

Alloy Materials and Their Allied Applications

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Alloy Materials and Their Allied Applications

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Preface

An alloy is an engineered material that is a mixture of one or more metals with nonmetallic elements. The search for innovative technologies to meet the needs of efficient and sustainable production has motivated the research and development of new alloy materials. Exploring the alloy composition is the first and, possibly, the best way to change the properties of materials. A well-defined combination of elements can create a very stable alloy with improved corrosion resistance in a wide range of adverse environments. The alloy materials possess immense compositional space and the possibility of creating materials that go beyond the binary and ternary systems. Alloys have been used in consumer products, automotive, robotics, aerospace, marine, and other industries owing to their excellent physical properties, lightweight, good corrosion resistance, and specific characteristics.

This edition of *Alloy Materials and Their Allied Applications* provides an in-depth overview of alloy materials and applications. It focuses on the fabrication methods and design of corrosion-resistant, magnetic, biodegradable, and shape memory alloys. The industrial applications in the allied areas, such as biomedical, dental implants, abrasive finishing, surface treatments, photocatalysis, water treatment, and batteries, are discussed in detail. This book will help readers solve fundamental and applied problems faced in the field of allied alloys applications. It is an archival reference guide for undergraduate and postgraduate students, faculty members, R&D professionals, engineers, and industrial experts working in the field of solid-state chemistry and physics, metallurgy, and materials science. Based on thematic topics, this edition contains the following eleven chapters:

Chapter 1 describes the production methods of amorphous alloys and their applications. Particular attention is paid to bulk amorphous alloys. The bulk amorphous alloys make up one of the most promising groups of functional materials. The basic applications of these materials are discussed

in areas such as electrical and electronic technology, jewelry, sport, military, and medicine.

Chapter 2 covers the role of composition, microstructure, processing, thermomechanical heat treatment, and surface finishing in the electrochemical properties of corrosion-resistant alloys. These factors are discussed in detail to guide the design of new optimized alloys to be used in adverse environments which are not susceptible to corrosion.

Chapter 3 details the influence of electrodeposition parameters on Ni-Co-W alloys. Parameters such as temperature, rotating cathode, electric current density, bath composition, and pH are discussed in detail. The focus is on the optimization of these parameters that can be obtained in the materials with characteristics suitable for industrial applications.

Chapter 4 deals with the synthesis of novel $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ alloy powders using a high-energy ball milling method. Several analytical techniques are employed to characterize the synthesized powders. X-ray diffraction (XRD) analysis revealed the formation of amorphous structures in the powder. Moreover, the degree of amorphization and microhardness values of the powders is also examined.

Chapter 5 reviews distinct magnetic alloy materials along with their applications in various fields. These alloys have gained much attention, and research is currently going on to introduce new kinds of magnetic alloys for applications in magnetic-storage devices, spintronics, etc.

Chapter 6 investigates the production of $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloys by ball milling and their photocatalytic degradation efficiency in decolorizing methyl blue dye. The color of methyl blue turned from blue to nearly colorless using catalyst of alloy $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ for only 60 min.

Chapter 7 contributes to a better understanding of the biocompatibility of frequently used metallic and polymeric dental materials, as well as the advancements in these materials. Additionally, detrimental effects and absorption routes of toxic agents, along with the significant factors affecting the degradation of dental restoratives, are discussed thoroughly.

Chapter 8 elaborates on the findings of experimental investigation carried out by eminent researchers for the surface treatment of alloys and ceramics using the magnetic abrasive finishing (MAF) process. The experimental,

modeling and simulation, and multi-objective optimization investigations laid major emphasis on revealing the contribution of process parameters (voltage, magnetic flux density, mesh size, working gap, rotation speed) concerning the finishing performance of different alloys and ceramics using the MAF process.

Chapter 9 describes the role of mechanical, chemical, and biological properties towards the performance of metallic alloys for biomedical applications. The major goal is to present the commonly used biomedical alloys besides the new metallic materials reported in the literature and to discuss the essential factors affecting their clinical performance.

Chapter 10 discusses the alloys of different elements for cathode and anode material and emphasizes their structural-performance relationship and how the performance of a particular cathode or anode will be enhanced by changing the composition and structural factor. Several elements form an alloy with potassium for cathode and anode electrode. The area of research on potassium ion batteries is in the immature stage; some models of potassium ion batteries have already shown good results and reveal potential applications for practical use.

Chapter 11 discusses how the shape memory alloys (SMAs) are evolved and the various classification of SMA according to its working principle. Pseudoelasticity is briefly explained and the biasing configurations of the shape memory alloy are also discussed in detail.

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Fabrication Methods for Bulk Amorphous Alloys

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Abstract

Amorphous alloys are one of the newer groups of functional materials that are widely used in many industries. Their properties are much better than materials with the same chemical composition and crystal structure. Amorphous alloys are produced by rapid cooling techniques. The most popular methods are: melt-spinning method, injection method, suction method, centrifugal method. Using these methods, products of various shapes can be produced. There are two groups of amorphous materials: conventional in the form of a thin tape and bulk amorphous materials with a thickness of more than 100 μm and various shapes, e.g. rods, tubes, plates, etc. The era of bulk amorphous material began when A. Inoue of Tohoku University in Japan developed three criteria. These criteria make it possible to systematically manufacture massive amorphous materials. Of course, there are many restrictions on their production, but the date 1989 is the date of birth of a new group of materials, i.e. bulk amorphous alloys. Material engineers need such materials and their development is continuous, as evidenced by numerous scientific publications in this field. It should be assumed that the growing demands on modern materials will promote the development of this group of materials.

Keywords: Bulk amorphous materials, injection casting, suction casting, application of amorphous materials

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1.1 Production Methods of Amorphous Materials

1.1.1 Initial Preparation for the Production of Amorphous Materials

Initial preparation of the specific chemical composition of the alloying components—prior to the main melting process—is a fundamental operation in the production process of amorphous materials. The results of many years of the Author's own research corroborate the fact that the initial ingot preparation, or even the material used to make the ingots in the first place, defines the quality of the amorphous materials. The most important criterion for success is to determine the correct weights of the alloying elements for the ingot. For example, in the case of rare-earth metal elements, the redundant mass of these elements has to be taken into account. The weight of the other alloying elements should be determined to an accuracy of ± 0.001 g. For the initial ingot preparation, high-purity elements should be used, as this gives a higher probability that the resultant alloy will have an amorphous structure. However, this increases the production cost of this type of material. Therefore, alloying elements with a purity of 99.99% are used only for the first test samples.

Generally, two alternative methods are utilized for the production of the ingots: using an induction furnace (Figure 1.1) or by arc-melting (Figure 1.2). The production process of a polycrystalline ingot, using an induction furnace, is a very long and labor-intensive process. The alloying components are usually placed in quartz capsules and re-melted several times using the induction (eddy-current) heating process. Each subsequent re-melting of the components results in improved homogeneity of the final ingot. However, this method struggles when it comes to some of the “hard to melt” metals. The presence of non-melted alloying components can be observed by various microscopy methods. In the case of the second ingot production method, using a plasma arc, a much higher degree of mixing of the elements in the alloy can be obtained, than by using the induction method. The temperature

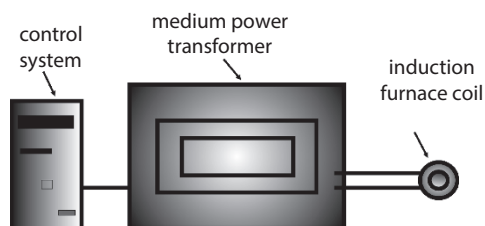


Figure 1.1 Schematic view of the induction method for the production of crystalline ingots.

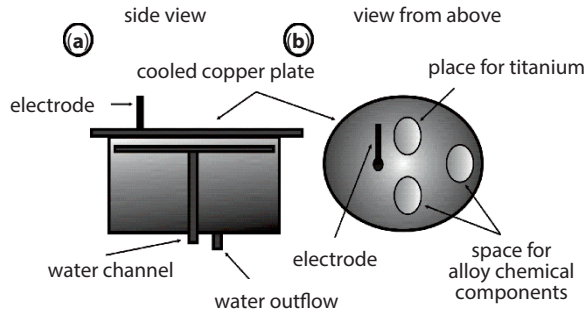


Figure 1.2 Schematic views of the arc-melting method for the production of crystalline ingots: (a) side view, (b) plan view.

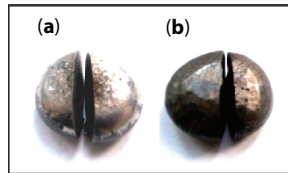


Figure 1.3 The surface of a crystalline ingot—arc-melting method: (a) after cleaning and (b) before cleaning.

of the electric arc depends on the current and can reach up to several thousand Kelvin. The ingot material is melted on one side; then, after allowing a few seconds for solidification to occur, it is turned over using a manipulator and melted again. The production of the ingot, using the arc-melting method, is a single-step process—which reduces the cost and time of the production process, in comparison to the induction method.

The initial preparation of ingots that are made from metallic materials is carried out in a vacuum, or under the protective atmosphere of a neutral gas (usually argon). This measure prevents the creation of oxides on the metal surfaces—heterogeneous “embryos”, which could become centers for crystallization, later in the production process.

The manufactured ingots are cleaned by abrasion and by an ultrasonic cleaner (Figure 1.3).

1.1.2 The Single-Wheel Melt-Spinning Method

The unidirectional cooling of liquid alloy at high speed on a rotating copper cylinder was one of the first methods used for the production of solid, metallic amorphous materials in the form of tapes (ribbons) [1, 2]. By the

1970s, this method had been used on an industrial scale for the production of materials for the electrical and electronic industries by the companies Metglas and Vacuumschmelze [3, 4]. The production process involves forcing the liquid alloy through an opening of small diameter, situated in the lower part of the melting crucible, onto a copper cylinder which is rotating at high speed (Figure 1.4).

On contact with the surface of the cylinder, the liquid alloy is cooled rapidly and solidifies at a rate of up to 10^6 K/s. Therefore, this method is often referred to as ultrafast (rapid) quenching. It has been concluded that the rate of cooling of the liquid alloy is determined by the linear velocity at the surface of the copper cylinder (Figure 1.5) [5, 6].

The pressure of the liquid alloy in the melting crucible is of lower importance. The shape (form) of the amorphous materials, obtained using this method, was in most cases ribbons of approximate dimensions: width = 3–5 mm and thickness = 35–60 μm (Figure 1.6).

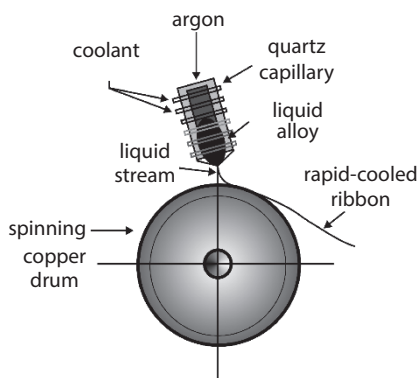


Figure 1.4 Schematic diagram of the continuous casting process for amorphous ribbons—high speed of quenching on the rotating, copper cylinder (side view).

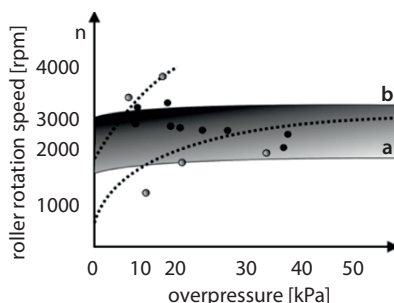


Figure 1.5 Relationship between the rotational speed of the cylinder with over pressure [7].



Figure 1.6 Amorphous ribbons [8–10].

This method allows the production of samples with thicknesses of greater than $100\text{ }\mu\text{m}$, which, by definition, could be classified as bulk amorphous alloys. However, the samples are produced in the form of flakes, and require detailed segregation, as over 70% fail to achieve an amorphous structure. Therefore, this method is not satisfactory for the production of bulk amorphous alloys.

Amorphous and nanocrystalline ribbons are used as materials for transformer cores with higher efficiencies when compared with ribbons made from transformer steel [11]. In Poland, since the 1970s, several scientific institutions have carried out research into the properties of amorphous and nanocrystalline ribbons (e.g., Finemet, Metglas, Nanoperm, and Hitperm), and also into the influence of thermal treatment on their microstructure and properties [11–16]. The specific thermal treatment of the amorphous ribbons allows their nanocrystallization. Usually, annealing of the material is performed at a certain temperature, and over a certain time, in the vacuum resistance furnace. The nanocrystalline ribbons could also be made directly, using a melt-spinning method. The advantages of amorphous ribbons, exhibiting soft magnetic properties, are very low magnetic hysteresis losses and near-zero magnetostriction. The lower hysteresis losses mean lower applied-energy costs, and the almost zero magnetostriction is an ecological factor which reduces the noise (“hum”), which accompanies transformers based on FeSi steel. Currently, amorphous ribbons are used, for example, in the reinforcement of the foundations of skyscrapers exposed to seismic stresses, and for multilayer tank armour. Ribbons of small width (narrow) are obtained by using melting crucibles with small single holes (Figure 1.7a).

Developments in electronic equipment, and enhanced requirements from Industry, have been major drivers in the increased interest in amorphous materials—in particular, wider and thicker amorphous ribbons. This has resulted in modifications to the original melt-spinning method, and a technique allowing the production of amorphous ribbons of width up to a few centimeters has been developed (Figure 1.6 and 1.7b); several

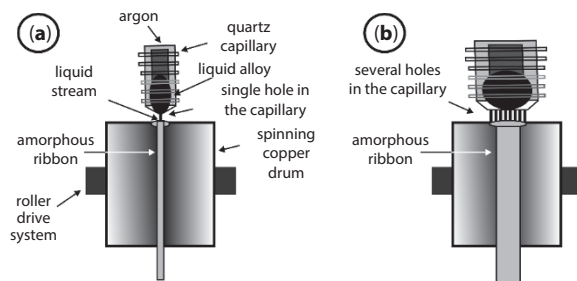


Figure 1.7 Diagram of the production process for metallic amorphous ribbons: narrow-cast using a single hole in the lower part of capillary tube (a) and wide-cast by forcing the liquid alloy through several holes in the capillary tube (b).

parallel nozzles apply the liquid alloy to the surface of the rotating copper cylinder. The “sprayed” metallic liquid meets the cylinder near its surface on a so-called “air bag” and, as a result, is solidified in the form of a wide ribbon. The thickness of the ribbon depends on its chemical composition. Unfortunately, even when using alloys with very good glass-forming ability, this method is not suitable for the production of bulk amorphous alloys.

1.1.3 Suction-Casting Method

The suction-casting method entails the suction of molten alloy into a copper die; this method is also often used and it allows for the production of the so-called “bulk amorphous materials” [17–34]. Using this method, a cooling rate of approximately 10^3 K/s can be achieved. One practical, and relatively simple, suction-casting method involves the use of the electric arc. The alloy material is melted on a copper or silver plate, and the liquid metal is then sucked into a cooled die (Figure 1.8). The bulk samples are made under a protective gas atmosphere; however, first, a high vacuum is created in the working chamber.

After this, a specific quantity of the protective gas is introduced (usually 0.3 atm of Ar). The minor adjustments of the indicated amount of gas are determined, depending on the chemical composition during the experiment. The arc-melting process is carried out in the air or in an atmosphere of the neutral gas. On the basis of the Author’s own research, it has been found that the melting of pure titanium—before the suction-casting process—enhanced the quality of the resulting amorphous materials. In order to melt the ingot and the titanium, a special design of plate is used.

In the suction-casting method, the induction furnace can also be used for the melting of the metallic ingots. However, the suction of the molten

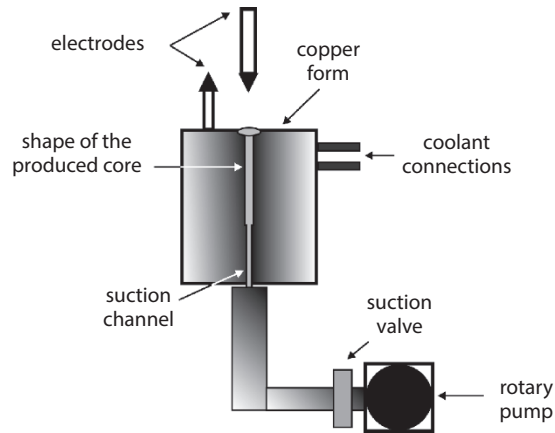


Figure 1.8 Diagram of the suction-casting process for production of bulk amorphous alloys.

liquid is difficult in this method, as the material is contained within the quartz capillary, and as soon as it is not subjected to the eddy current effect, it starts to crystallize on the wall of the capillary tube. The potential for manoeuvring the liquid alloy is very limited—which is a major drawback of this method.

1.1.4 Injection-Casting Method

Amorphous materials can also be made using an injection-casting method (Figure 1.9) [27]. Material is melted using an induction furnace.

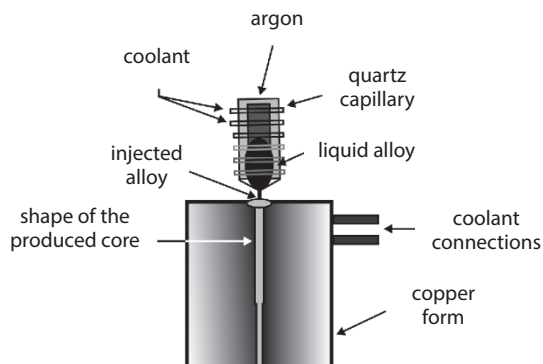


Figure 1.9 Diagram of the injection-casting process for production of bulk amorphous alloys.

The ingot is placed in the quartz capillary and subjected to induction heating using the eddy currents. The liquid metal is injected under pressure into the copper die. In the case of this method, the obtained cooling rate is similar to that achieved for the suction-casting method. Similarly, the procedure for obtaining the correct working atmosphere, before and during the melting process, is the same as that described for the suction-casting method. The melting of the ingots can be carried out in free air or under a neutral gas. The disadvantage of this method is the heating up of the intake in the quartz capillary, in addition to the heating of the copper die. It has been found that, often, the die could reach as high a temperature as 100°C, which unfortunately decreases the probability of creating bulk amorphous material. The use of a modern medium-frequency induction furnace allows this undesirable effect to be removed almost completely. The other way to remove this effect is to apply all sorts of thermal dividers between the copper die and the capillary tube. However, this hinders the production process, as the liquid alloy often stops and solidifies at these elements.

A good solution, allowing the elimination of all of the disadvantages of the aforementioned suction- and injection-casting methods, is to combine the methods, as described in [27].

1.1.5 Centrifugal Force Method

The centrifugal force method is mostly used for manufacturing amorphous materials for prosthetic use. Initially, it has been used to make titanium wires for prosthesis. In this method, the ingot is melted by induction heating. The liquid alloy is introduced into the copper die and then travels inside under centrifugal force (Figure 1.10): the ingot is effectively melted by eddy currents, and then pushed inside the horizontal rapidly-rotating die [35]. The shapes of samples, made using this production method, can be quite complicated [36]. In this method, the process of production of amorphous cores is carried out under a protective gas atmosphere, similarly to methods described previously in Sections 1.1.2–1.1.4.

1.1.6 Mechanical Synthesis

Amorphous, nanocrystalline and crystalline materials can be made by utilizing mechanical synthesis as the production method [29]. This method cannot be used to make some solid amorphous materials,

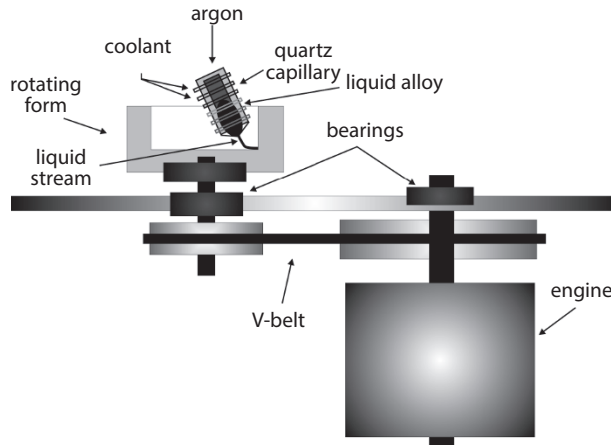


Figure 1.10 Diagram of the process for production of bulk amorphous alloys using the centrifugal force method.

i.e., bulk amorphous materials; however, it is worth noting that, on their basis, by utilizing powder metallurgy, powder cores can be made (and are often referred to as “bulk”). Therefore, this method should not be omitted when describing the production methods of amorphous materials. The selected components for forming the alloy are placed in a ball mill, in which multiple bonding and crushing processes occur as a result of the balls colliding [37]. The most commonly used material for the balls in high-energy milling machines is stainless steel. Using this production method, in which the deviation from thermodynamic equilibrium could be as much as 30 kJ/mol, the mixing range for the components can be widened, allowing mixing of elements which—in the state of equilibrium conditions—don’t mix. During the milling process, the chemical processes occurring at the low temperatures can start, as well as processes leading to creating of the amorphous, nanocrystalline and crystalline structures; also, synthesis of the new phases. During the milling process, numerous high-energy collisions of the steel balls occur. Between the balls are the components of the alloy, which as a result, are being squashed, and then crushed. The particle size of the mechanically powdered components depends mostly on the milling time [38–40]. Powder obtained in this way could be used, for example, in the production of composite cores [41–43]. A diagram of a ball mill is presented in Figure 1.11.

The process of high-energy milling can be presented schematically as shown in Figure 1.12.

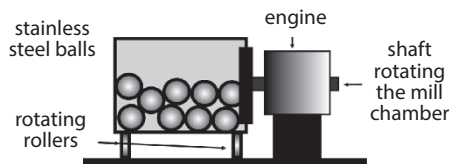


Figure 1.11 Diagram of a ball mill.

