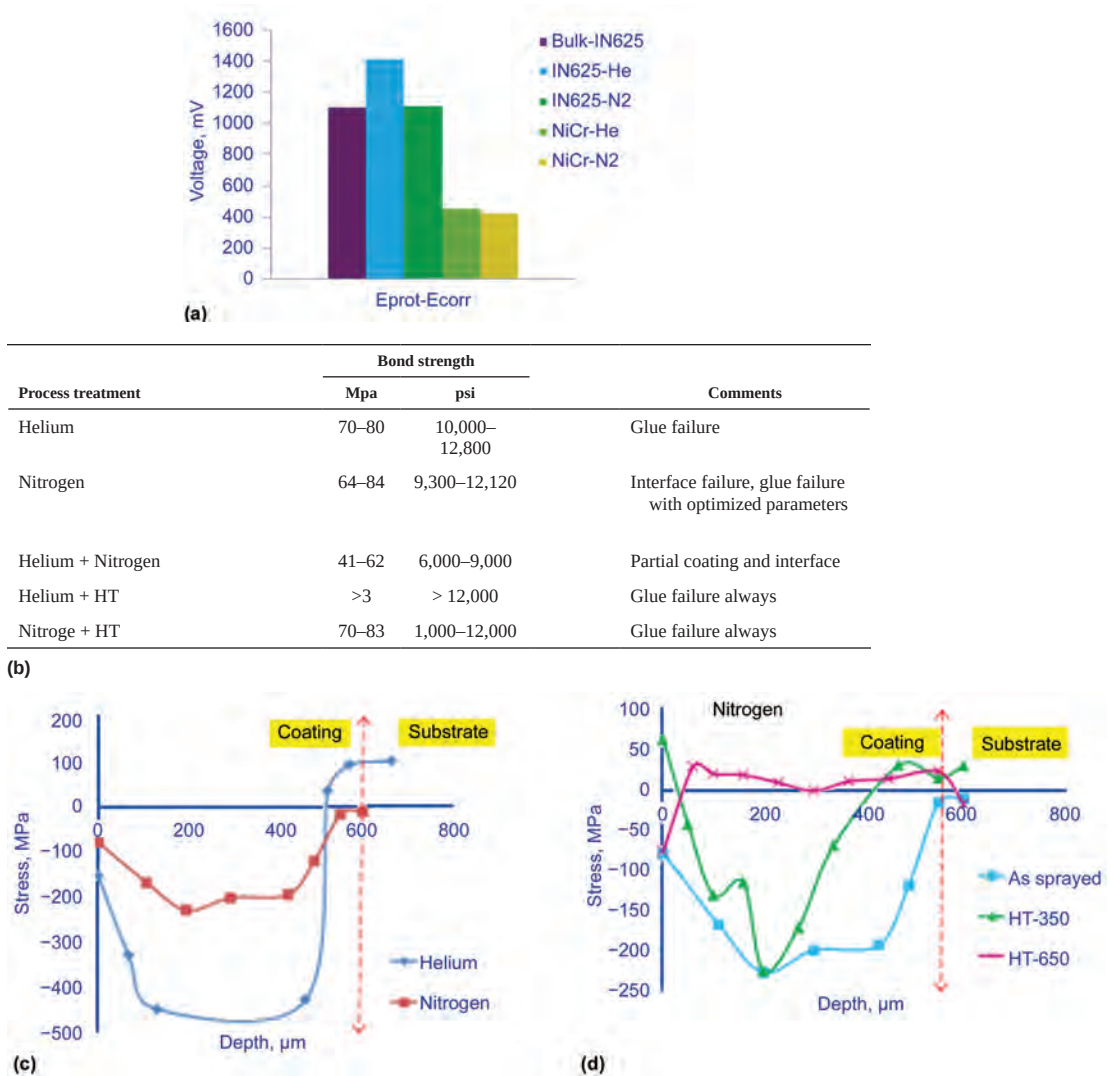


Fig. 11.18 Inconel 625 cold-sprayed coatings (helium vs. nitrogen). (a) Relative ranking of the pitting potential of Inconel 625 and NiCr cold-sprayed coatings. (b) Bond adhesion strength of Inconel 625 and NiCr coatings before and after heat treatment. (c) Residual stress behavior of helium vs. nitrogen. (d) Residual stress behavior of nitrogen before and after heat treatment. Source: Ref 11.23

ings, due to the proprietary nature of the technology and the highly competitive nature of the business in the services sector. However, a sufficiently large number of patents have been published to indicate the advances in repair in this domain, some of which are listed in Table 11.3. Niki has referred to the study of the durability of cold spray in the repair of degraded hot section components (Ref 11.29).

Ogawa and Seo have reported a detailed analysis of cold-sprayed Inconel 738 coatings (800 μm) on Inconel 738 substrates for possible repair of

Table 11.3 Patents related to cold spray applications in repair

Sl. No	Application No.	Title	Inventors (Affiliation)
1	US200729844A	Cold spray repair process	James Allister William, Gregg P. Wagner Brij B Seth (Siemens Westinghouse) Florida
2	US2007649574A	Sprayed weld strip for improved weldability	Davin Allen Allister James David Hunt (Siemens Energy, Orlanda, US)
3	US200883035A	Process for repairing a component with a directional microstructure	Jabado Rene, Jens Dahl Jensen Ursus Kruger Daniel Kortvelyessy Michael Ott Ralph Reiche Michael Rindler Rolf Wilkenhoner (Siemens, NY)
4	WO2013US72707A	Abrasive tipped blades and manufacture methods	Paul Faughnan R. Jr., Nardi Aaron Klecka Michael A UTC
5	US2004836560A	Component having wear coating applied by cold spray process	Seth Brij B., P. Wagner (Siemens, Energy)
6	US14066443A	Methods for cold spray repair	Chritian Widener Adam Well Owen Britton Brian James Rob Hrabe Victor Champagne
7	US13956431A	Localized repair of superalloy component	Anand Kulkarni JR, Ahmed Kamel Stefan Lampenschurf

gas turbine blades (Ref 11.30). Figure 11.19 shows representative micrographs from Inconel 738LC cold spray coatings for gas turbine repair. Figure 11.19(a) is a comparison of the porosity of coatings produced using nitrogen versus helium in the as-sprayed condition, with the nitrogen coatings having a higher porosity. There was an improvement in the coating density after heat treatment (Fig. 11.19c), along with improved tensile strength (Fig. 11.19d) and bond adhesion strength (Fig. 11.19e). Figure 11.19(f) is a representative microstructure after heat treating the cold-sprayed Inconel 738LC, displaying the γ' precipitates characteristic of the parent alloy. Optimizing nickel-base coatings for density and bond strength (>60 MPa, or 9000 psi) using a high pressure (2.5 to 3.5 MPa, or 360 to 500 psi) with helium as the process gas seems to be possible; however, there still remains work to be done on the use of high-pressure N₂ in terms of achieving good adhesion with the substrate for nickel-base superalloys (Ref 11.24, 11.27). In this case, enhancement in bond strength can be achieved by heat treatment, which also enables a better tensile strength and an improved ductility, in addition to diffusion between the coating and the substrate (Ref 11.20–11.22, 11.26).