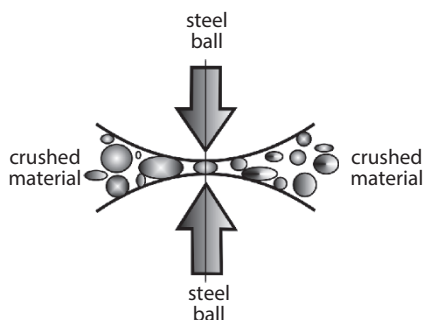


Figure 1.12 Schematic diagram explaining mechanical synthesis [6].

1.1.7 The Drop Method (Metal Granulation)

The so-called drop method is used for production of amorphous or nanocrystalline samples in the shape of a drop. The alloy is sprayed in liquid form onto a vibrating plate, where stream granulation occurs. The molten alloy also could be sprayed into the inside of a rotating cylinder. In the first case, the cooling medium is usually liquid nitrogen, and in the second case, water. The method using the vibrating plate is not suitable for making similar drops of alloys with high viscosity and refractory metals. It is an interesting fact that, in the first case, the hot alloy is cooled precisely in the liquid nitrogen vapor in a way that an issue of heat transfer caused by nitrogen evaporation around the drop has been almost completely eliminated. This solution gives the best cooling intensity through the duration of the process, until complete solidification of the product into the drop shape. The constant flow of the drops in the liquid nitrogen results in a high cooling speed of up to 10^4 K/s. On the basis of this method, during the production of aluminium flakes in the USA, a cooling speed of 10^9 K/s has been achieved. The technique was used by Erwin Mayer to develop theoretical and experimental models representing the disintegration of the hit wave of liquid metallic tape. The materials obtained as a

result of this production method are in reality granulates, which—due to their shape—are called drops. This method shows good prospects and is being developed constantly. The disadvantage of this production method is the wide dispersion of the final material, which is in the range of plus/minus 50%.

1.1.8 Water Quenching Method

This method is considered to be the simplest and the most commonly known. The cooling of steel in water has been used for the last few hundred years. This simple way of hardening has been used in the process of making the best-known bulk amorphous alloys based on palladium. The maximum cooling rate, achieved using this method, is 10^2 K/s. The preparation of the alloy is carried out using either the electric-arc method or the induction method. After this, the alloy is placed in a quartz capillary tube, where it is heated up to liquid temperature. Once all of the alloy in the capillary is in the liquid state, the tube is submerged in the cooling liquid, which is usually water. Despite the name of the method—i.e., the Water Quenching Method, the use of other cooling fluids is not precluded. This process is the same as the well-established steel hardening process. In order to restrict the influence of the quartz capillary tube on the cooling speed, the wall thickness is usually no more than 1 mm. The length of the capillary tube is also restricted and is usually several centimeters. Using this method, bulk amorphous materials could be made from alloys which require a low, critical cooling speed.

1.2 Applications of the Amorphous Alloys

The bulk amorphous materials currently find applications in many areas of technology; this is due to their unique properties (Figure 1.13, Table 1.1). The constant development of new technologies and increased possibilities of designing new materials have become the bases for the increase in thickness of amorphous products. At the same time, the range of possible applications increases. Amorphous alloys with thicknesses of greater than 100 μm are used as construction and functional materials, e.g., in the power industry (for cores of modern transformers), in medicine, electronics, and also in the production of sport and recreational equipment.

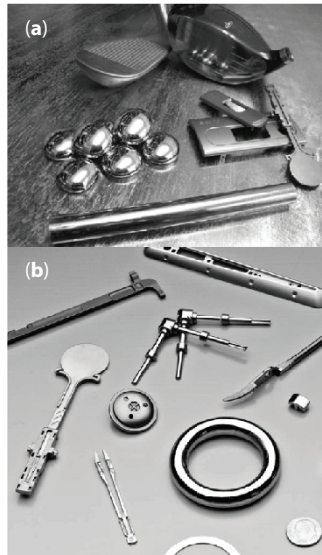


Figure 1.13 Components/assemblies made from metallic bulk amorphous materials: cores for golf clubs, casings for electronic devices or optical equipment, ingot, rod of approximate diameter 12 mm, amorphous ring, surgical scissors, medical implants; (a) Courtesy Hardware firm Liquidmetal[®] Technologies, (b)—[46].

1.2.1 First Commercial Applications of the Bulk Amorphous Alloys

Materials based on zirconium, with the chemical compositions ZrAlNCu and ZrAlCuNiTi , were first used in the sports industry in the cores of golf clubs [44]. The practical application of such Zr-based bulk amorphous alloys is due to the fact that they possess many advantageous properties: high tensile strength, high modulus of rupture, high value of hardness, high fracture toughness, high stress resistance, good fluidity, and good corrosion resistance.

1.2.2 Jewelry

Bulk amorphous materials can be used in jewelry due to two characteristics that characterize them: mirror reflection and brilliance, and environmental protection. The obtained dimensions of the amorphous samples are sufficient to produce rings, tags, chains, watch cases, and their elements. Amorphous materials are not mainly about Au and Pt-based alloys. Materials used in jewelry include amorphous titanium and zirconium

Table 1.1 Applications of the bulk amorphous alloys [45].

Properties	Potential applications
Tensile strength	Construction materials
Hardness	Cutting materials
Stress resistance	Materials used for making dies
Elasticity allowing applications in tooling exposed to varying dynamic loads	Tools materials
Fatigue strength	Materials used in joints
High value of elasticity limit	Sports equipment
Resistance to corrosion	Corrosion resistant materials
Wear resistance	Materials for stationery
Light reflection coefficient	Precision optical materials
Ability to absorb hydrogen	Materials absorbing hydrogen
Magnetic properties	Soft magnetic materials
Viscosity	Composites materials
Sound damping ability	Acoustic absorption materials (e.g., sound absorbing panel, sound suppressing mats)
Wear resistance and possibility of precision surface treatment	Medical tools and equipment

alloys. During the production of amorphous decorations, so-called allergic metals such as Ni were eliminated. In 2011, the companies: Liquidmetal® Technologies Inc. (OTCBB: LQMT) and Swatch Group Ltd. (SIX: Uhr/Uhr N) signed an exclusive licence agreement to use bulk amorphous alloys for component parts of cutting-edge watches. The LQMT amorphous alloys have been used in production of the Omega Seamaster Planet Ocean watch (Figure 1.14).

The advantage of amorphous alloys made by Liquidmetal® Technologies Inc. is the possibility of re-processing using technology similar to that used in polymer processing. This is due to the high forming-ability of the bulk amorphous materials in the supercooled liquid range.



Figure 1.14 Castings for a watch case. Post-production (prior to polishing and finishing processes). Courtesy Hardware of the company Liquidmetal[®] Technologies.

Amorphous metal casings are also used for electronic watches by the Swiss company TAG Heuer—for their Luxus product from the state-of-the-art Chronograph edition. Another luxury product made of amorphous material can be decorative feather nibs.

1.2.3 Electrical and Electronic Technology Engineering

The desirable mechanical properties of the metallic amorphous alloys, i.e., high tensile strength, corrosion resistance, and exceptional malleability, were the main reasons for their application in housings or cases for electronic measurement equipment. The sheen and attractive appearance are added benefits (Figure 1.15). For example, a manufacturer of flash memory cards has encased their offering, the SanDisc Cruzer[®] Titanium Flash Drive, in a hard and aesthetically-pleasing housing made from an amorphous alloy. The Apple company, in co-operation with Liquidmetal[®] Technologies Inc. (OTCBB: LQMT), is using amorphous alloys in the cases of electronic devices, and in particular for iPhone cases.



Figure 1.15 Housings made using Liquidmetal[®] Technology [48].

1.2.4 Sports Equipment

In 2003, the company, “Head”, introduced a new tennis racket called the Head Liquidmetal[®] Radical. The elements of the frame were made from an amorphous alloy designed by Liquidmetal[®] Technologies; and the frame possessed excellent elasticity and good energy transfer (Figures 1.16 and 1.17). The physical and mechanical properties of amorphous alloys

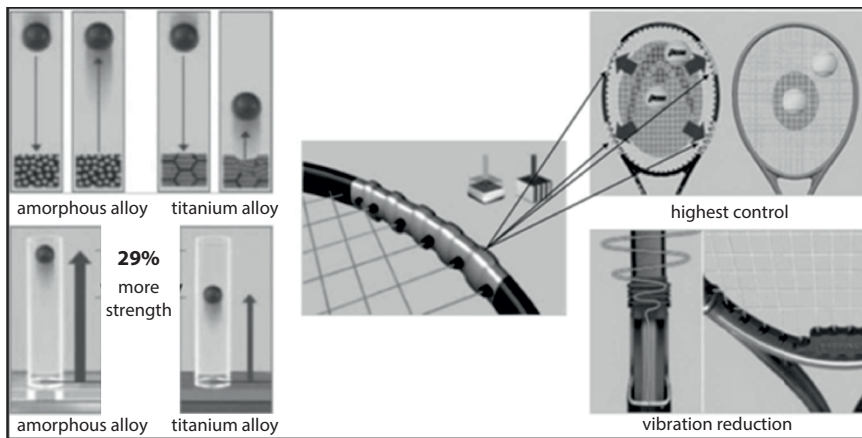


Figure 1.16 The Head tennis racket, featuring built-in amorphous elements [49].



Figure 1.17 Sports equipment featuring components made from bulk amorphous materials [50].

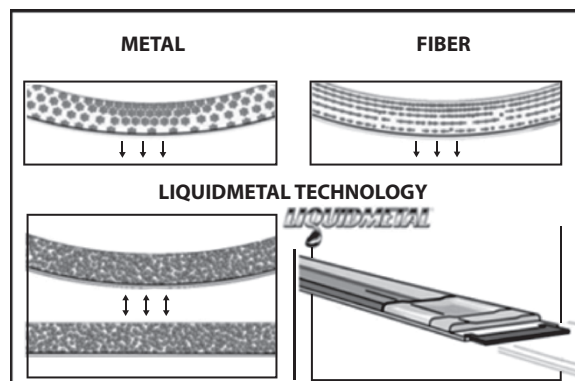


Figure 1.18 Amorphous materials used in the ski company HEAD [51].

have become a revolutionary solution in the design and construction of tennis rackets, and the product achieved the Laurel of the Best Product of 2003 in the Business Week and Fortune 25 contest review.

The company, Rawlings Plasma Technologia Fusion, used amorphous materials in the construction of baseball bats; the strength of these bats' was found to be 2.5 times greater than that of titanium baseball bats. The primary advantage of baseball bats, which feature components made from amorphous materials, is their high energy transfer ability. An additional advantage is the exceptional ability to dampen vibrations, created after hitting the ball, which substantially reduces the risk of contusion-type injuries.

The company, "Head", also used elements made from amorphous materials in the production of skis (Figure 1.18).

Skis based on a core made from amorphous materials feature the "Head Intelligence" and "How It Works Intellifiberus" technologies.

The patented technological solutions allow these skis to react rapidly to changes in their flexing during skiing turns, and to return instantaneously to their initial position. In addition, the Head skis have high stiffness during fast skiing, which immediately corrects deflections of the skis; this is also related to the use of amorphous materials within their core.

1.2.5 Electrical and Electronic Technology

The ferromagnetic metallic glasses and related soft magnetic materials have many applications within the electrical and electronics industries [52] (Figure 1.19). One particular application features nanocomposites based on an amorphous matrix, reinforced with particles of crystalline phase, with



Figure 1.19 Electrical/electronic components made from amorphous and nanocrystalline materials [54, 55].

grain sizes of less than 100 nm (at least in one direction). These materials are used for high-frequency transformer cores. The cores are wound from metallic tapes, and subjected to thermal treatment in order to create the nanocrystallites, embedded in the amorphous matrix. The thermal treatment can lead to improvements in the magnetic properties, in comparison to those of the amorphous precursor materials [52]. The nanocrystallization process can lead to an increase in the value of the saturation magnetization and decreases in the magnetostriction and coercive field values [52]. In addition, the application of thin ribbons in transformer cores decreases the tendency to create eddy currents. Usually, tapes of approximate thickness 30 μm are used for transformer cores. The Fe-based amorphous alloys are also used in magnetic sensors and for magnetic screens (thickness $>100 \mu\text{m}$). Currently, amorphous alloys based on palladium can be made in the shape of rods of diameter 72 mm. However, for iron-based alloys the maximum diameter reached has been 6 mm [53]. One difficulty in the production of iron-based bulk amorphous alloys is caused by the high affinity of the magnetic elements to oxygen. Heterogeneous “embryos” emerge on the surface of amorphous samples made using iron, cobalt, nickel, or gadolinium. The necessary restriction of the kinetics of nucleation is achieved by lowering the quenching speed. The largest thickness of an iron-based alloy, so far, has been achieved for the chemical composition: (Fe, Co)–Zr–(Mo, W)–B [53]. At the same time, casting amorphous rods with diameters of $>10 \text{ mm}$ has been found to be impossible. Analysis of the literature suggests the possibility of producing amorphous iron-based alloy castings using powder metallurgy technology.

1.2.6 Microelectromechanical Systems MEMS

During the process of heating-up from room temperature, oxides, polymers, and metallic amorphous materials possess a wide range of the so-called supercooled liquid region. In this temperature region, a bulk amorphous material forms a viscous super-cooled liquid—a Newtonian fluid. That means that they can be easily shaped; this property is referred to as the malleability of the bulk amorphous materials—this is comparable with polymers. The metallic amorphous alloys in the super-cooled state are basically stable. After annealing, they can be cooled again with insignificant shrinkage. The high elasticity of bulk amorphous materials has been used in nanotechnology and micro electromechanical systems (MEMS) [56–60]. In these systems, at least one of the specific dimensions is within the micro scale (0.1–100 μm) [61].

Microsystems are most commonly made from silicon using micro-processing methods (e.g., anisotropic etching in KOH). In recent years, there has been an increase in the production of microsystems made from polymers and bulk amorphous materials. The production methods of injection moulding or lithography are used to make microsystems from these materials. It can be assumed that obtaining MEMS from crystalline materials is complicated and expensive. MEMS can be produced in nano- or microsizes by utilizing the high malleability of bulk amorphous materials in the supercooled liquid region (Figures 1.20a–d).

Microelements that are made from bulk amorphous materials exhibit much better mechanical properties, in comparison with their crystalline counterparts. The size of the crystallites is an additional restriction in the mechanical properties of crystalline materials, and it is a characteristic parameter for the given crystalline structure. The introduction of the thermoforming method has facilitated the production of microelements with sizes of a few nanometers. Constant technological progress and miniaturization are driving the creation of more modern nanostructures, which in the very near future might be used in nanotechnology and bio-nanotechnology.

1.2.7 Medicine

The metallic materials: pure metals or their alloys, have a major influence on the development of the bio-engineering. Estimates show that, currently, about 70% of implants are made from metallic materials; these materials have found applications such as: hard tissues, screws for bones, acetabula, hip and knee joints, dental implants, and many others. The bulk amorphous alloys of titanium, magnesium, and zirconium form a new group of bio-materials used in medicine. It should be emphasized that these materials possess high bio-conformity,

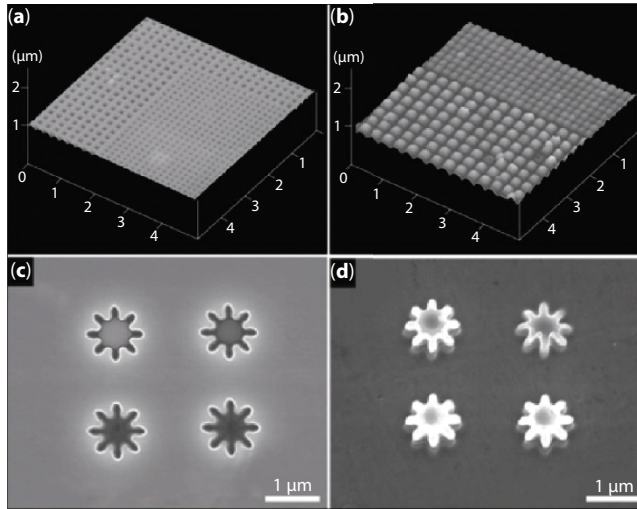


Figure 1.20 SEM image: (a) Silicon matrix with a system of concave nanopyramids, (b) Silicon matrix with a system of convex nanopyramids. (c) Made using ion beam concentrated microelements on the basis of Zirconium. (d) Cast microgears, based on bulk amorphous platinum alloy. (Courtesy of Y. Saotome, Tohoku University, Japan) [56].

high resistance to wear and corrosion, high malleability, and high strength [62]. In the case of implants made from crystalline materials, structural defects are usually the cause of: weakening of the material strength, inter-metal corrosion, and the creation of localized fractures in the biological environment. One of the major advantages of implants made from amorphous materials is that the chemical composition of the end product doesn't include elements that are harmful to humans—which leads to their better bio-conformity. On the basis of *in vitro* and *in vivo* studies that have been carried out, it has been shown that bulk amorphous materials (with appropriate chemical compositions) are non-toxic for cells and don't hinder the growth of body tissue [63–65]. The bulk amorphous glasses also find application as stents, due to their high elasticity.

In recent years, biodegradable amorphous implants, based on magnesium, have been developed. These are characterized by higher strength and elasticity in comparison to magnesium-based biodegradable implants with a crystalline structure. The major advantage of the amorphous variants is a significant reduction in the hydrogen emitted in the *in vitro* condition—which is the main cause of biological corrosion in the physiological solution. The effects of this corrosion are so-called “gas pockets” created around the implant (Figure 1.21). Figures 1.21a–d show pictures after implantation of biodegradable magnesium alloy: (a, b) amorphous material, (b, d) crystalline material. The pictures marked “A” and “B” were taken after

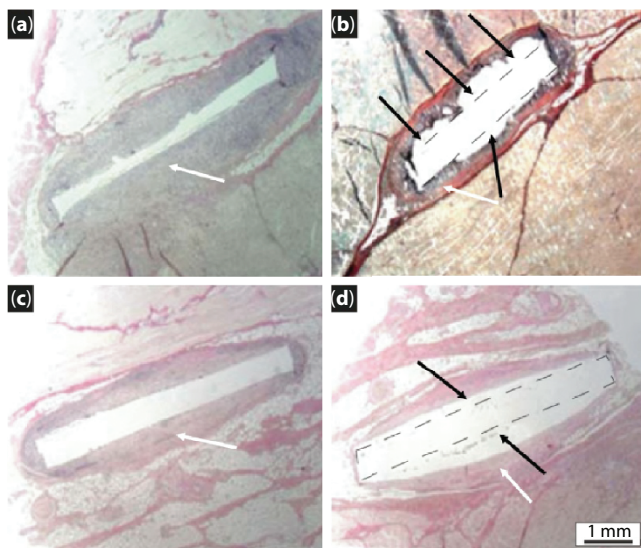


Figure 1.21 The process of dissolving of the magnesium-based implant in the tissue: amorphous alloy $\text{Mg}_{60}\text{Zn}_{35}\text{Ca}_5$ (a, c) and crystalline alloy WZ21 (b, d) [56].

27 days, and the pictures “C” and “D” after 91 days, following implantation. The white arrows highlight the pockets around the implant, caused by the reaction to the foreign body. The black, dotted lines indicate the implant (Figures 1.21b, d). The pockets of secreted hydrogen around the biodegradable, crystalline, implant are marked by black arrows.

On the basis of the presented pictures, it has been stated that the application of bulk amorphous materials as biodegradable magnesium or magnesium alloy implants is safer for health procedures. In addition, the chemical composition of biodegradable amorphous implants based on magnesium can be optimized, which allows control of the speed of degradation, and the rate of hydrogen secretion. This cannot be achieved with biodegradable implants based on magnesium with a crystalline structure.

1.2.8 Military Equipment, Munitions

Due to their properties, amorphous alloys based on zirconium have found application in the construction of specialist missiles: so-called kinetic energy penetrators (Figure 1.22). The working method of these missiles relies on uncontrolled deformation taking place on the shearing bands.

The first kinetic energy penetrators used depleted uranium in their cores. The use of standard bulk amorphous material based on zirconium for the cores of this type of missile is hindered by the low density of the



Figure 1.22 A missile with cores made from amorphous material, based on hafnium with tungsten particles (Kinetic Energy Penetrator) [67].

material and the lack of control over the deformation mechanism. The material developed for these missiles is a synthesized alloy based on hafnium (over 17 g/cm^3) with the addition of small tungsten particles in the form of a powder. Introduction of the tungsten into the hafnium matrix allows the control of deformation. As a result of the hot isostatic compression, the material is thickened in a way in which the processes occurring within its volume can be controlled.

Kinetic penetrators based on cores made from amorphous alloys were made for the first time during the Kinetic Energy Penetrator programme, co-ordinated by the Defence Department of the United States of America. As a result of ballistic tests, it was found that missiles with cores based on amorphous material had a similar destructive force to missiles with cores based on depleted uranium. An additional advantage of kinetic penetrators with amorphous cores is the relative absence of negative environmental impact. The experts taking part in the programme stated that the bulk amorphous alloys, due to their unique properties, are materials suitable for the production of special ammunition.

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Designing Corrosion-Resistant Alloys

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Abstract

Corrosion can impair the material durability and determine its applicability under realistic conditions. Although advances have been made, designing alloy materials to resist corrosion remains a challenge for engineering, dentistry, and medical fields. To create a corrosion-resistant alloy is necessary to consider the optimization of several factors involved on the manufacturing of alloys that may influence on corrosion kinetics. Exploring the alloy composition and processing are the main focus of materials research since they can affect the passive film growth and microstructure transformation. This chapter covers the role of composition, processing, thermomechanical heat treatment, and surface finishing on the electrochemical properties of corrosion-resistant alloys.

Keywords: Alloy, metals, corrosion, electrochemical, oxides, microstructure

2.1 Introduction

Corrosion is an electrochemical phenomenon that occurs when metals are exposed to challenging environments, specially that ones with high chloride concentration, high temperature, and/or high potentials, in which reactions between at least one anode and one cathode may lead to metal dissolution [1]. The corrosion resistance of a material is highly dependent

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on the oxide layer formed on the surface that acts as a protective barrier to ions transport, metal dissolution, and degradation. The passive film formed on materials surface will depend on its composition and processing, which can be changed by the needs of each area.