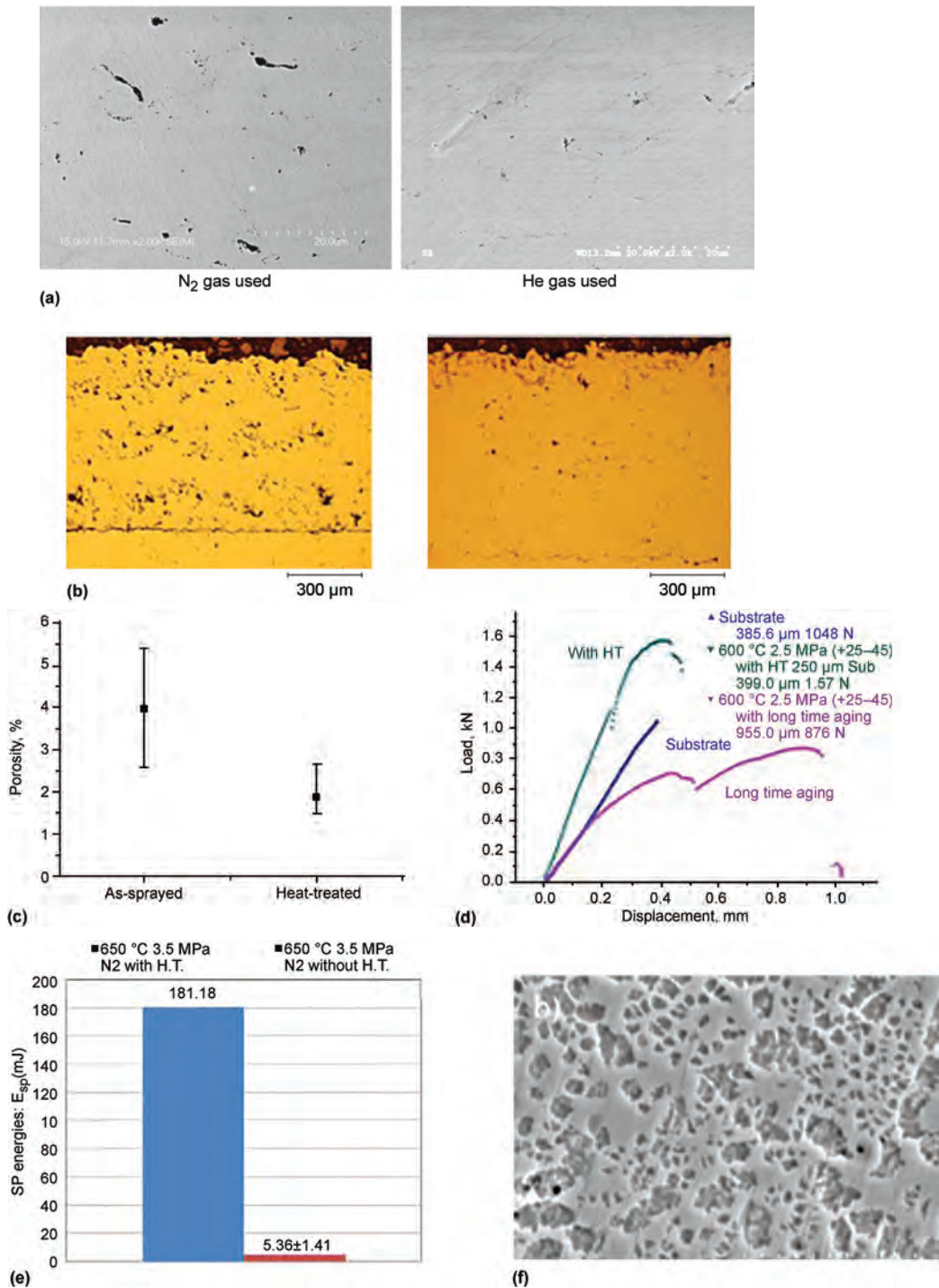


Fig. 11.19 Inconel 738LC cold spray coatings for gas turbine repair. (a) Nitrogen vs. helium in the as-sprayed condition. (b) Nitrogen coatings before and after heat treatment, revealing (c) decrease in porosity, (d) increase in strength and ductility, (e) increase in bond adhesion strength, and (f) γ' precipitates emerging in the heat treated coating. Source: Ref 11.26, 11.27

Stellite 6, a cobalt-chromium alloy, is well known for excellent wear resistance. Studies on using Stellite 6 coating for repairing gas turbine components reveal that the cold spray coatings predominantly consist of the high-temperature face-centered cubic cobalt solid-solution phase, rather than the hexagonal close-packed phase (Ref 11.31). During sliding wear, there is a martensitic transformation observed that leads to lower friction. The cold spray process is also being used to repair difficult-to-weld cast iron components (Ref 11.32).

11.5 Conclusion

Overall, cold spray technology has proven very versatile in saving millions of dollars in aftermarket repair, reclamation, and restoration in various industrial sectors. However, despite the success stories that have been highlighted in this chapter, there remain a number of unexploited opportunities to implement this technology for many repair applications. Some of the lessons learned from the last 8 to 10 years of research and development will pave the path for easier implementation. For instance, complex geometries such as tubing are better handled by using a hand-spraying technique for easy implementation in several applications (Ref 11.14).

Further efforts in developing a portable high-pressure system that can be used in the field are well worth the time and investment. Some of the challenges in a smooth repair include masking points and inside corners, internal grooves, and internal diameters. Overspraying must be accounted for in machining the component to the final print, and there may be discontinuity during blending at the interface or the original surface and the cold-sprayed coating. In addition, there still exist some challenges in obtaining a uniform coating for large-area buildups.

A vast majority of the success stories in using cold spray technology for repair applications include stationary components. The future of this versatile technology lies in being able to refurbish rotating components.