Corrosion of alloy materials is a concern of different areas, covering the engineering, dentistry, and medical fields, since corrosion can impair the material durability and determine its practical applicability under realistic conditions. The consequences can range from loss of equipment and components effectiveness to total failures [2, 3]. Specifically, the degradation of biomaterials used in orthopedic and dentistry rehabilitations with implants has a significant effect on their biocompatibility and treatment success [4].

Considering the negative impact of corrosion, efforts have been done to develop corrosion-resistant alloys by modifying the material-manufacturing-surface processes but maintaining their desirable property/performance combination that satisfy a variety of engineering and medical applications [5, 6]. To predict alloys corrosion performance is fundamental to understand the role of alloying elements and manufacturing processes on corrosion kinetics [7]. In this context, this chapter covers a range of subjects (composition, processing, thermo-mechanical heat treatment, surface finishing) that can influence on the electrochemical properties of corrosion-resistant alloys.

2.2 Alloy Design for Corrosion Resistance

Designing a new alloy is not an aleatory process and to achieve success is essential to anticipate the desired set of properties that this new material needs to fulfill (e.g., electrochemical, mechanical, and/or biological properties). A common approach is to improve an already existing alloy by changing one element in such alloy, adding additional elements or applying processing treatments [8].

2.2.1 Role of Composition in Corrosion-Resistant Alloys

Exploring the alloy composition is the first and, possibly, the best way to change materials properties. The corrosion resistance can be enhanced by adding alloying elements to one base element to achieve the materials passivity and create a protective barrier (stable passive films) on the surface that prevents the penetration of corrodants and minimizes the electrochemical reactions on alloy underneath [3]. Besides improving alloys passivity, other approaches are searching for alloying elements that

acts regulating the hydrogen evolution reaction [7, 9, 10] or reducing the anodic/cathodic activity directly [10, 11].

It is well known that stainless steels and alloys of Cr, Ni, Al, Mo, and Ti have the potential of growth a thin oxide or hydroxide film in aqueous and atmospheric environments (Figure 2.1) that, if it is maintained stable, it will guarantee an adequate electrochemical stability with low rate of corrosion [1]. However, this passive film can be disrupted by abrasion or other mechanical, chemical, and physical processes and be susceptible to accelerated localized corrosion and metals release (Figure 2.2) [12]. For this reason, alloys are designed taking in consideration the formation of an oxide layer with high thermodynamical stability to inhibit alloy degradation.

Designing corrosion-resistant materials has mainly focused on stainless steels, Co-Cr-Mo, Ni-based, and Ti alloys [3, 12]. The good corrosion resistance of stainless steels is owing to the presence of Cr (with >15 wt. %) as constituent and the consequent formation of a Cr-rich protective passive film [1, 13]. Indeed, Cr is an extremely easy-passivable element that is capable to ensure passivation of a non-passivating iron matrix [14]. For Ti alloys, TiO_2 -based oxide itself has great stability that generally is enhanced by Ta_2O_5 , Nb_2O_5 , and ZrO_2 oxides [11, 14–18]. Similarly, Ni-based alloy has high intrinsic corrosion resistance because of its thermodynamic stability. Normally, it is found associated with Ti [19] and Cr [7, 20].

A well-defined combination of elements can create a very stable oxide layer with improved corrosion resistance in a wide range of adverse environments. Nevertheless, the immense compositional space and the possibility of creating alloys that goes beyond the binary and ternary system,

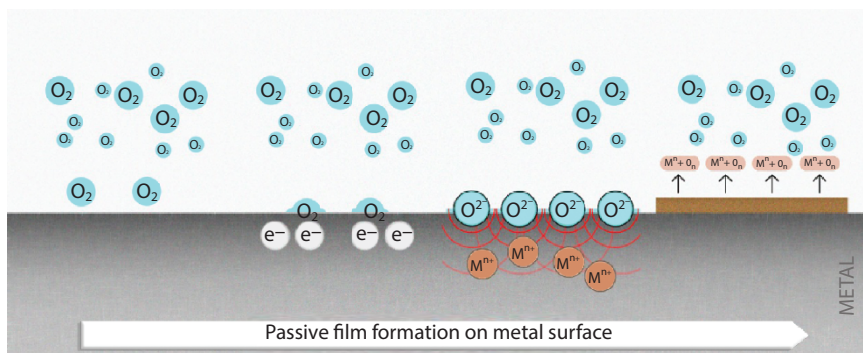


Figure 2.1 Schematic evolution of passive film growth on metal surfaces. When metals are exposed to air/aqueous environment, the interaction of its surface with O_2 molecules forms O^{2-} that are chemically bonded to available M^{n+} .

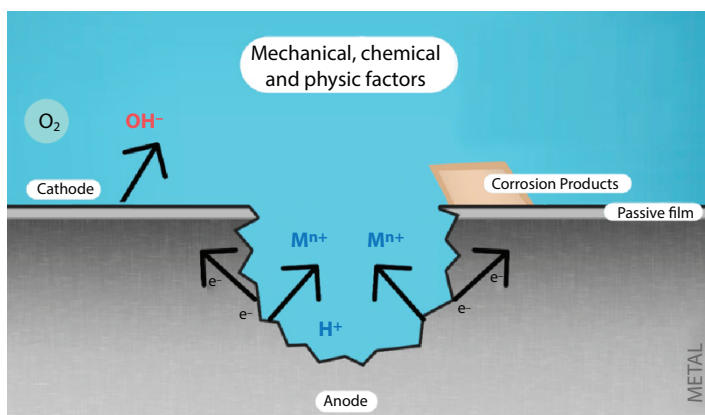


Figure 2.2 Schematic representation of metal corrosion due to mechanical, chemical, and physical factors. The disruption of surface passive film led to reactions with the environment and consequent metal ions release and corrosion products accumulation.

i.e., the class of high entropy alloys (HEAs) and compositionally complex alloys (CCAs), turn the experimental test of new designed alloys more difficult and complicated [21]. For this reason, computational tools have been proposed as a promising technique for designing better corrosion-resistant alloys, since they can quantitatively predict many materials properties and, in some cases, electrochemical mechanism taking in consideration first-principles calculations (e.g., *ab initio*, density functional theory) without empirical input [9, 21, 22]. Normally, this strategy drafts some criteria and theoretical approach to guide the calculations. Zhang *et al.* [9] defined three principles to study 68 different elements that could inhibit corrosion by their ability to diminish (or destabilize) H adsorption on second-phase particles and so reduce its corrosion rate. They found that As, Ge, Si, Ga, P, and Al are the best options as alloying elements to enhance the corrosion resistance of Mg alloys [8]. However, corrosion is a complex degradation process that can involve several factors that cannot be simulated by theoretical models alone, being necessary the *in vitro* and *in vivo* studies of newly developed alloys.

2.2.2 Influence of Alloy Microstructure on Corrosion Behavior

Alloy materials can be presented with a single- or multi-phase microstructure that is regulated by the composition. Each alloying element has a predominant crystalline phase at room temperature that when is added to

another element or experienced different thermomechanical processes can be changed due to a variety of phase transformation reactions [5, 23]. In this context, the same alloy can behave differently in terms of electrochemical activity when distinctive microstructures are produced.

Although some reports have stated a very clear relationship between microstructure and corrosive behavior, there is no consensus in the literature regarding the best crystalline phase to prevent corrosion and, not always, alloys with the same crystalline phase have the same performance. Three microstructure phases (α , $\alpha + \beta$, and β) with intermetallic variants are found for alloys in the literature [5, 10]. In general, the β crystalline phase is expected to be more resistant to dissolution than the α -phase, probably due to the passive film formed on the surface of β microstructure being more stable [24, 25]. Grimm *et al.* [28] stated that the protective behavior of β -phase is only evident when the surrounding presents a chemically less stable solid solution. The authors also observed that for corrosion inhibition, it is more important to have an α -phase with high stability than continuity of β -phase.

Studies that have investigated the direct correlation of microstructure on corrosion behavior of alloys mostly have tried the progressive incorporation of an element to alloys [10, 11, 26–30]. When Ta was gradually added (0 to 25 wt. %) to Ti, its increase in alloy composition resulted in superior resistance to pitting corrosion due to the formation of β solid solution and higher amount of Ta_2O_5 in the oxide layer that may avoid Cl^- ions intrude into the passive film [29]. Similarly, the incorporation of V (0 to 7 wt. %) to Ti-Zr-Al alloy displayed the typical β -stabilizer behavior that altered the microstructure, phase composition ($\alpha' \rightarrow \alpha'' \rightarrow \alpha'' + \beta \rightarrow \beta$), and internal stress values that were responsible to increase the corrosion potentials and to reduce the corrosion current densities [26]. The positive effect of increased amount of β phase on corrosion resistance was also observed for Ti6Al4V-xCu alloys [30]. However, Ti_2Cu intermetallic phase precipitation and porosities in the matrix also increased as Cu was added to alloy, which impaired the electrochemical behavior of such alloy with 6 wt. % of Cu. The increase of porosities in alloy structural may reduce corrosion resistance due to the increasement of the active surface area exposed to electrolyte [31].

Regarding to the precipitation of second-phases, it usually occurs with the incorporation of different elements to alloys. Although intermetallic phases may have nobler potentials than the matrix [32], if not stable, fine, and even distributed, they can dissolve preferentially on the surface [10, 30]. The presence of Al_2Cu , $\text{Al}_x\text{Fe}_{3-4}\text{Cu}$, and W-phase particles resulted

in dissolution of Al-matrix at their periphery in Al-Cu-Sc-Zr alloy since the second-phases act as cathodes to the matrix [32]. On the other hand, the absence second phase precipitations decreases galvanic effects associated with inhomogeneous distribution of alloying elements [14].

In line with this, not only the phase composition is important to understand the influence of microstructure on corrosion behavior, but also the grain size, refinement, distribution, and morphology. In general, the corrosion performance of alloys increases along with the grain size decreases [26, 32] and presence of single-phase alloys [23]. Besides, homogeneous microstructures and greater elemental distributions may result in better corrosion resistance [3, 33, 34].

Usually, passive films undergo breakdown at heterogeneous regions, namely, inclusions precipitations and grain boundaries [14]. When more than one phase and/or diverse crystallographic orientations are present, a galvanic cell may be formed and the least noble phase/element becomes more active and corrodes preferentially, impairing the alloy electrochemical stability [14, 33–36]. Similarly, the oxide layer tends to be more stable when alloying elements are homogeneously distributed, which may also avoid the galvanic interaction [14, 29].

2.2.3 Manufacturing Process to Develop Corrosion-Resistant Alloys

With a higher demand for efficient technique that is capable to fabricate materials with a complex design, new manufacturing technologies are emerging. Additive manufacturing processes, also called 3D printing, has grown in development and application in the last years. Among metal additive manufacturing processes, there are included powder bed fusion process [selective laser melting (SLM) and electron beam melting (EBM) and direct laser deposition (DLD)]. SLM is a technique that builds components layer-by-layer in a powder bed by using a high-powered laser with a computer aided design (CAD) model [37]. EBM is similar to SLM, but it uses an electron beam to generate melt metal powder in an evacuated build chamber, in which is possible the minimization of oxidation in the case of reactive powders [37]. DLD uses blown powder and energy source to build materials with large volumes; the advantage of this method is the ability to fabricate materials with gradient design using different alloys, but have limitations regarding the creation of complex shapes [37].

Most of studies that have tried to understand the influence of different manufacturing techniques (e.g., conventional casting, milling, and laser sintering) on alloys corrosion do not compared all techniques. But, studies

that have done this showed that laser sintering or/and milling shows comparable [38], or even greater corrosion resistance and lower amount of ions release [39] than the cast Co-Cr-(Mo) alloys. Specifically, SLM can be subjected to several thermal cycles, which induces the formation of alloy microstructures with refined grain structures, unique second phase precipitation, and solute segregation [40]. Ni-Ti alloy fabricated by laser based additive technology promoted a shift of corrosion potentials toward noble direction due to the increase in the grain size and associated decrease in grain boundary area and surface energy of samples when higher laser power and scan speed were used [19]. In fact, the microstructure of alloys produced by additive manufacturing depends on the process variable, such as scan-speed, laser power, and hatch distance [37].

Besides manufacturing, thermomechanical processing has demonstrated to be an excellent approach to improve the corrosion resistance, mainly by altering and refining the alloy microstructure. Aging (heat) treatments are commonly applied to change the microstructure of alloys systems with predictable phase behavior [13]. Annealing is a modality of heat treatment that is used to diminish or eliminate precipitates on grain boundaries after cold rolling [41]. In fact, solution annealing reduced the corrosion rate of wrought high-carbon Co-Cr-Mo alloys owing to grain coarsening (decrease in vol% of the phase boundary and grain boundary) and partial dissolution of second phases, without significative influence on passive film [42]. The precipitation of these secondary phases as well as the dissolution of casting precipitates in the matrix is dependent of the time and temperature of heat treatment, which can consequently result in the change of galvanic corrosion of the alloy [43]. Differently, the thermal treatment (cold-rolled/annealed) of Al-Fe-Ni alloy has no impact on the corrosion kinetics, since microstructure is not affected by annealing [44]. In some cases, it can influence negatively the material corrosion resistance when compared with the as-cast condition [28].

Surface finishing is another tactic to achieve alloy corrosion inhibition. It is well known that unpolished surfaces corrode faster than the polished ones [44]. Alloys with poor surface finishing present imperfections and impurities than may badly affect corrosion resistance owing to favor passive layer disruption and thus leading to high local corrosion rates [45]. Conversely, smoother surface of Al-Li alloy abraded from 600- to 5,000-grit finishing papers presented lower pitting susceptibility and better corrosion resistance due to the reduction of intermetallic particles (density, size, and the area fraction) [46].

Burnishing is a type of finishing process that generates a nobler and more corrosion-resistant surface compared to only cut surfaces due to the

increased level of compressive residual stress and sealed microcracks and pores produced by rolling [47]. Other technique that has been used is shot penning. It generates plastic deformations on alloy surface by the impact of high-speed particles that results in microstructure recrystallization and grain refinement [48]. Laser surface treatments also is applied to materials surfaces to improve corrosion resistance by inducing the complete oxidation of alloying elements, namely, formation of a uniform surface film [16], suppressing solute segregation [49], and generating grain refinement [50].

2.3 Final Considerations

To predict the performance of corrosion-resistant alloys is indispensable to align the intrinsic variables involved on its manufacturing, as well as to consider the constants involved on corrosion kinetics. Understanding these factors is necessary to optimize alloys to be used in adverse environments without being susceptible to corrosion. Firstly, alloy composition is the main factor that drives the growth of highly stable passive film and microstructure. However, manufacturing techniques and thermomechanical/finishing processes are efficient alternatives to inhibit corrosion on alloys materials by creating a solid and refined microstructure, with homogeneously element distribution.

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Ni-Co-W Alloys: Influence of Operational Process Conditions on Their Electroplating

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Abstract

The search for innovative technologies to meet the needs of efficient and sustainable production motivates the development of research on new materials. Ni-Co-W alloys have been studied for replacing chromium due to their superior wear, hardness, and corrosion properties. In addition to these properties, Ni-Co-W alloys have remarkable mechanical resistance and thermal stability, which confers the various applications, such as microsensors, thermostable films, anticorrosive coatings, electrocatalysts, and generation of electronic images, among others. However, the management of the parameters that influence the electrodeposition of metallic layers, whose features can be obtained by the optimization of the operational and solution parameters, has attracted the attention of researchers. The change of parameters such as speed agitation, electric current density, temperature, reagent concentration, and pH can modify and improve the features of the electrodeposited layer (accession to the substrate, homogeneity, hardness, corrosion resistance, and embrittlement by hydrogen), which is of great importance for industrial applications. In this sense, this chapter aims to demonstrate the effect of operational parameters on morphology, corrosion resistance, and composition.

Keywords: Anti-corrosive materials, microstructure, magnetic materials, electrochemical synthesis, electrodeposition, adhesion, corrosion resistance, bath composition

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3.1 Introduction

Coatings containing chromium are widely applied in engineering due to the anti-corrosive properties and for presenting a low coefficient of friction and detachable hardness [1]. However, the solution contains toxic chromium ions and by European directives legislation (2000/53/WE and 2011/37/UE) should no longer be used. With the challenge of replacing chromium by other metals, Ni coatings combined with refractory metals have become a source of study for appropriate, promising, and environmentally friendly alternatives [2, 3]. Other common challenge is to use less current density without impairing the alloy characteristics.

The electrodeposition of alloys using electrolytes allows uniform coatings to be obtained, being an economical and simple method, and quite applicable when the melting point of the metals involved has a larger range (Ni - 1,445°C, Co - 1,495°C, W - 3,410 °C). In addition, the conventional method could lead to the embrittlement by hydrogen, due to the release of hydrogen that would diffuse between the lattices of the substrate, generating failures in the sample [4]. Industrially, the electrodeposition using direct current is the most applied. Savale (2018) considered that this method is easier to reproduce and can provide more control over film thickness when compared to methods as anodization or sputtering deposition [5]. Moreover, metals used to form alloys have an important role to attribute specific characteristics.

Ni-Co alloys have been studied because of the characteristics of a micro mechanically hard material. The researchers have sought to investigate correlations between operating conditions that confer microstructure, microhardness, and specific mechanical properties in the material [6–10]. Besides, the electrodeposition process is complex, which involves transport phenomena, material and surface science, and solid-state physics [11]. Thus, there is a range of parameters that can influence the alloy, according to Figure 3.1, so that the variation of these provides the fabrication of materials with specific properties and applications.

In this sense, this chapter approaches with the Ni-Co-W ternary alloy development techniques and studies addressing each metal isolated and together with another metal, highlighting the tendencies of the use of these materials and the influence that the electrodeposition parameters have on the characteristics of the final material.

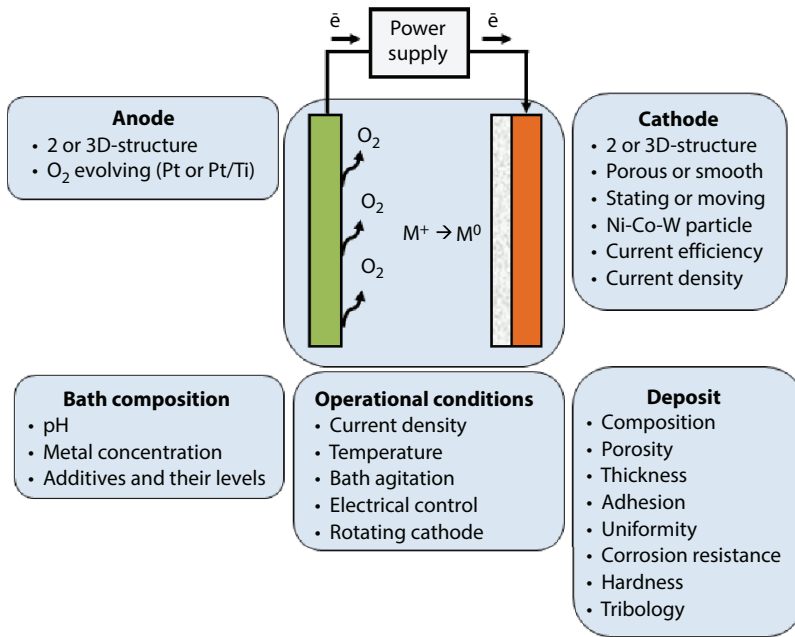


Figure 3.1 Representation of the parameters studied in the electrodeposition process of Ni-Co-W alloys. Adapted [12] Copyright 2019, Surface & Coatings Technology.

3.2 Metallic Alloys

The electrodeposition of coatings allows the synthesis of materials for various applications, such as computer industry, anti-corrosion materials, heat conduction, anti-erosion coatings, fuel cells, anti-wear and magnetic materials, connectors, and electrocatalysts [12]. In the coating of metallic parts, the electrodeposition is quite accepted and relatively simple, which produces coatings with nanocrystalline or amorphous structures. There are cases which the alloy structure can be modified by the operating parameters such as the change in current density, which produced different crystal structures, as shown in Figure 3.2.

At 10 A/m², the Ni₁₇W₃ with crystallographic planes (200), 50.88°; (220) 74.82° (JCPDS n° 65-4228); and Co₄ (111) 43.90° (JCPDS n° 01-2927) indicated a cubic crystalline system for both elements. For the same temperature of 30°C, 15 rpm and 50 A/m² were obtained crystalline structures of

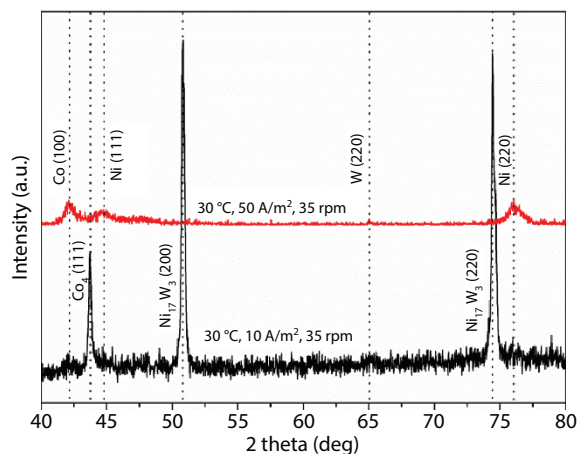


Figure 3.2 X-ray diffraction patterns of the Ni-Co-W alloys under different electrodeposition conditions.

Co (100), 41.68° (JCPDS n° 05-0727); Ni (111), 44.60° (JCPDS n° 03-1043); and W (220), 64.91° (JCPDS n° 88-2339), indicating hexagonal crystalline system for cobalt and cubic for nickel and tungsten.

3.2.1 Nickel Alloys

Nickel is one of the most commonly used metals in the galvanizing process and can be introduced into various metal alloys. Binary or ternary alloys are commonly found with combinations of nickel, iron, zinc, cobalt, copper, and aluminum. Ni coatings with other metals promote modifications in the crystalline structure of Ni. The nickel binary alloy containing iron is commonly studied since it can the junction of these metals promote the formation of a cubic crystalline structure with a centered body, which attributes hardness to the material. However, the combinations between metals must be evaluated, since, during the formation of coatings with two or more metals, the interaction of the particles does not occur in the same way as if there were only one metal. For example, the Fe-Ni alloy provides improvements in the characteristics of the material, however, in the electrodeposition process, microcracks can arise due to internal stress during the formation of the crystalline lattice [13, 14].

One of the main applications of nickel in industry and the urban environment is in anti-corrosive materials. The corrosive process in metals, especially in more aggressive environments, can be controlled with nickel-enriched sacrificial alloys, replacing toxic alloys composed of chromium

and cadmium. In Ni alloys used to retard corrosion, the weight percent of that metal is between 10% and 15%. This amount of nickel allows the formation of a more evident γ phase in the morphology, which consequently makes the coating more regular and hard [15].

Ni-Fe and Ni-Zn binary alloys are preferably used to improve the corrosion resistance of metals such as steel, which is one of the metals most consumed. Other combinations, such as the Ni-Co-Fe ternary alloy, impart ferromagnetic properties to the material; however, in ternary alloys, strict control is required during electrodeposition, since these are more susceptible to cause changes in the material due to phenomena such as anomalous co-deposition [16].

3.2.2 Tungsten Alloys

Tungsten has the characteristic of being co-deposited only with other metals, that is, it is not deposited alone, and this characteristic is known as induced co-deposition, as shown in the diagram of Figure 3.3. The process of co-deposition occurs because a metal, generally, of the ferrous group begins to undergo reduction and forms a layer that catalyzes the tungsten allowing its deposition. As a consequence of the induced co-deposition process, the tungsten alloys are not able to reach 100%

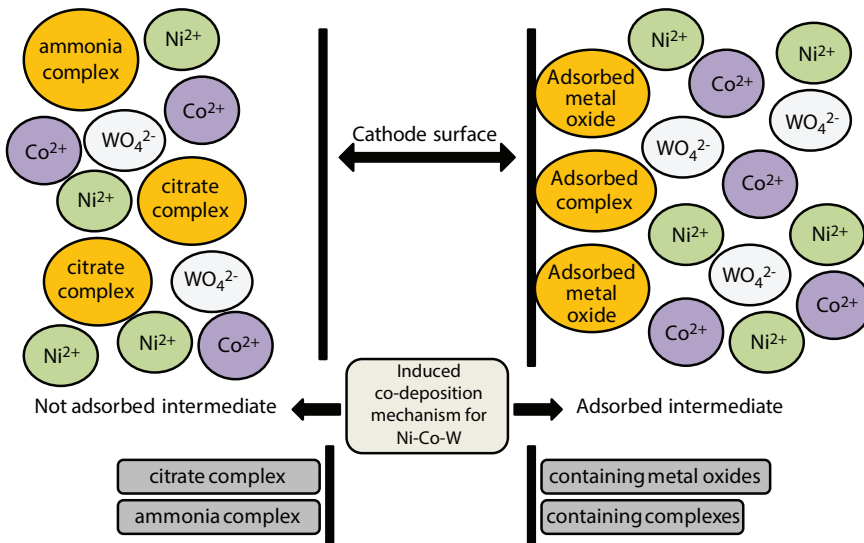


Figure 3.3 Proposal for an electrodeposition mechanism of Ni-Co-W alloy. Adapted [19]
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of the faradaic efficiency, because during the electrodeposition of this metal, even with low currents, the hydrogen evolution and the increase of the tungsten percentage in the alloy form oxide plates [17]. During the electrodeposition, the hydrogen can be adsorbed on the inductive metal layer, requiring a greater transfer of the payload and decreasing the faradaic efficiency [18].

Despite the specificities to occur the electrodeposition of tungsten, this metal can be easily deposited and attribute improvements to the characteristics of the coating. Studies indicate that materials containing a certain amount of tungsten have amorphous properties, producing a material with thermodynamically stable intermetallic components [17]. An amorphous structure can be active incorporating tungsten into the crystalline layer of metals such as iron, nickel, and cobalt. Tungsten atoms can increase the main internal distance of the atoms and changes crystals arrangement. The crystallinity of the coating directly interferes with the abrasion resistance and corrosion protection. Corrosion resistance can be improved in alloys with percentages tungsten about 18%, with structure is partially amorphous. Due to certain concentrations of the induced metal, large deformations of the intermetallic structure can be generated, being able to form partially amorphous structures with percentages between 10% and 20% of tungsten, and amorphous structures with percentages above 20% [20].

Depending on the internal structure of the tungsten alloys, the coating has similar mechanical and tribological properties to the chromium-containing materials, and tungsten has the advantage of being non-toxic and does not harm the environment. These characteristics of the metal are also added to the corrosion resistance, temperature resistance, and magnetism of the alloy, which allows the use of tungsten alloys in electronic equipment. Other uses for these alloys are the electrocatalysis of hydrogen, deposition in the reentrance of microstructures, and electrodeposition of alloys in nanotubes, foams, and gas diffusion layers for application as electrocatalysts in oxygen reduction/evolution reactions [21, 22].

The parameters of the electrodeposition (rotating cathode, current density, temperature) of metals interfere in the formation of the material, for example, tungsten alloy with cobalt deposited at a low current value tends to be magnetic. Nevertheless, it is not only the tungsten that modifies the coating properties, but the association between this metal and the parameters used is also another important factor.

3.2.3 Cobalt Alloys

The use of cobalt is common in superalloys applied in gas turbines and aerospace vehicles. Cobalt superalloys were originally used to withstand internal stress arising from temperature. With the development of new materials and the need to replace toxic metals, other properties of cobalt were explored, some of them were the resistance of the metal to oxidation and corrosion. Ni coatings containing W and P, and Co-W have become potential substitutes for hard chromium, while cobalt-rich alloys have stood out due to low coefficients of friction and good properties related to wear. Sliding wear tests on the Co-W alloy presented better results in wear rate for high loads, with a lower coefficient of friction, compared to chromium [23]. These tribological properties of the alloy containing cobalt are associated with its compact hexagonal structure and the resistance of adhesive interactions with the counterface of the coating.

Cobalt coatings can be obtained by applying alternative methods to electrodeposition, however, this makes the process of formation of hexagonal structures more unpredictable. With the use of electrodeposition to apply thin layers of cobalt, there is a control of the magnetic properties of the coating, creating ideal materials to be applied in electronic equipment. Current applications in electrocatalysis suggest cobalt as one of the elements responsible to the catalysis in the oxygen evolution/reduction reaction in metal-air cells [24–28].

Cobalt magnetic films with low coercivity, which applications are ideal for motors and generators, were prepared from an electrolytic bath. The authors proved the direct relationship between magnetic morphology, structure, and property, with control of the electrodeposition parameters [29]. Saturation magnetization and coercivity are dependent on the amount of cobalt in the film and the electrodeposition temperature [30].

In the electrodeposition of cobalt and its alloys, nanocrystalline materials can be obtained with grains smaller than 100 nm, and as the grains decrease, there is a tendency to increase hardness. Polycrystalline (4.8 μm) and nanocrystalline (12 nm) cobalt coatings were studied [31]. In the stress of the nanocrystalline coating due to deformation was made difficult, due to the need for greater energy to promote grain slip.

Tensile and elasticity tests on nanocrystalline coatings were better, suggesting that the plastic deformation properties of the material may be altered.

Cobalt is preferably deposited with lower currents and in some situations its co-deposition is anomalous. Generally, the anomalous co-deposition aim to be avoided, because it occurs when the less noble metal is dominate. In this case, the concentrations of metals obtained in the deposit have non-linear proportions and inverse to the concentrations of the metals added in the bath [30].

3.3 Ni-Co-W Alloys

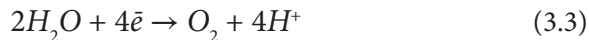
The control of the coating characteristics towards electrodeposition parameters is still established trough experimental process. The effects of several parameters on the passive behavior of alloys have been studied to better understand the phenomena attributed to the characteristics of the alloy [13, 14, 17].

Results published on Ni-Co [12, 32] and Ni-W [19, 33] alloys indicated an improvement of properties of Ni coating, by adding Co or W. Ni-Co-W alloys demonstrated a substantial reduction of microcracks on their nodular surface when compared to Co-W alloys [34]. Studies indicate the application of Ni-Co alloys in parts requiring ductility, wear-resistance, and electrocatalytic activity, whereas Ni-W alloys present amorphous microstructure, excellent corrosion resistance, hardness, and magnetic properties [35–37]. Thus, it is important to consider that the combination of these metals may promote specific properties in the material.

When there is a soluble anode, the metal ions are generated according to Equations (3.1) and (3.2):



When there is an insoluble anode, such as a platinum electrode, the oxygen is evolved:



In the cathode, the main reaction is the electrodeposition of Ni and Co, according to Equations (3.1) and (3.2). In some cases, when the target is a ternary alloy, these are accompanied by deposition of another element such as phosphorus, boron, or tungsten.

The evolution of hydrogen occurs secondarily in the cathode surface:



This reaction decreases pH and efficiency and can result in porous deposits if there is no surfactant in the bath composition. Other consequences of the hydrogen evolution are the cracks that are caused by hydrogen embrittlement due to stress among the ions [38]. High current efficiency means that the metal deposition reaction is dominant, which minimizes the electrochemical hydrogen source, preventing cracks to appear [39].

The variation of Ni and Co in the bath alters the coating of the metal alloy [40]. Studies used the fixed experimental conditions used were 5 A dm⁻² and 20 rpm for 60 min at room temperature, as shown in Table 3.1, which shows the most recent studies of ternary/quaternary alloys containing Ni-Co in the composition. By varying the concentrations of Ni and Co, a direct relationship between higher faradaic efficiency in baths with a higher proportion of nickel was observed. During the study, it was concluded that in the higher Ni level of the factorial design, Co and W were deposited with greater difficulty, however in the inverse situation, ie, for the lower proportion of nickel of the planning, there was a high deposition rate of tungsten and higher deposition of cobalt. For the authors, the crystallinity of the coating depended on the presence of boron and the Ni and Co concentration in the solution, which provided a greater deposition of Co and W with a disordered arrangement. And although amorphous alloys were more suitable for corrosion resistance, corrosion tests proved to be better in crystalline alloys with higher nickel concentration.

The current density applied and adsorption of active species can alter the morphology and features of Ni-Co, Ni-W, and Ni-Co-W alloys [33]. The current density used by the authors in the assays was between 2.5 and 50 mA cm⁻² with W concentrations varying from 11.3% to 4.2%, Co ranging from 28.2% to 11.9% and Ni ranging from 62.3% to 84.9%. The evolution of the corrosion resistance obtained in the linear potentiodynamic polarization provided the values of corrosion current 3, 4.5, and 4.5 μA cm⁻², values referring to the increasing order of the current densities used. Observations regarding the electrochemically active species of the Ni-W and Ni-Co-W alloys demonstrated that during the electrodeposition the adsorption of complex ions containing tungsten plays an important function in the morphological formation of the coatings.

Table 3.1 Summary of Ni-Co-X deposits.

Alloy	Source of the third/ fourth element	Temperature (°C)	pH	Current density ($A\ dm^{-2}$)	Reference
Ni-Co-W	Na_2WO_4	25	7.5–8.0	5 (DC)	[40]
Ni-Co-W	–	30–60	4.5	2.6 (DC)	[43]
Ni-Co-Fe	$FeSO_4 \cdot 7H_2O$	55	4	4 (DC)	[44]
Ni-Co-P	H_3PO_3 and/or NaH_2PO_2	80	2	6.25 (DC)	[45]
Ni-Co-Fe-P	$FeSO_4 \cdot 7H_2O$	65	1.8	2 (DC)	[46]
Ni-Co-Cr	$Cr_2(SO_4)_3$	30	6	0.25 (DC)	[47]
	$Cr_2(SO_4)_3 \cdot 6H_2O$	25	2.4, 2.8, and 3.2	6 (DC)	[48]
Ni-Co-Cu	$CuSO_4$	25	3.25	–0.58 V vs. SCE for Cu between –1.00 and –1.5 V vs. SCE for Ni-Co	[49]
	$CuSO_4 \cdot 5H_2O$	40	5	–1 to –5	[50]
Ni-Co-Al	–	Room	4	1.6 (DC)	[51]
Ni-Co-Mn	$MnSO_4 \cdot H_2O$	55	4.5	3 (DC)	[52]
Ni-Co-Sn	$SnSO_4$	50	5, 6, and 7	5 (DC)	[53]

(DC) - Direct current

SCE - Saturated Calomel Electrode

It was concluded that under the same deposition conditions Ni-Co-W coating presented a high Co content in the deposit, compared to Ni-Co binary alloy, thus raising the hypothesis that tungsten acts as a catalyst. The authors reported that in Ni-Co-W alloys, some characteristics such as the size of the nodules (6–10 nm), the orientation of the grains and the spherical morphological structure are not directly related to the variations of current density, because the elements Co and W have opposite and simultaneous effects.

The composition phases of the electrodeposited coatings, the microstructure, the nucleation, and growth mechanisms of the grain were studied for Ni-Co-W alloy [37]. The electrodepositions were performed on a polished copper surface, from a solution of sulfuric acid with the addition of sodium tungstate and citrate, pH 6–7, temperature 20–30°C and current density between 50 and 400 A m⁻². The studies were carried out based on the data obtained by scanning electron microscopy associated with an electron transmission microscope and X-ray diffraction. The amorphous alloys had a composition of Co₃₈Ni₃₆W₂₆ and Ni₅₀Co₂₅W₂₅.

In the composition phase of the ternary alloy, solid solutions are formed, in which the cobalt replaces the nickel, as much in the crystalline state as in the amorphous state. Tungsten has catalytic action on cobalt, facilitating the deposition of cobalt.

A heterogeneous phase, centered and hexagonal cubic, in the ternary alloy with tungsten concentrations between 12% and 14% and an amorphous homogeneous phase with tungsten concentrations above 20%, which tends to occur with the highest incidence of the hexagonal phase, was obtained in Ni-Co-W coatings [37]. The ternary alloy presented a network of microstructures, which varied according to the percentage of elements in the coating. The crystalline structure was altered as the cobalt concentration was increased.

The relation of the operational parameters with the corrosion resistance and alloy co-deposition efficiency was discussed in the literature [32]. For this, some techniques were used, such as scanning electron microscopy, chemical analysis by X-ray dispersive energy, X-ray diffraction, linear potentiodynamic polarization, and electrochemical impedance spectroscopy. The pH was maintained at 8, the temperature ranged from 30°C to 70°C and the current density from 200 to 600 A m⁻². Corrosion tests were performed at 0.1 g mol⁻¹ sodium chloride at room temperature and linear potentiodynamic polarization and electrochemical impedance spectroscopy measure the tendency for corrosion in a three-electrode cell.

Through statistical analysis of a complete factorial design, the authors obtained results for the Ni-Co-W alloy behavior varying temperature and current density. They observed that the current density variable had little influence on electrodeposition; however, the interaction of the applied current density with the solution temperature was significant in the process, evidencing a synergistic involvement. The deposited alloy presented good adherence and quality, certified by the outcomes of X-ray diffraction that presented an amorphous structure. The values optimized for the operational conditions in terms of deposition efficiency were a cathodic current density of 600 A m^{-2} , solution temperature of 30°C , 8.0 pH, and rotating cathode of 20 rpm, with 46% of deposition efficiency. The optimum coating in terms of corrosion resistance of the alloy had a deposition efficiency of 36% and was obtained with a current density of 600 A m^{-2} , the temperature of 70°C , 8.0 pH, and rotating cathode of 20 rpm. The average composition of the most corrosion-resistant alloy was 70% Ni, followed by 22% W, and Co at a lower proportion (8%). The corrosion potential and bias resistance for this corrosion efficiency were respectively 508 mV and $4.56 \times 10^4 \text{ ohm}$.

The pH values between 2 and 9 could be correlated with their effects on electrodeposition [41]. In the baths, with higher acid concentration, the reduction of the faradaic efficiency occurred and the tungsten concentration remained constant. Varying the percentage of each metal in the electrolyte can increase the tungsten concentrations in the alloy, however, the increase of tungsten in the bath allowed the evolution of hydrogen. The composition of the alloy also changed with variations in current density and temperature. The study of the current density was carried out with a density between 20 and 400 A m^{-2} . The deposits were bright and adherent with 150 A m^{-2} , and for values of current density above 150 A m^{-2} , the deposited tungsten concentrations were higher. The temperature directly influenced the adhesion, composition, and alloy efficiency. Alloys deposited at temperatures above 35°C were more adherent, in addition to the decrease of the cobalt concentration and increase of the other compounds, there was an improvement in the faradaic efficiency.

The chemical composition and crystallite size can be altered according to the thickness of the Ni-W-Co (Al_2O_3) nanocomposite by the electrochemical technique of reverse pulse [42]. The authors verified that cathodic and zero current times altered the percentage of elements, impacting the thickness, while the anodic reverse current promoted the reduction of the cracks in the coatings, removing the hydrogen from the cathode surface and taking away the residual stresses. Corrosion and wear properties were also affected by the parameters of the electrochemical procedure.

3.4 Operational Parameters in the Electrodeposition of Alloys

Crystalline structure control, morphology, and composition of metal coatings are important to maintain quality in the production of the alloys. Among the several studies, some affirm that solution composition, temperature, and current density indirectly influence the structure of the alloy [54]. Other studies indicate that the change of parameters, such as current density, causes direct changes in grain nucleation [55]. Therefore, operational parameters of electrodeposition are still widely studied, to understand the changes generated in the material, whether due to the variation of an isolated parameter or their association.

3.4.1 Temperature

The temperature interferes in the diffusion and migration of the metal ions. The increase in temperature accelerates the availability of ions on the cathode since the movement of ions at the interface of the cathode is a function of temperature. Thus, there is an increase in the kinetic energy of the particles, which reduces the cathodic overpotential and the electric field. In experiments with nickel, the increase in temperature led to an increase in the Ni content in the coating.

Figure 3.4a shows micrographs of Ni-Co-W alloy deposited on the copper substrate under temperature conditions at 60°C, a current density of 500 A m⁻², and rotating cathode 10 rpm with the presence of chips and cracks. Figure 3.4b occurred at 80°C, showing similarity in morphology; however, the faradaic efficiency increased from 53.35 to 68.46% as the bath temperature was increased by 20°C. Figure 3.4c shows the Energy-Dispersive X-Ray (EDX) mapping to the ternary alloy at 60°C and Figure 3.4d at 80°C, which composition of the three metals were Ni - 72.68, Co - 9.47, and W-17.85% for temperature at 60°C and Ni - 74.02, Co - 5.57, and W - 20.41% for temperature at 80°C, agreeing with the literature that the percentage of nickel is favored with temperature increase.

In addition to the coating composition, the temperature can alter the crystal structure of the film. During the electrodeposition, the increase in the temperature of the solution leaves the coating more crystalline and increases the growth of the grains. The structure tends to be more crystalline, since the temperature promotes the incorporation of more atoms of metal in the layer of the host metal, distorting the diffraction peaks, commonly seen in X-Ray diffraction patterns [30].

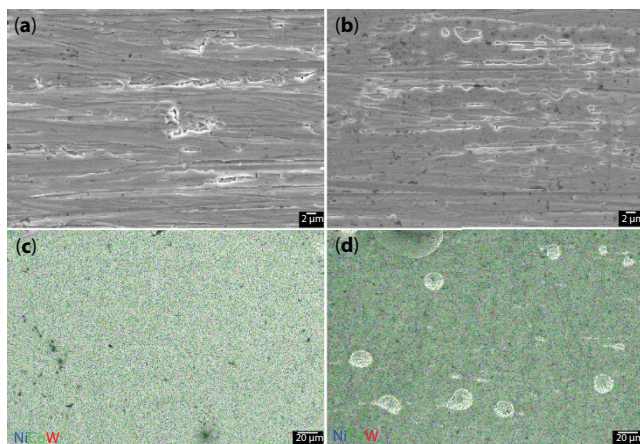


Figure 3.4 (a) Ni-Co-W alloy electrodeposited at 60°C, 50 mA cm⁻², and 10 rpm; (b) Ni-Co-W alloy electrodeposited at 80°C, 50 mA cm⁻², and 10 rpm; (c) EDX mapping of the Ni-Co-W at 80°C; (d) EDX mapping of the Ni-Co-W at 80°C.

High temperatures positively influence the cathodic efficiency of the deposition process of the metal phase, although it is not the most significant parameter to alter the cathodic efficiency [34]. Some metals are favored by the intense mobility of the ions, in tungsten co-depositions, the increase in temperature favors the concentration of reducible species present in the diffusion layer, which reduces the viscosity of the electrolyte, increases the formation of the film and makes the co-deposition of the atoms easier and more solid [18]. On the other hand, some metals are harmed by the rise in temperature, as with cobalt. In the experiments conducted at 48°C demonstrated the decrease of the adsorption of complexed cobalt species on the cathodic surface [32].

Performing electrodeposition without heating the electrolyte or with little heating can help to obtain some expected results since it allows greater control of the hydrogen evolution (release of H₂ bubbles). High temperatures increase the hydrogen evolution, being able to surpass the deposition rate and to decrease the faradaic efficiency in the electrodepositions in which the cobalt is present in a great amount [56]. Jeffrey *et al.* (2000) studied the temperature effect on the electrowinning process efficiency and observed that hydrogen evolution reactions increasing in electrodeposition process as cobalt concentrations and temperatures increases [56]. Inhibition of some molecules may also occur due to the elevation in temperature, and surface energy of crystallines. During electrodeposition at high temperatures, the grains become coarser, due to the decrease of

the generation of new nuclei and acceleration of the development of the nucleus of existing grains.

3.4.2 Rotating Cathode

Rotating cathode ensures homogenization of the electrolyte and current density at the cathode surface. The particles transfer step from the dispersed metal in the electrolyte to the cathode surface differs according to the variables used in the electrodeposition. Among the variables can be cited the effects of rotation under a perspective of kinetics, hydrodynamics, and control of mass transport during electrodeposition. A study indicates the increase of metal particles in the deposit due to the increase of the agitation; however, the excessive agitation can also damage the deposition of the particles, caused by the hydrodynamic forces in the solution that give off micro particles already deposited [57].