Based on laboratory trials, there is a specific need for niche custom-made repair-application-based qualification tests, with realistic test conditions, to capture the true benefits of this technology for component life extension. The repair risks must be evaluated with specific regard to the service-exposed component and not the new-make original material. Figure 11.20(a) compares the probability of failure between a new, pristine component and a service-returned one and estimates the overall risk of failure (Fig. 11.20b) (Ref 11.14). One must weigh the repair risks against the return on investment (Fig. 11.20c) and be able to take a calculated engineering risk in implementing this technology for use in repair and refurbishment.

On the whole, only a limited amount of information about cold spray in repair and refurbishment has been made publicly available, because most

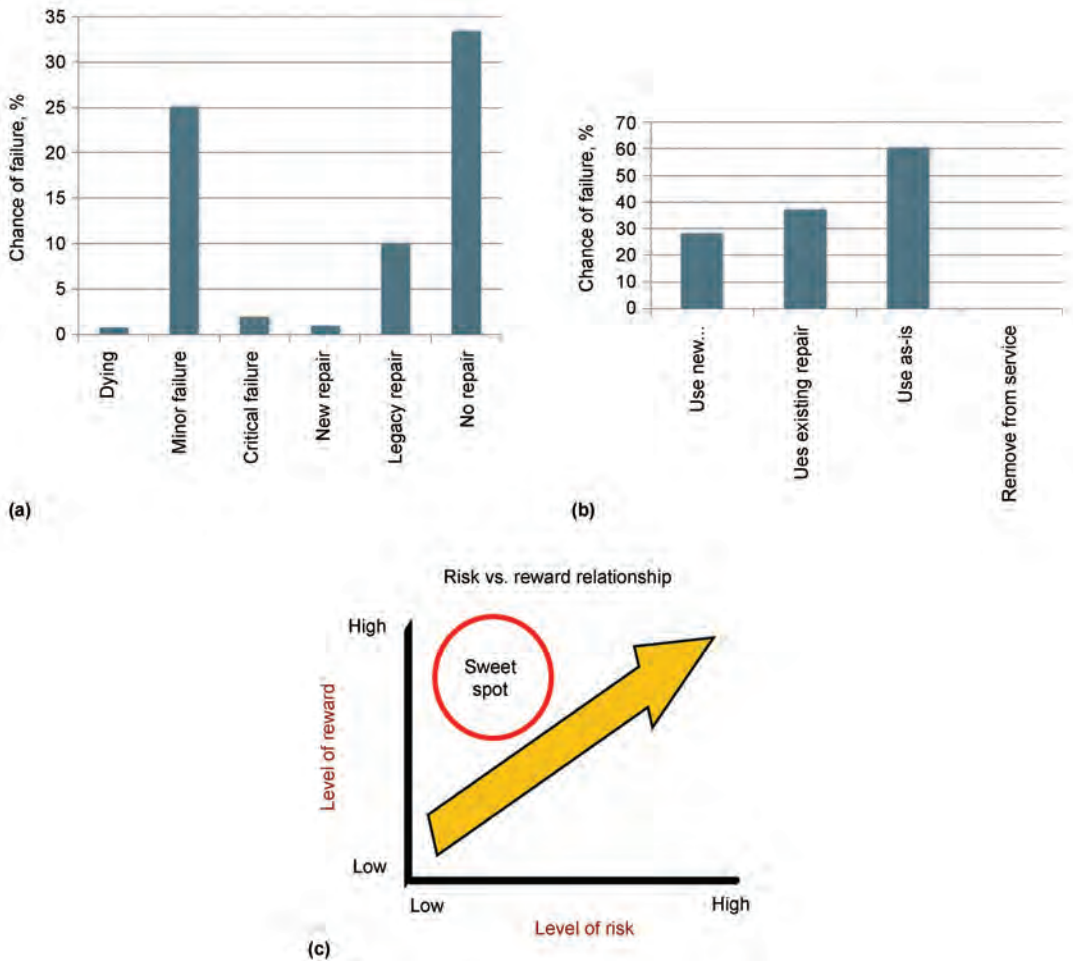


Fig. 11.20 (a) Probability of current vs. repair risk. (b) Estimated total repair risk. (c) Risk vs. reward based on the risk analysis. Source: Ref 11.14

advancements in cold spray repair are quickly patented by various OEMs before they are put into practice, or they are guarded as trade secrets by the OEMs that perform the repairs.

Overall, there exists the possibility of developing the technology for repair applications within a fairly short time, perhaps 6 to 7 months, from laboratory scale to prototype to implementing in the field, thus dramatically reducing cycle time and improving system reliability.

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