The vigorous agitation of an electrolyte which has in its composition a surfactant facilitates the release of bubble and can control the hydrogen pites [58]. The intense stirring of the fluid generates a turbulent flow with a high Reynolds (Re) number, which can interfere with the potential difference measurements in a galvanostatic electrodeposition system. However, for rotations less than or equal to 11 rpm, the Re number is below 50 and the mass transfer occurs mainly through natural convection [59]. The rotation used during electrodeposition has a participation in the deposition rate and can be calculated considering a diffusivity coefficient (D_{AB}), the Reynolds number (Re), which describes the flow of the fluid, and the number of Schmidt (Sc), which describes the transport properties of the electrolyte.

One of the complexities of analyzing ionic mass transfer in the electrodeposition of alloys is due to the formation of intermediate complexes, reduced in parallel and simultaneous stages during adsorption, which increases the resistance to mass transfer [59]. Besides, this parameter should not be studied singly, since it will be at least related to current density. Therefore, the study of mass transfer is necessary, since just as the effects of the rotation variation can change the rate of deposition, there can also be changed in the characteristics of the alloy.

3.4.3 Current Density

Applied current can directly affect morphology and consequently alloy structure. The application of the current density in the electrodeposition can be carried out potentiostatically, where the potential is kept constant

in the system, or galvanostatically, in which current is applied in the system. The galvanostatic form is the most used for the deposition of alloys, which the current can be applied using techniques of direct current, pulsed current, or reverse pulsed current, being the first technique the most industrially employed. The choice of technique and how it is applied may affect the deposited final mass and grain size, being a relevant tool to control the crystallinity of the material. Depending on the value of current density and the technique used, the size of the deposited grains can be gradually reduced or increased. The outcome of current density on the grain size occurs, because at a high cathodic overpotential, the nucleation process is accelerated and the grains are refined, this electrocrystallization theory has already been observed in several studies [58, 60, 61]. The hydrogen evolution may also increase the size of Ni grains and the tensile strength of the coating [14].

The function of current in the deposition of metal atoms has significant interferences caused by variables such as metal concentrations, pH, and temperature. The set of parameters that will promote the catalysis of this metal needs to be considered. For deposition of tungsten, for example, the electrodeposition needs to be under high currents and the solution pH is close to 8 for the generation of the tungstate complexes.

The impact of current density, in the range of 50–1,000 A m⁻², on the morphology and magnetic features of the (Co_{100-x}Ni_x)_{100-y}W_y electrodeposited alloys were evaluated from a glycine-containing solution [62]. The W content decreases with increasing current density magnitude. The current density variation allowed the formation of two-phase structural transitions: the hexagonal close-packed that occurred at a current density of 200 A m⁻² and cubic crystalline phase at 500 A m⁻². The observed Co face-centered cubic phase depended on the adsorption/incorporation and the effect of grain size reduction. The relation between current density and crystallinity was observed by Sakita *et al.* (2013), which proved that an amorphous state occurs for values higher than 500 A m⁻² [62].

As in the other parameters, the hydrogen evolution affects the deposition of metals, mainly with the use of high currents. The incorporation of hydrogen in the deposit causes changes in the surface energy, in the mechanisms of growth and the distribution of the applied current [14, 60, 63].

3.4.4 Bath Composition and pH

The initial concentration of metal added into the bath is an important parameter and can interfere directly on morphology [40]. However, the

final proportion of the metal which composes the alloy also has an intrinsic dependence with the cathodic overpotential during electrodeposition. Qiao *et al.* (2013) observed a constancy in the alloy composition when the cathodic potential was fixed during electrodeposition [64]. Together with the salt source of a metal that composes the bath can add other reagents to improve electrodeposition efficiency. Their addition is with the purpose of complexation, bath stabilization, the formation of amorphous structures in the alloy and surfactants to reduce hydrogen bubbles during deposition [32, 65]. Lupi *et al.* (2017) analyzed the electrodeposition with and without sodium citrate, a complexing agent [43]. The use of a complexing agent promoted high efficiency and specific energy consumption. Using citrate in solution the tungsten contents increased with temperature, however, without citrate W remain quite constant.

The pH adjustment is necessary to obtain better current efficiency and avoid anomalous electrodeposition due to the chemical species correlation with the potential [66]. In Ni-Co-W alloys, ammonium hydroxide is used for pH adjustment due to its complexing action [32]. Baths such as Watts type have low pH and high nickel concentration. Authors who tested different alloys using acid baths showed good results for the deposits [33, 66–68].

3.5 Conclusions and Future Perspectives

Researchers have spared no effort to develop new materials capable of replacing coatings that use toxic metals that harm human health and the environment. Ni-Co electroplated alloys have been widely applied in magnetic devices such as sensors and inductors. Ni-W alloys demonstrate high hardness and corrosion resistance. The introduction of W in Ni-Co coatings favors durability, increases hardness, and resistance to high temperatures.

It was discussed the tendencies of Ni-Co-W ternary alloy applications including electrodeposition conditions, parameters affecting various properties (magnetic, mechanical, and thermal stability) and nanocrystalline morphology. The topics implicit in this chapter are some among a huge list of study objects potentially innovative for future research. We hope that this chapter will motivate the research in the field of metallic alloys, in particular in the influence of the electrodeposition parameters, since the literature is still deficient of recent studies.

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Synthesis and Characterization of Al-Mg-Ti-B Alloy

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Abstract

In this study, novel $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloy has been synthesized by using high energy ball milling method. The structural, morphological, thermal, and mechanical properties of synthesized alloy were examined by using different analytical techniques including scanning electron microscopy (SEM), energy dispersive spectrometry (EDX), differential thermal analysis (DTA), and X-ray diffraction (XRD). The micro-hardness value was also investigated by Vickers micro-hardness (HV) tester. The degree of amorphization, crystallite size, and lattice strain were calculated for the different milled powders (5, 30, 50, 100 h, and 150 h). The glass formation of synthesized powders is clearly observed and the optimum milling time is found as ranging between 50 and 100 h. Moreover, thermal stability of mechanically milled alloy is suitable to applications working under 800°C. The crystallite sizes of different milled powders were decreased gradually with increasing milling time up to 100-h milling. The micro-hardness value of 100-h milled powders was found as 859.7 HV.

Keywords: Mechanical alloying, crystallite size, XRD, SEM, amorphous phase

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4.1 Introduction

Mechanical alloying (MA) has been used to synthesize wide range of materials from its discovery in 1966s to present day [1, 2]. Cold welding and fracturing processes are two well-known phenomena that repeated during MA of powders. During mechanical alloying, the energy of balls in milling medium transfer to elemental powders and these powders undergo atomic diffusion and solid state reaction to produce final material [3]. Although MA is a simple working principle, milling speed ball to powder ratio, milling atmosphere, and process control agent are significant parameters that affect to final produced materials [4, 5]. Various novel materials can be synthesized by this routine; metallic glasses, quasicrystalline alloys, intermetallic compounds, nanocrystals, and high entropy alloys are some examples of these materials [3, 6].

Aluminum alloys have been used in automotive, aerospace, marine, and other industries owing to their excellent physical properties and lightweight [7]. Al-Mg alloys attract attention of researchers due to high specific strengths and good corrosion resistance [8, 9]. Moreover, it was founded that solubility of Mg in Al was increased by mechanical alloying process [10, 11]. AlMgB₁₄ attract scientific interest due to their extremely low friction coefficient and high hardness about 28–32 GPa [12–14]. In different study, the hardness of Al-10%Mg-0.1%Ti alloy is gradually increased with addition in Si wt% content [15]. The effect of addition of Cr and Mn on microstructure and mechanical properties of Al-10%Mg-0.1%Ti alloy was also investigated [16].

Therefore, the aim of the present study is an analysis of effect of milling time on microstructural, morphological, and micro-hardness properties of Al₇₈Mg₁₅Ti₆B₁ powders mixture during mechanical alloying process.

4.2 Experimental

In the present study, the powders purity metal basis of aluminum (99.5%), magnesium (99.8%), titanium (99.5%), and boron (99.1%) mixtures were then mechanically milled Al₇₈Mg₁₅Ti₆B₁ (at.%) alloy in ball milling (Fritsch Pulverisette-5 planetary mill). The elemental powders of Al, Mg, Ti, and B were weighed in the appropriate ratios before start into the milling. The powders with the stainless-steel balls were mixed into a stainless steel cylindrical vial (250 ml) under room temperature. The milling was carried out at room temperature for different durations of 10 min, 5 h, 30 h, 50 h, 100 h, and 150 h in mechanical mill with a rotation speed of 300 rpm with balls that were used with ball to powder weight ratio of 10:1. To avoid heating during the mechanical alloy process, ball milling was programmed

to operate for 30 minutes and waited for 30 minutes. O-ring to prevent air from leaking in avoids agglomeration of the powder onto the walls to prevent excessive cold-welding.

The structure and the crystallite size of the mechanically milled powders were examined with a Panalytical Philips X'Pert PRO diffractometer (XRD) with Cu-K α radiation ($\lambda = 0.154056$ nm) at 40 kV and 30 mA in a fixed at angles from 20° to 100° with a step size of 0.02° and a count time of 1 second per step. The microstructures of the milled powder particles were observed by SEM (scanning electron microscopy) using a ZEISS EVO LS10 microscope operated at 15 kV and 0.4 mA and BSD detector. Bruker 124 eV of energy-dispersive X-ray spectrometer (EDX) was used for composition dispersion analysis after the milling process. Thermal behavior of the alloys powders which obtained at 10 min, 5 h, 30 h, 50 h, 100 h, and 150 h of milling were analyzed by differential thermal analysis (DTA) using a Perkin-Elmer Sapphire where the samples were heated at 20°C/min from 400°C to 800°C in high-purity nitrogen atmosphere. The Al₇₈Mg₁₅Ti₆B₁ powders after 100-h and 150-h milled times were selected to investigate micro-hardness values. They were cold compacted into compacts of 13 mm in diameter and about 1 mm in height. The Vickers micro-hardness tests were carried out with Shimadzu HMV-2 micro-hardness tester at a load of 19,614N (HV2) and a waiting time of 15 s.

4.3 Results and Discussions

X-ray diffraction results of Al₇₈Mg₁₅Ti₆B₁ powders milled for different periods (5 h, 30 h, 50 h, and 100 h) are given in Figure 4.1. After initial milling (5 h), all the elemental powders peaks are clearly seen. The XRD peaks of elemental powders of aluminum (Ref. code:00-001-1176), magnesium (Mg₄O₄ Ref code:96-901-3225), titanium (Ref.code:01-088-2321), and boron (B₂O Ref code:01-088-2485) give peaks that are very close to each other resulting wide diffraction pattern is formed. Also, after 5-h milling interval, Mg and B elemental powders oxidized have been observed. With increasing milling time, X-ray diffraction peaks gradually decrease as seen from Figure 4.1, the peak intensity from low to is 100 h, 50 h, 30 h, 5 h, respectively. Moreover, the bordering of most intense peak gradually decreased and after 100-h milling only main broad diffraction peak is seen. The disappearing of all crystals peaks and the broad diffraction pattern indicates the formation of amorphous structures. So, this main broad peak implies that Al-based amorphous alloy is successfully generated. Figure 4.2 demonstrates XRD pattern of

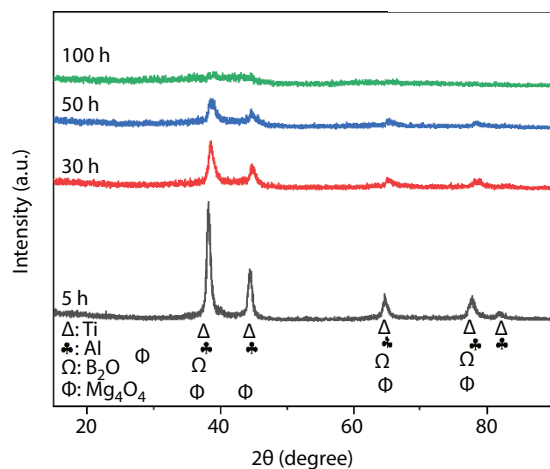


Figure 4.1 XRD diffraction pattern of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders milled for 5, 30, 50 and 100 h.

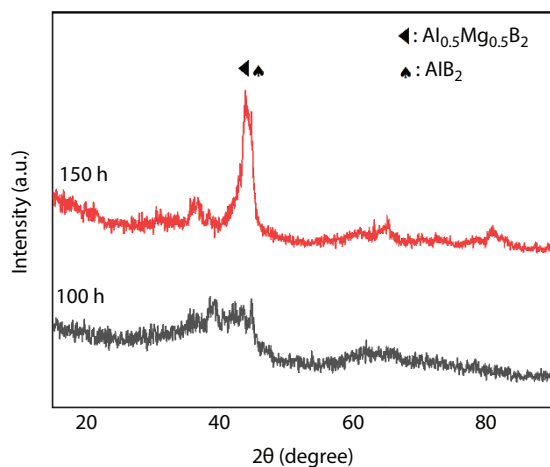


Figure 4.2 XRD diffraction pattern of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders milled for 100 h and 150 h.

$\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders after amorphous phase generated for 100-h milling. The amorphous powders were subjected to 50-h further milling. As shown in the figure, broad diffraction peak of 100-h milling is disappeared and new sharp crystalline peaks generated by further milling. It is assumed that these new peaks correspond to $\text{Al}_{0.5}\text{Mg}_{0.5}\text{B}_2$ and AlB_2 phases. Local increased temperature and severe deformation might be the possible reason of formation of these new phases [17].

The amorphous alloy formation of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders as a function of milling time was calculated by using formula [18]:

$$X_a \% = 1 - \frac{I_a}{I_c} \times 100 \quad (4.1)$$

where X_a is the degree of amorphization, I_a is the intensity for major peaks of milled powders, and I_c is the intensity of initial powders. Therefore, the degree of amorphization for different milling times is given in Figure 4.3. From this figure, the glass formation of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders is clearly observed and the optimum milling time that is ranging between 50 and 100 h is founded. After further milling, the degree of amorphization has decreased the crystals was occurred.

It was known that microstructures and some physical properties of materials are affected by the change in crystallite size. For this reason, examining crystallite size of synthesized $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders as a function of milling time is important. The crystallite sizes of the powders were calculated by using Debye-Scherrer analysis

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (4.2)$$

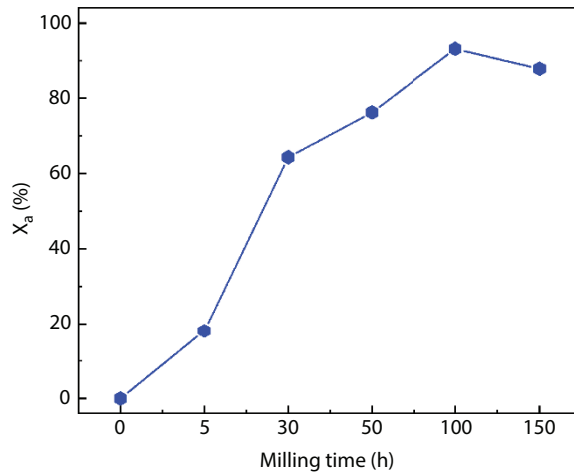


Figure 4.3 The milling time dependence of amorphization of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloy.

Here, D is the average crystallite size, λ is the wavelength of X-ray, B is the full width (in radians) at half maximum intensity, and θ is the Bragg diffraction angle. The variation of crystallite sizes of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloys for different milling intervals are given in Figure 4.4. When the crystallite size change up to 100-h milling was examined, it was observed that the crystallite size was calculated as 35.6 nm, the early stage of milling (5 h), and decreased to 8.9 nm after 100-h milling. However, the milling time is increased further and after 150 h of milling, the crystallite size has increased as opposed to the previous decreasing situation. The increase of particle size might be stream from decrease of degree of amorphization for milling time after 100-h milling [19]. The milling time dependence of lattice strain is given in Figure 4.5. The lattice strain decreased with increasing milling time as opposed to behavior crystallite size as a function of time. The lattice strain increased up to 100-h milling since heavy plastic deformation can cause high fraction of dislocations and increase in grain boundaries during milling process also positively affect increase in lattice strain [20, 21]. The lattice strain was decreased after 150-h milling.

The morphological evolution of the micro structured powders alloy for different milling times was investigated by the help of Scanning Electron Microscopy (SEM) and it is demonstrated in Figure 4.6. SEM images show an $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloy after different ball milling times (a) 5 h, (b) 30 h, (c) 50 h, and (d) 100 h that are given in this figure. It is known that cold welding and fracturing are common processes during ball milling. Here, at the earlier stage of milling, different size distribution and special

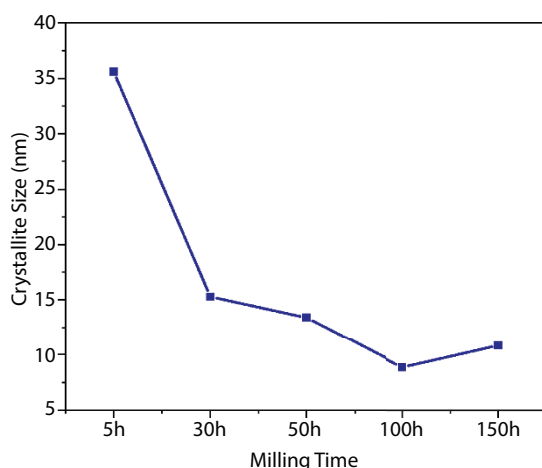


Figure 4.4 Crystallite size as a function of milling time.

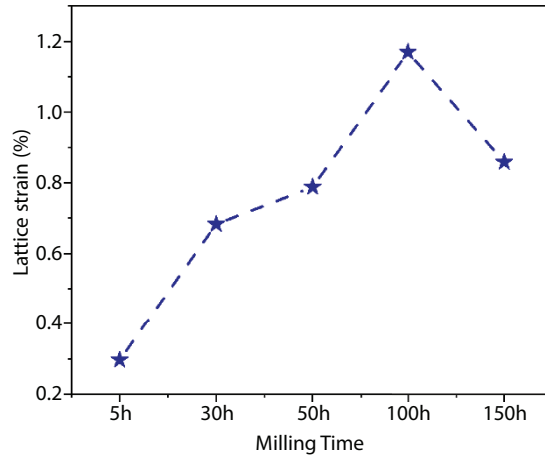


Figure 4.5 Milling time dependence of lattice strain.

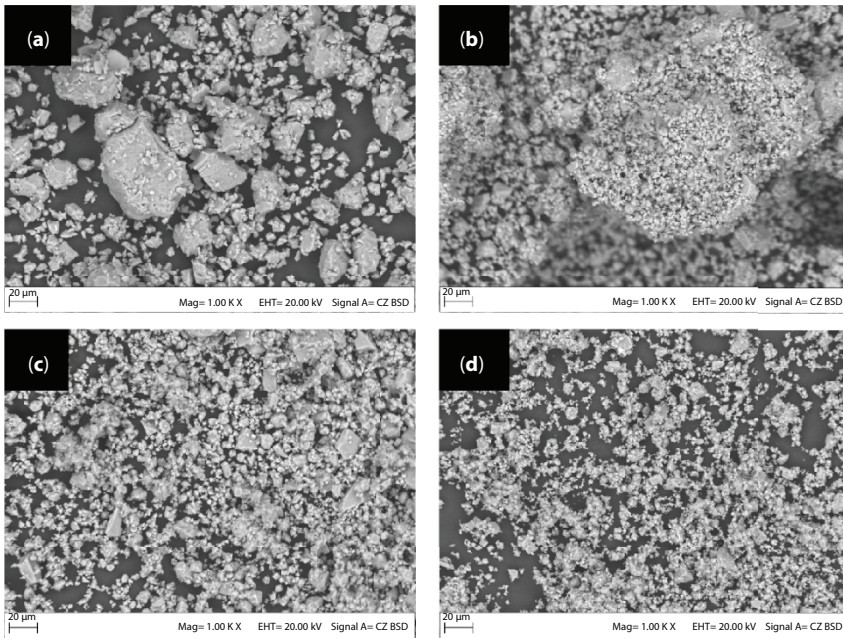


Figure 4.6 SEM micrographs (1000x magnification) morphological changes of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ (at.%) alloy powder after different ball milling time: (a) 5 h, (b) 30 h, (c) 50 h and (d) 100 h.

shapes of elemental powders are clearly seen in Figure 4.6a. The cold welding process of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloy is shown after 30-h milling and it is given in Figure 4.6b. From this figure, it is seen that the initial elemental

powders come together and they form large particles. In Figure 4.6c, after the cold-welding process, the milling powders undergo fracturing process. At this stage, homogeneity of particle shape was increased and particle size of powders was decreased. Re-welding and fracturing occur repeating with increasing milling time. After 100-h milling, particle homogeneity enhanced and micro-grain size of powders drastically decreased which is demonstrated in Figure 4.6d. Figure 4.7 shows the SEM morphology of 100-h and 150-h milled $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloys. As a result of XRD, the degree of amorphization is decreased after further milling from 100 h to 150 h, and then, partial crystallization occurs in powder alloys with a grinding time of 150 h. The effect of further milling after amorphization region on morphological features was investigated in this figure. There are no extreme differences between 100-h and 150-h milling were found from SEM observation but grain sizes of powders were further decreased for 150-h milled sample were found.

SEM photograph and EDS elemental maps spectrum of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloy milled for 100 h are shown in Figure 4.8. EDX analyses can resolve the presence of multiple phases observed by XRD. Surface scanning of the $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders is shown in this figure. It can be seen in the figure that the elemental powders, Al, Mg, Ti, and B, are distributed mechanical alloying and they are shown red, green, blue, and yellow colors, respectively. Furthermore, Mg was distributed into the Al matrix; hence, Mg rich particles were found in the powders sample. The $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ alloy powders were mixed with elemental according to a nominal stoichiometric composition. The EDX analysis confirmed the compositional homogeneity of the $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ alloy for 100-h milling time. At this step, the colloidal force between balls and all elemental metals of Al, Mg, and

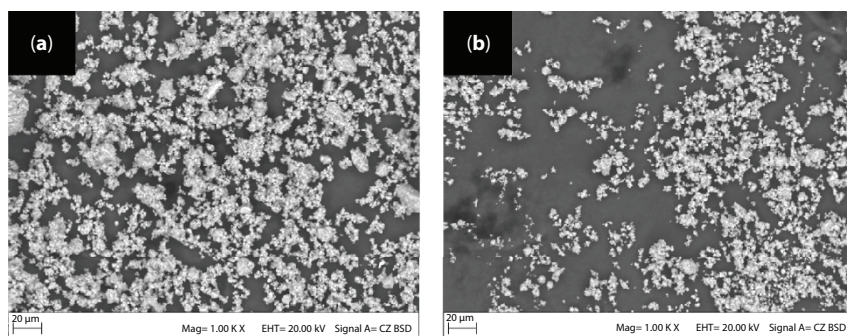


Figure 4.7 Microstructural changes of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ (at.%) powder as a function of MA times: (a) 100 h and (b) 150 h.

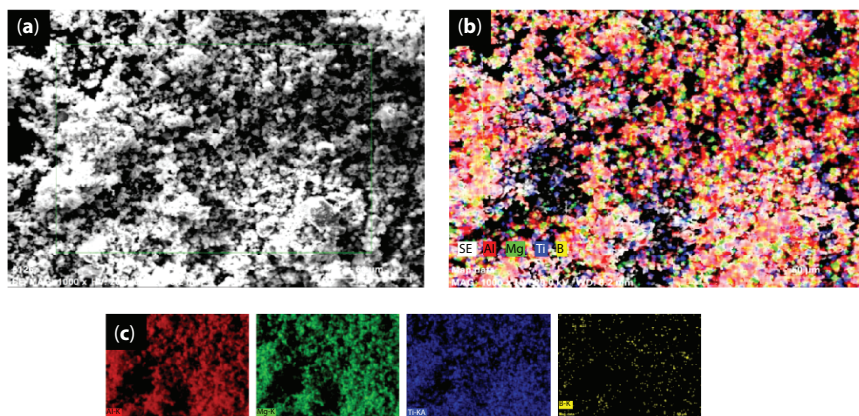


Figure 4.8 EDX results of (a) SEM image, (b) The corresponding elemental maps and (c) The powders elemental surface distribution of Al, Mg, and B in $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ (at.%) alloy milled for 100 h.

B was mostly used in the deformation process. This reveals Mg and B elements dissolve into the Al.

The physical behavior of the mechanically milled $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ alloy was investigated by Vickers micro-hardness measurements to study the influence on the hardness of degree of amorphization especially for 100-h and 150-h milled samples. Since degree of amorphization is the best value with 93.1% for 100-h milled sample and further milling caused partial crystallization occurs in powder alloys. The degree of amorphization is decreased to 87.8% for 150-h milled sample. It is known that the hardness of powders increased with increasing milling time since powder tends to more regular shapes and some atoms dissolved atom generates solid solutions [22]. Figure 4.9 shows the micro-hardness values of $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ alloy after 100-h and 150-h milling. As seen from this figure, the micro-hardness value of 100-h milled samples is higher than 150-h milled sample. The calculated micro-hardness values were found as 859.7 HV and 534.4 HV for 100-h and 150-h milled samples, respectively. While the micro-hardness increased proportionally to with the rate of amorphization, crystallization of the amorphous structure adversely affected the hardness of the alloy.

Figure 4.10 shows the DTA curves of the $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloy at a heating rate of 30 K/min for 100-h and 150-h milled samples. As a result of this figure, thermal behavior of mechanically alloys $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ powders alloy was found as stable meaning that the synthesized alloy can work well in the 200°C–800°C temperature range.

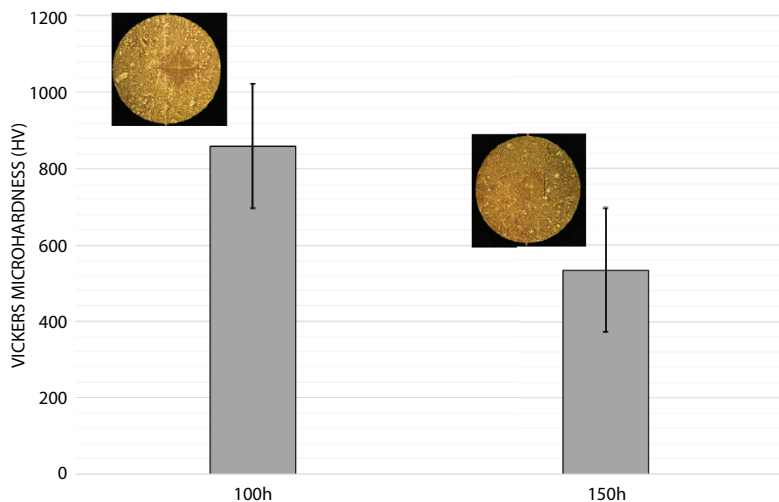


Figure 4.9 Average microhardness as a function of milling times.

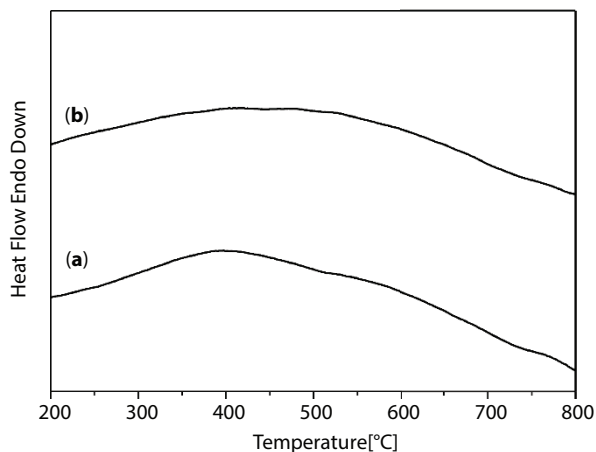


Figure 4.10 DTA graphs of (a) 100-h and (b) 150-h ball milling time.

4.4 Conclusion

In this work, $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ alloy powders were synthesized by mechanical alloying method. The effect of milling time on their microstructural, morphological, mechanical, and thermal properties of the synthesized $\text{Al}_{78}\text{Mg}_{15}\text{Ti}_6\text{B}_1$ alloy was investigated. The following results and conclusions appear from the experimental work:

1. The degree of amorphization reaches to maximum at 100 h milling and after further milling the crystallization of the amorphous structure begins.
2. According to EDX results, the compositional homogeneity of alloys is in harmony with the intended composition ratios.
3. The micro-hardness values were found as 859.7 HV and 534.4 HV for 100-h and 150-h milled samples respectively.
4. The thermal stability of mechanically milled alloy is suitable for applications that work up to 800°C.
5. The crystallite size of mechanically alloyed samples decreased with increasing milling time up to 100 h and the crystallization of the amorphous structure for 150-h milling increased it.

Acknowledgments

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Magnetic Alloy Materials, Properties and Applications

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Abstract

The magnetic materials in element form have some limited applications. Thus, the magnetic alloyed materials acquired much attention to fulfill the further applications. In case of any kind of magnetic alloy material, the basic parameters such as coercivity, retentivity, saturation flux density, magnetization, magnetic permeability, magnetic loss, etc., are considered. Thus, we pointed out the efficiency of magnetic alloys towards the industrial applications. This chapter is mainly aimed at the discussion on various magnetic alloys (soft and hard) along with their different parameters for magnetic storage devices, spintronics, transformer and inductor cores, etc.

Keywords: Magnetic alloys, coercivity, retentivity, saturation, flux density

5.1 Introduction

A physical phenomenon that is arbitrated by magnetic fields is magnetism. Magnetic field is created by the electric currents and the magnetic moments of electrons. A simple bar magnet is shown in Figure 5.1. The

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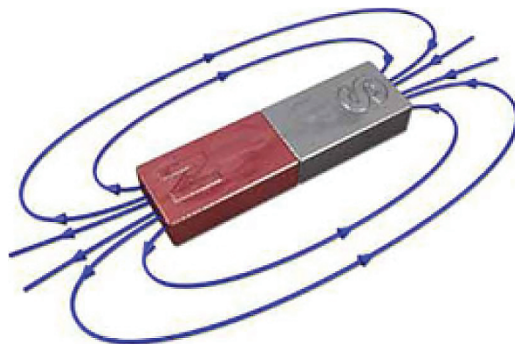


Figure 5.1 Bar magnet.

materials which are strongly attracted by the magnetic fields are ferromagnetic materials. These materials can be magnetized easily because of spontaneous magnetization and exhibit domain structure and hysteresis. Examples are iron, cobalt, nickel, and alloys like steel. The phenomenon of magnetism was first observed in lodestone which is a form of natural iron ore called magnetite (Fe_3O_4). Many magnetic effects which we come across in day-to-day life is due to ferromagnetism. The materials which are weakly attracted in the presence of magnetic field are paramagnetic materials. Examples are aluminium, oxygen, etc. The materials like copper and carbon which gets repelled in the presence of magnetic field are diamagnetic materials. Materials like chromium called as antiferromagnetic possess a complex relation with magnetic field. Generally, para, dia, and antiferromagnetic materials are considered as non-magnetic materials because these materials will experience a weak magnetic force which can be detected only in laboratories.

Magnetic materials enacted a pivotal role in the advancement of modern civilization. The compass invented by the Chinese is the very first application of magnetic material in the Qin dynasty between 221 and 206 BCE. Compass was made up of lodestone or magnetite. French scholar P. de Maricourt has written the existing description of magnetic materials in 1269 by introducing the concept of magnetic poles and explaining the attraction and repulsion concepts [1]. For centuries, magnetic compass was used for navigation and became an important pre-requisite for the exploration of our planet [2]. Oersted made a scientific and technological breakthrough by discovering the interaction between electric current and magnetic field which later on become the basis for the development of

generators used for producing electricity and also often applications like electromotor, telecommunication, electric light, etc. [3]. Invention of magnetic tape recorder by Valdemar Poulsen is another breakthrough in the technological advancement of magnetic materials [4]. Pierre Weiss proposed a theory to explain the magnetism in solids, according to Weiss, owing to interactions (magnetic) between the adjacent atoms, the atoms exhibit magnetic properties at molecular level [5]. Especially, in case of ferromagnetic materials, he introduced the concept of domain theory, i.e., the ferromagnetic material consists of large number of small regions with spontaneous magnetization called domains. In addition, this theory also explains the temperature dependence of magnetization. Nevertheless, the explanation of origin of magnetic field in solids is not clear at ambient temperatures due to classical approach. The exchange interaction between electrons was shown by Werner Heisenberg in 1928 which was originated from Pauli's exclusion principle. This gives an effective interaction among the spins of the electrons [6]. This quantum approach overcomes the above said problems for explaining the magnetic ordering at ambient temperatures in solids.

Until 1930, ferromagnetic materials were considered to be strong magnetic materials because it was assumed that entire magnetic moments of atoms were parallel. But according to Louis Neel complex magnetic structures could exist where resultant magnetization vanishes due to opposite magnetic moments as in the case of antiferromagnetic materials or its magnitude reduces as in the ferromagnetic materials [7]. He also said that tiny particles of the magnetic materials might show superparamagnetic behavior at finite temperatures, i.e., due to thermal agitations direction of magnetization may oscillate. Discovery of magnetic neutron diffraction (MND) by Clifford G. Shull has unveiled large number of magnetic structures in solid objects [8]. The distinctive magnetic field that captivated attention in spin glasses, which contains frozen atomic magnetic moments in arbitrary directions [9].

Later half of the twentieth century witnessed advancement of current information technology in the form of data storage in magnets. It is worthy to note that nanostructured magnetic materials find place in many modern applications such as multilayer structures, nanowires, thin films, etc. Nanoparticles exhibiting magnetic properties generally differ from that of bulk materials. For example, hard disks consist thick layers of iron (Fe) in nano range and chromium (Cr) exhibiting giant magnetoresistance resistance (GMR) discovered by Fert, Grünberg & co-workers [10, 11]. From these nanostructured magnetic materials, nanoparticles are the

potential candidates for many technological applications like magnetic storage devices because of their unique properties. Ferrofluids are the stable supervisors of magnetic NPs having wide technological applications and currently is in biotechnology and in biomedicine. These magnetic NPs also play a major role in nature, because soils and rocks also consists of these particles. Based on the nature of magnetic materials in external field, they are classified mainly into two types which are soft magnetic materials and hard magnetic materials.

5.2 Types of Magnetic Materials

5.2.1 Soft Magnetic Materials

These are a class of ferromagnetic materials with low coercivity and high permeability. When soft magnetic materials are subjected to the magnetic field which is time changing both magnetic and core loss arises in electric machines. Core losses are due to eddy currents losses which in turn are due to circulating electrical currents in conducting material. In magnetic materials, the loss due to hysteresis is proportional to area of hysteresis loop. These materials should possess

- high saturation induction
- high permeability
- low coercivity
- high resistivity

The above said properties may be tailored by adding chemicals and by subjecting them to heat. Silicon-iron electrical steel usual soft magnetic material is utilized in the electrical machines. By adding Si (silicon) to soft-iron coercivity reduces significantly, saturation magnetization decreases slightly and resistivity increases. Soft magnetic nanopowder is made up of bonded Fe powders. The Fe powder is layered with an insulating layer and compelled into a solid before heat treatment to cure the bond. These soft magnetic composites are isotropic which helps in the design of magnetic circuits with 3D flux paths and small eddy currents. The major disadvantage is high core loss at 50 Hz [12]. Figure 5.2 indicates some simple soft magnetic alloys.

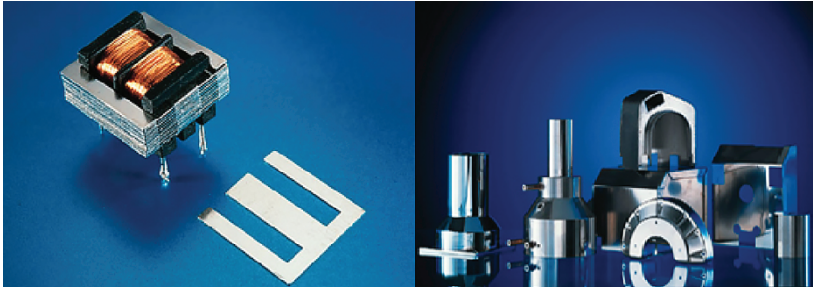


Figure 5.2 Soft magnetic alloys.

5.2.2 Hard Magnetic Materials

The ferromagnetic materials with high coercivity and low permeability are hard magnetic materials. Some hard-magnetic alloys are shown in Figure 5.3. These are mainly used in making permanent magnets. These are generally used in the preparation of permanent magnets. For example, AlNiCo alloys show nonlinear demagnetization behavior. In general, the casting or powder metallurgy process is used to prepare AlNiCo magnets which are existing in both anisotropic and isotropic forms. Compared to other permanent magnets the main advantage of these alloys is their good temperature stability which makes that use of these magnets in different devices such as voltmeter, ammeters, small servo motors in military and aviation, etc. [13, 14].



Figure 5.3 Hard magnetic alloys.

5.3 Magnetic Alloy Materials

Energy problems have become one of the important current issues. According to literature, US greenhouse gas emission reported that due to usage of coal combustion in electric sector caused the production of highest greenhouse gas emission (nearly 30%) which is followed by transportation sector (nearly 26%) [15]. The demand has been increased to overcome the energy problem. Scientists suggested that the usage of magnetic materials can save the electrical energy and also reduces the emission of dangerous gases like CO_2 , S_xO_y , and N_xO_y into the environment [16–18]. Even nonpolluting renewable energy resources like hydropower dams, windmills, etc., use the permanent magnets to convert the energy [19]. Instead of using permanent magnetic materials, the usage of soft magnetic materials decreases the energy losses in transportation and power generation [20]. Furthermore, some magnetic materials produce heat during magnetization-demagnetization process, which is also known as MCE (magnetocaloric effect) [21]. In general, devices like air conditioners, refrigerators, etc., play a vital role in energy consumption and utilization of MCE in such devices creates a huge reduction in energy consumption. In addition, the magnetic materials used in spintronics, magnetic memories in alloy form, magnetocaloric effect, permanent magnets, electric steel, etc. Nowadays, in order to meet the demand to develop good magnetic alloy materials, researchers introduced some alloys like NANOPERM ($\text{FeZrB}(\text{Cu})$), KITPERM (FeCoZrBCu), and FINEMET (FeSiBNbCu) [22, 23]. Especially, nanocrystalline alloys have attracted much attention for the applications in energy storage and electronics industry [24–26]. In this chapter, we focused on different types of magnetic alloy materials and their applications in distinct fields.

One of the major industrial applications of the magnetic materials is usage of the magnetic materials in magnetic recording system. In this connection, the research is going on to find new materials for magnetic recording application for high information recording capacity [27–29]. At high-frequency region, some of the magnetic alloys (for example, Fe-SiO_2) have attracted much attention as new recording media [30]. Hashimoto *et al.* [31] synthesized CoPd alloy films by rf magnetron sputtering technique. They investigated the magnetic properties of the prepared alloy films as function of Pd composition. They reported that Pd-rich alloy films exhibit excellent magnetostriction is of the order of 10^{-4} , also shows the magnetic anisotropy perpendicularly related to the magnetostriction effect. Thus, the CoPd alloys with perpendicular anisotropy can serve as a

perpendicular magnetic recording system which can also be used in magneto-optical recording systems.

In the process development, through hardening sputter-deposited non-crystalline alloy films, N. Hasegawa *et al.* [32] prepared nanocrystalline films which are Co-M-C, Ni-M-C, and Fe-M-C ($M = \text{IV}^{\text{th}}$ and VI^{th} group metals), in which very thin M-carbide particles are spread. Among these, Co-M-C and Fe-M-C films display decent soft magnetic behavior. Even after annealing, the magnetic properties in the films are continued due to dispersed M-carbide particles. In addition, these carbide particles significantly slow down the grain growth of Co-rich and Fe-rich nano crystallite films. Further, the films which contains Hf or Ta shows high thermal stability and in contrast, films containing Hf and Zr are much appropriate for attaining large saturation magnetization (Fe-M-C films 1.7T and Co-M-C films 1.6 T). Furthermore, through regulating the hardening condition, it is possible to prepare zero magnetostrictive films. Moreover, the effective functioning of Fe-Hf-C films, high value of saturation (2.0T) is accomplished through multilayering the Fe-Hf-C with iron. Hence, the carbide dispersed films are prominent candidates for high dense magnetic recording applications. Later, Kim [33] synthesized Co-rich amorphous alloys such as $\text{Co}_{75.26}\text{Fe}_{4.74}\text{Si}_2\text{B}_{18}$ and $\text{Co}_{74.26}\text{Fe}_{4.74}\text{Si}_3\text{B}_{18}$ which in turn proved to be potential candidate for magnetic recording applications. Honshima and Ohashi [34] introduced new preparation method that involves two alloy systems which mainly focused on producing the magnets with compatible retentivity and coercivity. They described that this new technique is used to improve the magnetic properties of NdFeB alloy. First, they took $\text{Nd}_2\text{Fe}_{14}\text{B}$ along with rare-earth rich alloy, after that they melted individually and mixed together followed by sintering. This new technique reduces the liquid phase level which is necessary to keep the coercivity at useful level. The magnets produced by two alloy technique are used in Voice Coil Motors (VCM) for hard drives which can downsize the hard disk and shorten the access.

In general, the magnetic behavior depends on the size of the crystallites. By subjecting the samples to thermal treatment, we can alter the size of the crystallites which influence the magnetic nature. The co-based matrix having the composition $\text{Co}_{71.5}\text{Fe}_{1.5}\text{Mn}_1\text{Si}_{13}\text{B}_9$, exhibits soft magnetic nature (coercivity nearly 0.001 Oe). Bottoni *et al.* [35] reported that the same composition after annealing with suitable temperatures (above crystallization temperature = 480°) shows hard magnetic property with a coercivity of around 400 Oe which is suitable for magnetic recording. Also the influence of residual amorphous matrix on the interactions of the particles

and existence of superparamagnetic particles is reported. By using field annealing technique followed by domain wall pinning, C.K. Kim *et al.* [36] fabricated a high-frequency harmonic sensor for the applications in EAS (Electronic Article Surveillance) industry. They reported that the usage of amorphous magnetic materials ($\text{Co}_{95-x}\text{Fe}_5(\text{BSi})_x$) can enhance the properties of sensors. The usage of magnetic materials can improve the sensor properties like signal-to-noise ratio, stability, etc., Kishi *et al.* [37] investigated on magnetic properties and microstructures of the CoNiGa alloys (ferromagnetic shape memory alloys). They reported that the coercive force and magnetization is strongly dependent on applied magnetic field direction. The characteristics of the alloys are much similar to those of bulk materials but the process of annealing raised the transition temperatures. In addition, the studies of transmission electron microscope revealed the precursor tweed and arc typical twin structures, which consists small boundary energies.

Inoue *et al.* [38] synthesized a new type of glassy alloy [$\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$] with the help of arc-melting technique. They reported that the prepared alloys exhibit high mechanical strength (5,185 MPa), high specific strength ($6.0 \times 10^5 \text{ Nm Kg}^{-1}$), high specific young's modulus ($31 \times 10^6 \text{ Nm Kg}^{-1}$) and high young's modulus (268 GPa). These values are very high compared to previous reports [39–40]. In addition, the prepared alloy material also shows the soft magnetic nature with enormously high magnetic permeability (550,000). Hence, these ultrahigh-strength alloys show soft magnetic properties with good deformability. Sahingoz *et al.* [41] examined effect of annealing on microstructure and magnetic properties of metallic glass $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ alloys. DC inductive magnetometer is used to study the magnetic properties of $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ alloys. They reported that the samples are annealed at a temperature of 773 K and the variation of coercivity with respect to annealing time is observed and graphs are plotted which are shown in Fig. 1 of the reference [41]. Also, Fig. 3 of reference [41] indicates the XRD pattern of the metallic glass $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ alloys at different annealing times.

Zhu *et al.* [42] synthesized single phase magnetic (MnB) alloys by using arc-melting technique. They reported that the single phases of the prepared alloys are confirmed by using X-ray diffraction studies. In addition, the magnetic properties are carried out by SQUID and VSM at wide temperature range. From those studies, they observed that the prepared alloy materials exhibit high value of magnetization of around 113 amu/g which is different from the previous reports [43]. They concluded that the prepared MnB magnetic alloy exhibits strong magnetic behavior which may act as a potential candidate in spintronics and magnetic recording. Y. Ogawa *et al.* [44] studied the magnetic properties of Fe-based amorphous alloys

prepared through melt spinning technique. They reported that the newly developed alloys show an improved value of B_s of around 1.64 T and low core loss of around 0.065 W/kg at 50 Hz. In addition, a trial distribution transformer using new alloy shows small core loss and low noise level compared to distribution transformer using other alloys.

Du *et al.* [45] prepared Heusler alloys $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sb}_x$ ($x = 12, 13, 14$) via arc melting technique at high pure atmosphere. They investigated the shape memory effect, martensitic transition temperature, and magnetocaloric effect of the prepared alloys. They observed that a large change in entropy at near martensitic transition. This change originates to a high-temperature ferromagnetic parent phase from a low-temperature martensitic phase. In addition, the martensitic transformation was reversed at low magnetic field of about 1.2 T and shape recovery strain of around 15 ppm at room temperature. So, this shape memory effect and field-induced magnetocaloric effect in $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sb}_x$ alloy system make it a potential candidate for room temperature application. Makino *et al.* [46] reported the effect of copper (Cu) and phosphorous (P) on the structural and magnetic properties of FeNiB alloys. From the outcomes, it is clear that, the addition of Cu or P alters the magnetic softness a little. While the simultaneous addition of P and Cu considerably expands the magnetic properties of crystallized $\text{Fe}_{83.6}\text{Nb}_{6.6}\text{B}_{9.6}$ alloy. The attained results are low coercivity (5 A/m) and high permeability (45,000) and saturated flux density (1.54 T).

Later, N. Kasapoglu *et al.* [47] synthesized $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ (where $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) magnetic alloys by using hydrothermal technique followed by annealing maintaining at a temperature of 300°C for three hours. They investigated the influence of Ni composition on the structural and magnetic properties. The cubic spinel structure of the prepared alloys is confirmed by XRD and the presence of metal oxide bonds is investigated by FTIR. In addition, the morphology is studied by using SEM and the results indicate that the particle size lies in between 30 and 35 nm. Furthermore, ESR studies revealed the increase in resonance with increase in nickel composition. Fig. 5 of the reference [47] represents the ESR spectrum of the nickel doped cobalt ferrites. Ohta and Yoshizawa [48] prepared $\text{Fe}_{82.65}\text{Cu}_{1.35}\text{Si}_x\text{B}_{16-x}$ alloys by melt spinning technique. They examined the variation in the properties of Fe-Cu-B alloys with the replacement of Si in B place. Further, reported that in $\text{Fe}_{82.65}\text{Cu}_{1.35}\text{Si}_x\text{B}_{16-x}$ alloys for $x = 2$ composition, they observed excellent soft magnetic properties, i.e, small $H_c = 6.5$ A/m and high flux density (B) = 1.84 T. In addition, the prepared materials show the average grain size of around 20 nm for x is less than or equal to 2, while for x greater than 2, the grain size also increases with x composition.

Subsequently, Ohta and Yoshizawa [49] also studied the effect of copper on Fe-Si-B alloys. Using melt spinning method, they prepared $\text{Fe}_{84-x}\text{Cu}_x\text{Si}_2\text{B}_{14}$ and $\text{Fe}_{82-x}\text{Cu}_x\text{Si}_4\text{B}_{14}$ alloys. For $x = 1.35$, the annealed $\text{Fe}_{84-x}\text{Cu}_x\text{Si}_2\text{B}_{14}$ alloy system exhibits excellent properties such as high magnetic flux (B) = 1.84 T and low magnetic intensity (H_c) = 6.5 A/m. for the same value of x , the $\text{Fe}_{82-x}\text{Cu}_x\text{Si}_4\text{B}_{14}$ alloy system magnetic intensity (H_c) = 5.7 A/m. Finally, high copper content leads excellent magnetic properties for enriched silicon content. Fig. 4 of the reference [49] represents the B-H curves of the prepared alloys. Yoshimura *et al.* [50] developed a new Fe_2CrSi Heusler alloy synthesized *via* ion beam sputtering technique. They reported that the prepared alloys exhibit excellent properties such as high spin polarization ($P = 0.98$), low saturation magnetization ($M_s = 385 \text{ emu/cm}^3$), and low Curie temperature ($T_c = 630 \text{ K}$). Furthermore, with the help of optimized thermal treatment the Heusler alloys is used to fabricate the MTJ (magnetic tunnel junction) with high performance, i.e., with high magneto tunnel resistance. The results are evident that the Fe_2CrSi Heusler alloys are appropriate ferromagnetic material for high-performance magnetic random-access memory.

Long *et al.* [51] prepared Fe-based nanocrystalline magnetic alloy $((\text{FeCu})_{80}\text{Zr}_x\text{Si}_{20-x})$, where $x = 5, 6, 8$ by using arc melting technique. Further, single roller melt spinning method has been used to prepare thick ribbons (25–30 μm) of the prepared alloys. In addition, the prepared samples underwent annealing process at the temperatures 450°C, 480°C, and 550°C. The outcomes of XRD and TEM analysis revealed that the prepared alloys exhibit amorphous nature with an average particle size of 10 nm. Further, the core loss of the prepared alloys is very small as compared to other commercial soft magnetic materials. So, Fe-Zr-Si-Cu alloy can act as promising candidate for the applications in cost-effective soft magnetic materials.

With the help of non-aqueous solution technique, Elango *et al.* [52] synthesized manganese doped cadmium sulfide nanocrystalline materials with altering Mn concentration. To investigate the structural, optical, and magnetic properties, the prepared materials have undergone different characterizations. The XRD studies revealed that the prepared materials exhibit two phases which are cubic zinc blende structure (CdS:Mn , primary phase) and cubic structure ($\alpha\text{-MnS}$, secondary phase). The morphology of the prepared nanoparticles is analyzed by using TEM and the size of the nanoparticles is of around 15–20 nm which is confirmed by TEM studies. In addition, in the optical absorption spectra, they observed that the blue shifts are altering in maximum characteristic wavelength region with varying Mn-concentration in cadmium sulfide host material.

The FTIR studies revealed the existence of weak interactions between the sulfur (anion) and manganese and cadmium (cation) ions. Further, VSM results confirmed that the prepared nanomaterials exhibit considerable magnetic nature which is mainly due to spin magnetic moment of manganese ions in CdS:Mn structure. So, owing to the replacement of manganese in cadmium enhances the magnetic behavior which acts as a potential candidate in spintronic device applications. Mejia *et al.* [53] investigated the temperature dependence magnetic properties of Ni-Mn-In Heusler alloys by applying pulsed high magnetic fields. Fig. 1 in reference [53] shows the M-H loops of $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ alloys at different temperatures. They reported that the entropy of the specimen and magnetocaloric effect decreases with decreasing temperature.

Till now, a variety of methods are used to synthesize the magnetic materials. Among those melt spinning is considered as the best technique. But, Alvarez *et al.* [54] introduced an alternative technique synthesis route called gas atomization for the preparation of materials. By using helium gas atomization technique, they prepared amorphous Fe-Si-B alloys. They reported that the prepared powder alloys exhibit non-crystalline nature and the particles are in spherical shape as confirmed by SEM results. Fig. 3 and Fig. 4 of the reference [54] show the SEM image and microstructure of the Fe-Si-B alloys. From the outcomes, they suggested that gas atomization is a mass production technique that can improve the technical applications of Fe-Si-B ternary systems. Specifically, by considering the outstanding soft magnetic properties exhibited by Fe-Si-B ternary system, the new studies are underway to enhance the magnetic nature through annealing treatments. Khandy [55] introduced a new Heusler alloys (FeVRuSi) and presented the first principle calculations of the structural, electronic, and magnetic properties of the prepared alloy materials. He reported that the FeVRuSi alloy in spin-down configuration exhibit the ferromagnetic property along with indirect semiconducting bandgap. The electron density maps (Fig. 5, Fig. 6, and Fig. 7 of the reference [55]) revealed that the existence of covalent bond between Fe and Si as well as Fe and V (Ru) atoms. Owing to high spin magnetic moment (ferromagnetic) the prepared alloys can be used in memory devices, spintronics, etc.

Akamaru *et al.* [56] investigated the properties of Pd-Co alloys before hydrogenation and after hydrogenation. They reported that Pd-Co alloys exhibit simple ferromagnetic nature and attained Curie temperature is of around 220 K, 315 K, and 350 K for the compounds $\text{Pd}_{0.96}\text{Co}_{0.04}$, $\text{Pd}_{0.92}\text{Co}_{0.08}$, and $\text{Pd}_{0.90}\text{Co}_{0.10}$. Further, under hydrogen gas pressure (100 KPa), the Pd-Co alloys were hydrogenated. The properties of hydrogenated Pd-Co alloys are different compared to non-hydrogenated samples as the

magnetization of the samples is reduced and the magnetic moment is nearly half of the non-hydrogenated alloys. Hou *et al.* [57] prepared the $\text{Fe}_{83.2-x}\text{Co}_x\text{P}_{10}\text{C}_6\text{Cu}_{0.8}$ where $x = 0, 4, 6, 8$, and 10, nanocrystalline alloys *via* induction melting technique. Fig. 6 of the reference [57] indicates the TEM images of the prepared alloys and Fig. 5 of the reference [57] represents the magnetization performance and evaluation of microstructure during annealing. From the results, they reported that the prepared alloys exhibit good amorphous nature and soft magnetic properties. Besides, addition of small cobalt content effectively enhances the saturation value of magnetic flux density from 1.53 T to 1.61 T. After proper heat treatment, especially, the $x = 4$ composition, i.e., $\text{Fe}_{83.2-x}\text{Co}_x\text{P}_{10}\text{C}_6\text{Cu}_{0.8}$ alloy shows good magnetic properties which includes low coercivity of 6.6 A/m, high permeability of 15,510 and high saturation flux density of 1.8 T. These values indicate that FeCoPCCu alloys can serve as a good soft magnetic material.

By using induction melting technique Fan *et al.* [58] synthesized novel $\text{Fe}_{83.3}\text{Si}_4\text{B}_8\text{P}_{4-x}\text{C}_x\text{Cu}_{0.7}$ where $x = 0-4$, alloys and explored the structural and magnetic properties. The analysis of microstructure revealed that the substitution of C for P increases the amorphous nature in the prepared alloys with the critical thickness of around 35 nm. Further, the addition of C also improves the saturation flux density of about 1.84 T, low coercivity of around 4.8 A/m, and high permeability of 13,540. Therefore, the prepared alloy materials can be a potential candidate for the application of DC superposition as they exhibit high amorphous forming ability and excellent soft magnetic properties. A. Makino *et al.* [59] investigated the structural and magnetic properties of $\text{Fe}_{83.3}\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_{0.7}$ and $\text{Fe}_{84.3}\text{Si}_4\text{B}_8\text{P}_3\text{Cu}_{0.7}$ alloys synthesized through melt-spun technique. They reported that the prepared alloys exhibit hetero-amorphous structure with an average particle size of around 10 nm and 17 nm. However, owing to the uniform nanostructure formed by small grains and small magnetostriction, the nanocrystalline alloys shows excellent magnetic properties which are as follows, coercive force is 7 A/m and 10 A/m, saturation flux density is 1.88 T and 1.94 T and permeability is 25,000 and 16,000 at the frequency of 1 kHz. Therefore, compared to other soft magnetic materials, the proposed Fe-rich FeSiBPCu alloy materials exhibits good soft magnetic properties which can be considered as promising magnetic materials for the spintronics, magnetic recording applications.

In the process of searching new magnetic alloy materials, Pang *et al.* [60] synthesized a new Fe rich FeBSiCu alloy materials *via* melt spinning technique. The prepared $\text{Fe}_{82-85}\text{B}_{13-16}\text{Si}_1\text{Cu}_1$ alloys exhibits excellent soft magnetic properties along with good mechanical strength. They reported

that the alloys show improved properties with decreasing B content. From the result, it is clear that for higher values of B composition the values of Vickers hardness (H_v), flux density (B_s), coercivity (H_c), and permeability (μ) are as follows 803, 1.7 T, 4.72 A/m, and 7,100. But, the same values for 13B composition are 867, 1.74T, 5.62 A/m, and 10,100, respectively. The addition of copper played a vital role in improving the hardness and other properties. Therefore, the proposed Fe-based alloys are hopeful as future high strength and soft magnetic materials with low cost. R. Zhu *et al.* [61] used electromagnetic smelting technique to prepare $\text{Co}_{90}\text{Nb}_{10}\text{Ta}_3$ alloys. They explored the effect of cobalt on the prepared alloys and observed that the Curie temperature (T_c) of the Co-based alloys is very low (360°C). Compared to other alloys (Fe-B-Cr, Fe-Cr-Cu-Nb-Si-B, Fe-Co-Si-Al-Ga-P-C-B, etc.) besides near T_c , second-order phase transition is observed, i.e., ferromagnetic to paramagnetic. In addition, the alloys show high magnetocaloric effect near the Curie temperature. Owing to good chemical and mechanical properties, the CoNbTa alloys are prominent MCE materials. Further, in $\text{Ba}_4\text{Nd}_2\text{Fe}_{2-x}\text{Ni}_x$ where $0 \leq x \leq 1$ alloys, Zhang and Zuo [62] observed large retentivity ($2M_r = 0.13 \text{ emu/g}$) at 300 K temperature. Besides, the ferromagnetic properties are ascribed by Dzyaloshinskii-Moriya interaction. X. Yang *et al.* [63] investigated the effect of Co, Pt, and MnIr layer on coercive field and exchange bias field in perpendicular exchange biased $[\text{Pt/Co}]_3/\text{MnIr}$ multilayers through magneto-optical Kerr effect. First, PMA increases with increase in Pt thickness and reached to saturation. In addition, the saturation damping constant also increases with increase in Pt thickness, whereas the same content decreases with increase in Co thickness. Spin pumping effect may be the reason for this. These materials are useful in spin valves, spintronics, magnetic tunnel junctions, etc.

In general, the spin electronic devices contain electrodes that insert electrons with perpendicular magnetic anisotropy (PMA) and high spin polarization. Some full-Heusler alloys are assumed to be half-metallic ferromagnets. But, maximum cubic full-Heusler alloys exhibit small magneto-crystalline anisotropy, i.e., it is difficult to achieve PMA in thin films. To overcome this, A. Basha *et al.* [64] reported PMA in sputter-deposited ultrathin Co_2MnSi films. The magnetron sputter-deposition technique is used to prepare the alloys, adjacent to this MgO layer act as tunneling barrier and Pd-buffer layer. Fig. 6 [64] represents the HRTEM images of the prepared alloys. When the Pd layer is adjacent to Co_2MnSi films they observed the PMA with an energy density ($7.8 \pm 1.8 \text{ merg/cc}$) at 5 K followed by annealing at a temperature of about 350°C. While the

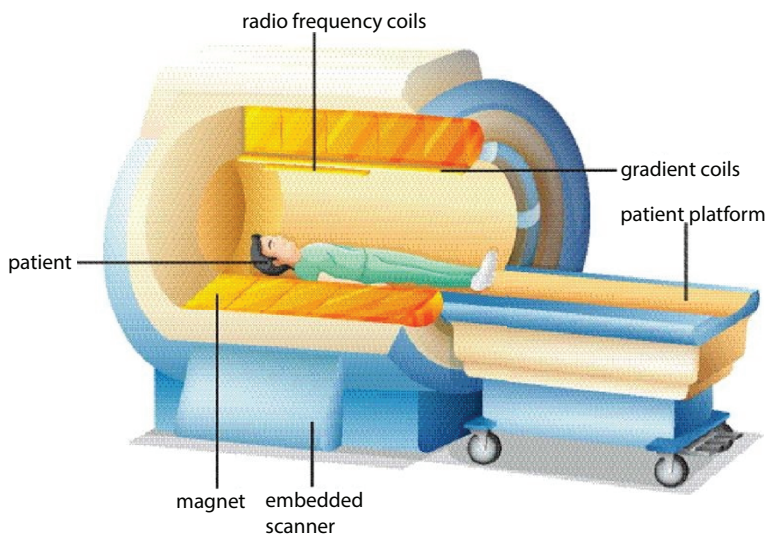


Figure 5.4 Magnetic resonance imaging machine.

paramagnetic properties without anisotropy is observed at same conditions when MgO layer is adjacent to Co_2MnSi films. Hence, the presence of Pd is v as the source of PMA. The prepared alloys are useful in spintronics and information storage devices.

Therefore, in particular, the magnetic alloy materials are much suitable for the applications in spintronics, wind turbine technology, magnetic storage devices (hard disks, magnetic random-access memory), telecommunication, magnetic sensors, microwave devices such as circulators, insulators, phase shifters, transformer cores, inductor cores, etc. In addition, some alloys like Al-Ni-Co are used in MRI (magnetic resonance imaging) which can sense the small magnetic field intensities. Figure 5.4 represents the magnetic resonance imaging unit.

5.4 Conclusions

We discussed the distinct magnetic alloy materials along with their applications in various fields. It was concluded that, due to excellent magnetic properties, the magnetic alloy materials gained much attention and research is going on to introduce new kinds of magnetic alloy materials for the applications in magnetic storage devices, spintronics, transformers, etc.

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Microstructural Characterization of Ball Milled $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ Alloys and Their Photocatalytic Performance

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Abstract

In this work, the quaternary $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy was produced by planetary ball milling in order to investigate the influence photocatalytic degradation efficiency of methyl blue dye. The quaternary $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy powder was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDX), UV-Vis spectroscopy (UV), and transmission electron microscopy (TEM) techniques. The nanocrystalline and amorphous structure was demonstrated in XRD patterns and it was also supported with TEM observation for 50 h of milled the powders alloy. The composition of the powders after mechanical alloying was determined by EDX analyses. The nanostructured morphology of the synthesized alloy after 50-h milling was seen from the SEM analyses. The time-dependent photocatalytic degradation of methyl blue (MB) sample was investigated under UV light by using UV-Vis spectrometer at room temperature. The color of methyl blue turned from blue to nearly colorless using catalyst of alloy $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ only in 60 min. The degradation efficiency of methyl blue was examined and their results fitted to the first order kinetic.

Keywords: Mechanical alloying, photocatalytic degradation, XRD, SEM, UV-Vis

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6.1 Introduction

Colors have drawn significant attention of humans from the beginning of life. The consumption of colors has exponentially increased with industrialization of the society and limited natural colorants have been replaced by synthetic dyes. The usage of synthetic dyes have been increasing day by day [1, 2]. The synthetic dyes, however, are polluting the environment because of their large stability against physicochemical attack and low removal rate during aerobic waste treatment [3–6]. Today, the synthesized azo dyes are approximately as much as all other different dyes that are synthesized. They are generally used in textile, cosmetics, food, printing, and pharmaceutical industries [7, 8]. The textile industry is one of the most widely used industries in the consumption of azo dyes, and they produce large volume of effluent after dyeing operation [2, 9]. The discharges from factories including dyes effluents are unsafe chemicals and some of the used dyes are dangerously toxic, mutagenic, and carcinogenic to living organisms [10–13]. Therefore, the treatment of waste dye effluent is necessary. Photocatalysis has an important place in eliminating dyes in wastewater due to its efficiency and wide applicability [14].

Although, zero-valent metals (ZVM) are one of the important catalysts to remove textile effluent due to their degradation efficiency, low cost and simple operation, ZVM is limited due to easy agglomeration, lack of stability, problem of separating solids from dye solution after operation, and their restricted surface area [15–17]. Therefore, the development of new photocatalysts is needed [18]. In literature, amorphous and nanocrystalline alloys are utilized to obtain new types of catalysts. Generally, Fe-based, Mg-based, and high entropy alloys have been investigated [9]. The degradation capacity of gas-atomized Mg-Zn-Ca glassy powders is considerably higher than Fe powders which were found by Zhao, Y. F. [19]. Hou *et al.* shown that the addition of Co element to Fe-based alloy enhanced catalytic decolorization performance of the used Fe-based alloy [20]. Moreover, Co-based metallic glass showed outstanding catalytic performance and stability with little mass loss as compared to reported Fe-based and Mg-based metallic glasses found by Qin *et al.* [21].

It is well known that surface area of used catalytic materials has considerably effected decolorization performance of the materials. Generally, the melt spinning method was used to obtain metallic glasses and ball milling method was used to generate powders form of the synthesized alloy to increase their surface area. For this reason, selecting a single-step ball milling method to synthesize powders provides advantages in terms of time, cost, and complexity. This methods also suitable for mass production [22, 23].

Photocatalytic activities of the $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy were investigated using methyl blue solution in water under Xenon light. The $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy showed very good photocatalytic activity in methyl blue degradation using under Xenon light. The degradation of methyl blue was followed while measuring the absorbance at 590 nm in UV-Vis spectrophotometer.

6.2 Experimental

6.2.1 Mechanical Alloying

In this work, cobalt, iron, titanium and neodymium elemental powders (not boron) were obtained from Alfa Aesar. The powders were accurately weighted in a glove-box under an argon atmosphere to avoid oxidation. The ball milling process of $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy was carried out in planetary ball mills (Fritsch Pulverisette 5) using 125-ml stainless steel with rotational speed of 300 rpm. The ball to powder ratio was selected as 20:1 with different sized steel balls. The different physical and mechanical parameters of used elements are given in Table 6.1.

6.2.2 Characterization

X-ray diffraction (XRD) with Cu K α radiation was used to investigate crystal structural of the synthesized samples. The morphology of the powder particles was investigated by scanning electron microscopy (SEM) with ZEISS EVO LS10 with a voltage of 15 kV. Transmission electron microscopy (TEM) characterization was also performed with JEOL JEM 2100 (UHR). UV-Vis spectroscopy (Shimadzu-1800) was used for the photocatalytic degradation experiments.

Table 6.1 Some physical and mechanical properties of the used elements.

Element	Atomic number	R (pm)	T _m (K)	K (GPa)	V ^{2/3} (cm ² /mol)	n _{ws} ^{1/3}
Co	27	125	1768	180	3.5	1.75
Fe	26	126	1811	170	3.7	1.77
Ti	22	147	1941	110	4.8	1.47
Nb	41	146	2750	170	4.9	1.62

R = Atomic radius, T_m = Melting point, K = Bulk modulus, V = Molar volume, n_{ws} = Electron density.

6.2.3 Photocatalytic Degradation of Methyl Blue

Photocatalytic degradation of methyl blue ($C_{37}H_{27}N_3Na_2O_9S_3$) was investigated in water samples using $Co_{60}Fe_{18}Ti_{18}Nb_4$ alloy. The optimized method in our previous studies was applied for the photocatalytic degradation of methyl blue ($C_{37}H_{27}N_3Na_2O_9S_3$) [24, 25]. Solar simulator cabin (300 W Luzchem Photo reactor calibrated AM1.5 spectrum) was used as a light source for photocatalytic experiments. The degradation efficiencies of the powders were recorded by using UV-Vis spectroscopy while the photocatalytic degradation reaction going on. Maximum absorption was observed at 590 nm for methyl blue in water sample in the scanning range was of 400–800 nm with a 1-nm interval. The absorbance decrease was collected at 590 nm in the scanning range between 400 to 800 nm for all the photocatalytic degradation samples. 10 ppm ($mg.L^{-1}$), 200-ml methyl blue dye solutions were prepared in a beaker, and 0.2-g alloy was added to this solution. Then, the prepared dye-catalyst mixture was magnetically stirred for more than 30 min to obtain dye adsorption-desorption equilibrium on the surface of the powders alloy. Because of having magnetic properties of the synthesized powders, any magnetic stir bar was not used throughout the photocatalytic experiments. Water samples were taken at regular intervals up to 60 min. and analyzed at UV-Vis spectrophotometer ranging from 400–800 nm. Degradation Efficiency (DE) was calculated using the equation;

$$DE = \left(1 - \frac{C_t}{C_0} \right) \times 100 \quad (6.1)$$

Here, C_0 represents the initial concentration, and C_t represent concentration at the sampling time.

6.3 Results and Discussion

6.3.1 Characterization

X-ray diffraction method was employed to investigate structural evolutions of mechanically milled $Co_{60}Fe_{18}Ti_{18}Nb_4$ powders during 10-min, 1-h, 10-h, 20-h, 30-h, 50-h milling time intervals. XRD patterns of $Co_{60}Fe_{18}Ti_{18}Nb_4$ powders after different time intervals are given in Figure 6.1. After 10-min milling process, the crystalline peaks of element Co, Fe, Ti, and Nb are given. Two different types of Co structure Co_{hcp} and Co_{fcc} are present. From this figure, it is clear that crystalline intensity and structure of the powders were

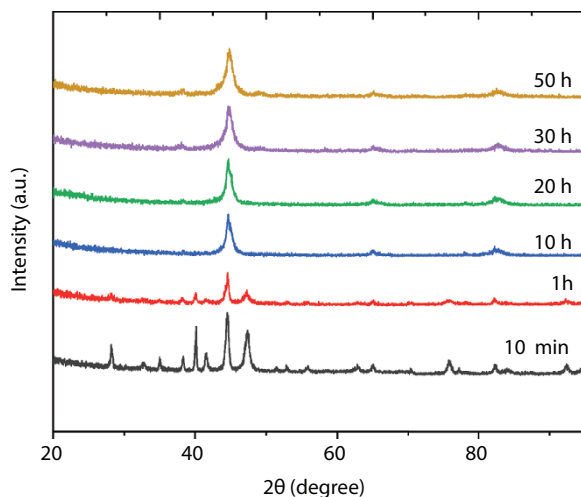


Figure 6.1 XRD patterns of the mechanically milled powders at 10 min, 1 h, 10 h, 20 h, 30 h, 50 h milling time intervals.

changed with milling intervals. Fracturing and cold welding is the main reason of this phenomenon. After 50-h milling, the peak intensity of elements decreased and one wide diffraction peak corresponding to amorphous structure observed. This observation is an agreement with earlier reports [26–28].

EDX mapping of elemental powders after 10-min milling process is given in Figure 6.2. From this analysis, the morphology and geometry of

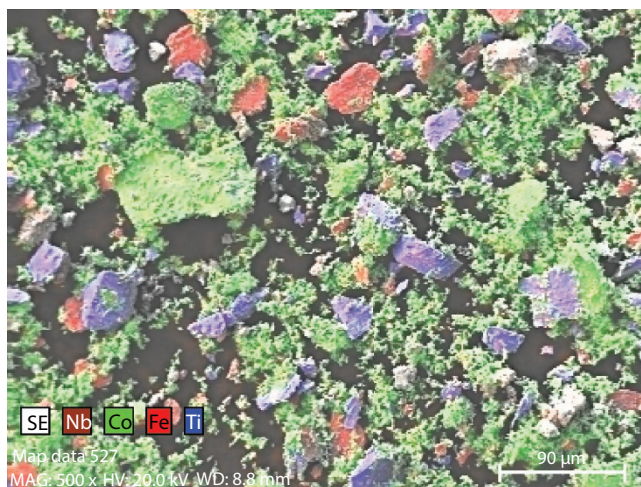


Figure 6.2 EDX elemental mapping of the mechanically alloyed $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ powders after 10 min milling.

used elements are found. The Co, Fe, Ti, and Nb elements are clearly seen from this figure. EDX mapping helps to demonstrate morphological evaluation of initial elemental powders with ball milling process. The morphology of mechanically milled $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ powders after 10-min, 1-h, 10-h, 20-h, 30-h, and 50-h milling time intervals is represented in Figure 6.3. During mechanical milling, powders undergo flattening, cold welding, fracturing, and rewelding [29] which is a known process of this alloy synthesis method. Figure 6.3a demonstrates powders after 10-min

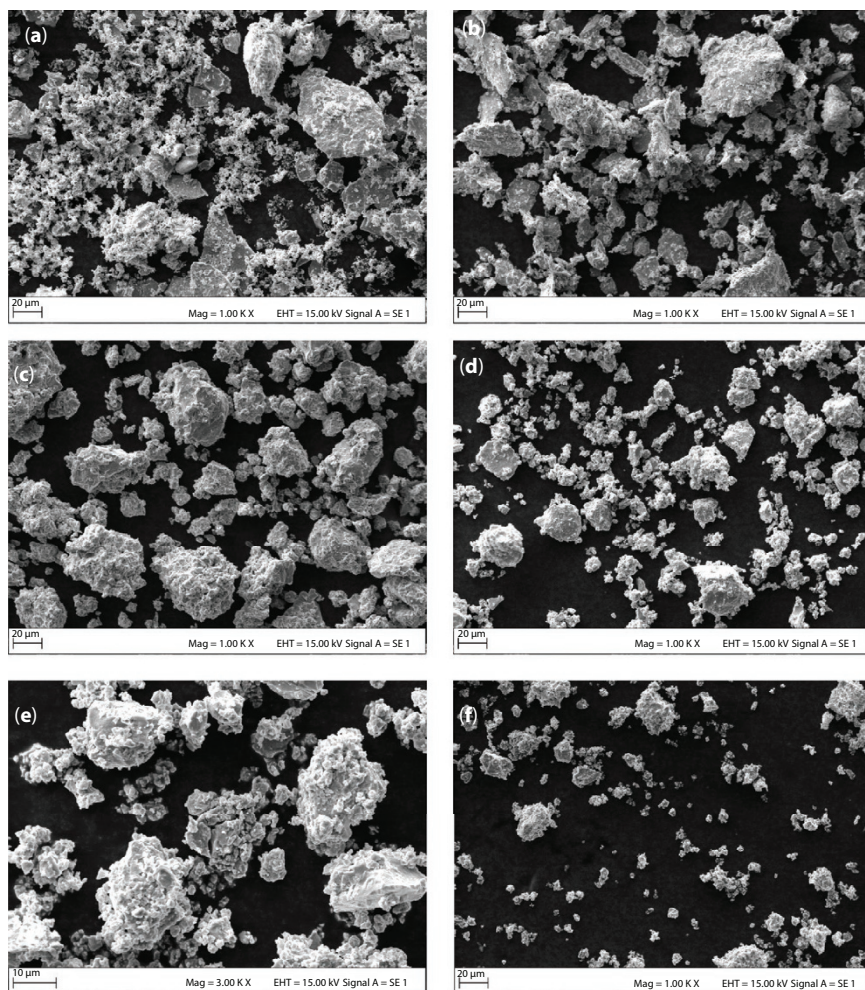


Figure 6.3 SEM micrographs of mechanically milled powders after (a) 10min, (b) 1h, (c) 10h, (d) 20h, (e) 30h, (f) 50h milling time.

milling process and the elements which different shapes and morphologies can be seen from this figure as the easier stage of milling process. Figure 6.3b represents powders after 1-h milling. At this stage, powders have begun to flatten. The mean particle size of powders increased after 10-h milling and the morphologies of increased particles size given in Figure 6.3c. At this stage of milling, bigger particle size and morphologies attributed to agglomeration of smaller powders particles; in other words, here, dominantly cold welding process occurs. Figure 6.3d represents powders after 20-h milling; as seen from this figure, powders have relatively regular morphologies and smaller mean particle size than 10-h milled powders. Fracturing process is attributed to this morphological change. For 30-h and 50-h milling times powder morphologies undergo cold welding and fracturing process again, respectively. The morphological feature of $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ powders after 50-h milling process also investigated by TEM analysis and the TEM image of 50-h milled powders is shown in Figure 6.4a. The bright field TEM image demonstrated amorphous phase in which small nanocrystalline regions are shown in Figure 6.4b [30].

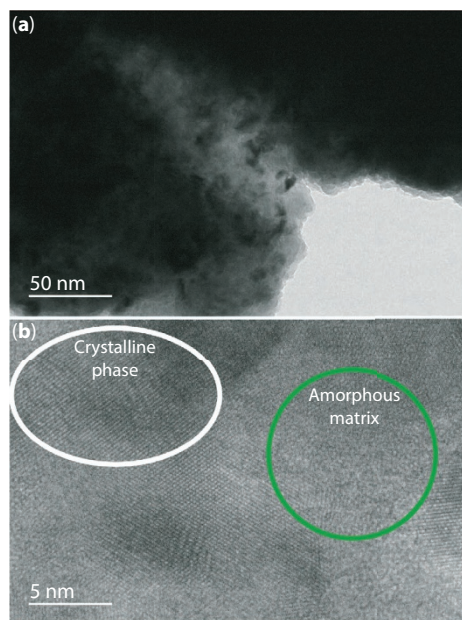


Figure 6.4 50h milled $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ powders, (a) TEM micrograph, (b) HRTEM image amorphous matrix and crystalline phases.

6.3.2 Photocatalytic Studies

The photocatalytic degradation of methyl blue ($C_{37}H_{27}N_3Na_2O_9S_3$) using $Co_{60}Fe_{18}Ti_{18}Nb_4$ alloy as a catalyst was investigated in water samples. Figure 6.5 demonstrates self-degradation of methyl blue dye without any catalyst. From this figure, it was clear that methyl blue dye is largely stable under solar simulator for 60 min. Time-dependent changes in UV-Vis spectra of photocatalytic degradation of mechanically alloyed $Co_{60}Fe_{18}Ti_{18}Nb_4$ powder are given in Figure 6.6. The color of the reaction medium turned from blue to nearly colorless approximately in 60 min.

In the possible mechanism, the valance electrons might be excited to the conduction band from the valence band in the alloy with the light effect. The formed positive holes in the conduction band on the surface of the powders play a role as photo-generated electrons in conduction band formed a radical anion $O\cdot^{2-}$ as a result of reaction with acceptors. When the nanostructured alloy $Co_{60}Fe_{18}Ti_{18}Nb_4$ powder receives an electron for positive holes from water, $OH\cdot$ radicals form. Methyl blue having negative sulfonate groups electrostatically attracts the positively charged the surface of the nano-alloy during the reaction. Finally, the dye is oxidized by the radicalic moieties to carbon dioxide and water [24, 25].

The photocatalytic degradation efficiency of the sample is given in Figure 6.7. Although self-degradation efficiency of methyl blue was found under 10%, the efficiency of catalyst alloy powders reached to

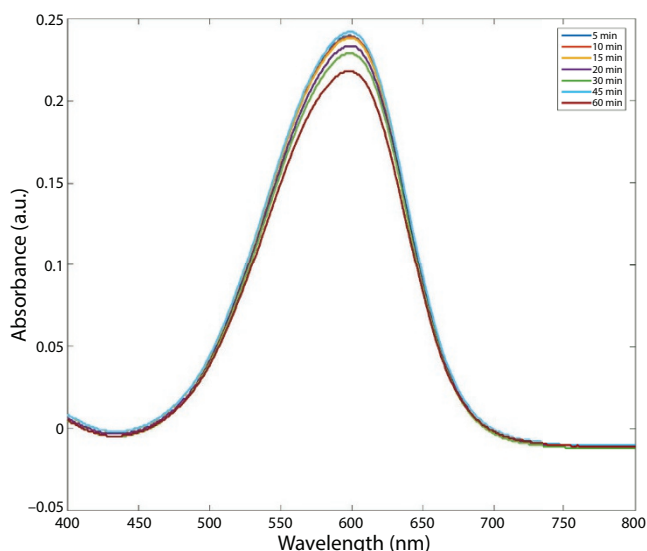


Figure 6.5 Time-dependent UV-vis absorption curve of methyl blue.

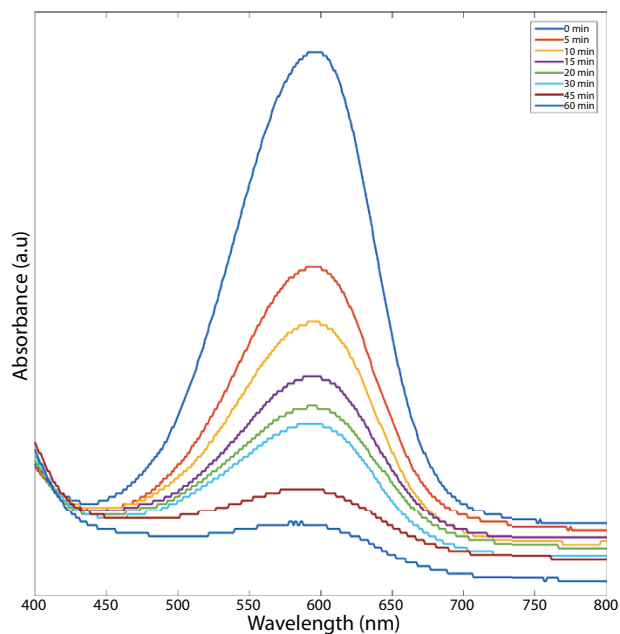


Figure 6.6 Time dependent changes in UV-vis spectra of photocatalytic degradation of mechanically alloyed $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ powder.

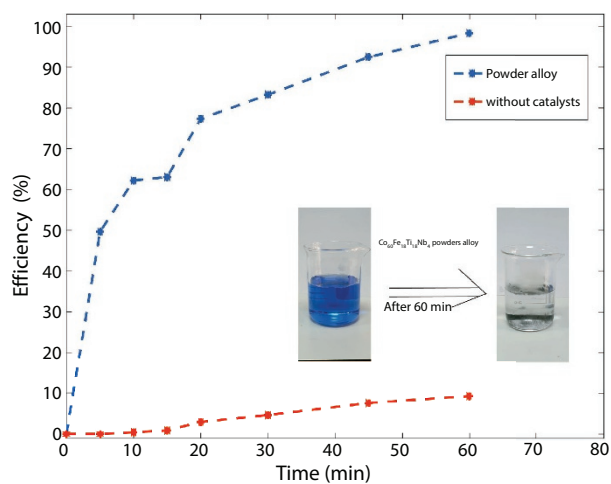


Figure 6.7 Photocatalytic degradation kinetic curve for photocatalytic degradation of melty blue over mechanical alloyed $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ under UV irradiation.

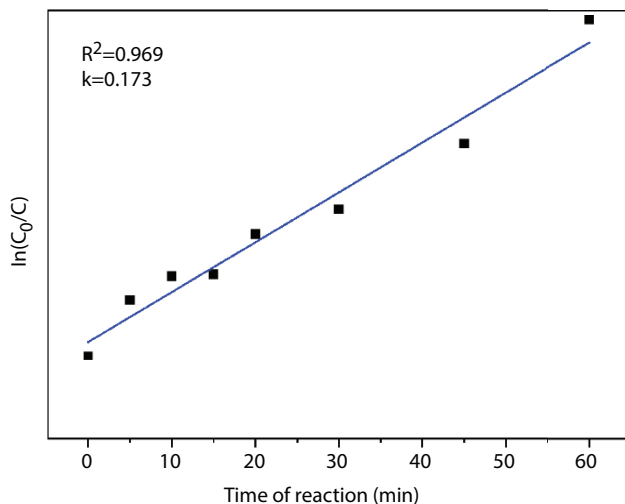


Figure 6.8 Photocatalytic degradation kinetic curves for photocatalytic degradation of MB over $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ under UV irradiation.

98.3% in 60 min. The digital images of methyl blue aqueous solution with catalyst for 0 min and 60 min are given Figure 6.7 inset. The kinetics of photocatalytic degradation was calculated as pseudo first order with the fitting coefficient 0.969 in Figure 6.8 [31, 32]. According to the degradation efficiency (Figure 6.7), the photocatalytic degradation of methyl blue was nearly completed in 60 min. The first ordered kinetics is expressed as:

$$\ln(C_0/C_t) = k.t \quad (6.2)$$

where k is the photo-degradation rate constant (min^{-1}) and C_0 and C_t are the concentrations (mg/L) of methyl blue at different photocatalytic degradation times, respectively.

6.4 Conclusions

In the present study, nanostructure and partially amorphous quaternary $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy was successfully manufactured from their elemental powders using the mechanical alloying technique. The synthesized powders alloy was investigated by variety of analytical techniques including SEM, TEM, XRD, and EDX. The quaternary $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy was confirmed stoichiometric composition by EDX analyses. The methyl blue dye

degradation evolution of catalyst $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ alloy was examined by help of Uv-Vis spectrometer at room temperature. The color of methyl blue turned from blue to nearly colorless using catalyst of alloy $\text{Co}_{60}\text{Fe}_{18}\text{Ti}_{18}\text{Nb}_4$ in 60 min. The kinetics of photocatalytic degradation was calculated as pseudo first order with the fitting coefficient 0.969.

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A Narrative Insight on the Biocompatibility Issues for Dental Alloys and Other Materials

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Abstract

Over the past few years, the rapid advancement in the adhesive dentistry has evolved the importance of biocompatibility of dental restoratives. It has been grown as a comprehensive, intricate, and independent field of restorative dentistry. Since, these dental restoratives constantly interact with the dental tissues that may affect both the material and the immediate tissues. Even though these restoratives varied significantly in their characteristics and developed to be as inert and durable as possible, it may fail or degrade during its functionality because some constituent may release from the restoration into the oral cavity. Besides their significant role in curing and enlightening the functionality of oral tissues, the released constituents from restoration may illustrate some side effects in some cases, which lead to severe infections. In such harsh oral conditions, these materials need to preserve their integrity as well as functioning features over a prolonged period. However, the safe use and cytotoxic effect of distinct dental materials remain a controversial point. The aim of this paper is to contribute a better understanding for the biocompatibility issues of frequently used metallic and polymeric dental materials as well as the further advancement in these materials.

Keywords: Dental restoration, biocompatibility, toxicity, metallic alloys, polymeric resins

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7.1 Introduction

Over a decade, significant developments have been done on the utilization of biomaterials for dentistry to rehabilitate dental tissues and teeth structures damaged/disoriented by accidents or any kind of infection; these requirements have empowered experts to use ground-breaking therapeutic rehabilitation, regenerating the physiological, social, and physical outcomes. Although, there is an extensive range of dental materials used in adhesive dentistry including liners, intercanal fillings, irrigants, subgingival implants, restorative, and prosthetic materials, etc. [1, 2]. Ideally, dental restoratives should be compatible with oral tissues, mucosa, pulps, bone, and gingiva. Furthermore, it should not release any toxic or diffusible constituents that may be fascinated into the circulatory system of the human body, causing an allergic or systemic response, i.e., carcinogenic or teratogenic effects [3].

Biocompatibility of dental implants is one of the essential considerations for the human being, clinician, laboratory personal, and producer. It is the ability of dental restoratives to trigger appropriate biological response without producing a continual inflammatory reaction, toxicity, or foreign body response when implanted in the body [4, 5]. The longevity of them is the common measure for the knowing the efficacy of these restorative materials in the oral cavity over a period without leading to any undesirable event with the patient. Many distinct alloys and materials are now easily accessible in the market for fixed prostheses and dental restoration purposes. Developing countries like Europe, USA, and Japan widely use ceramics and cast gold alloys for fixed dental implants, whereas developing countries like South America and Middle East countries prevalently use base metal alloys and stainless-steel crowns [6]. Dental alloys play a prominent role in the treatment of dental caries over pure metals because it does not have considerable physical characteristics such as density, etc., as required for dental restoration.

Dental amalgam is one of the metallic alloys used around 200 years as restoration material in dentistry in the form of cavity filling material [7–10]. It was identified as a metallic alloy of silver, mercury, copper, and tin along with some other metallic elements to improve the physical and mechanical characteristics of restoration [11]. Nowadays, the use of dental amalgam is limited due to the high concentration of mercury vapor vulnerability that leads to the detrimental effect on the kidney and brain of the patients. However, enough literature data is available to contradict this shortcoming of dental amalgam and claiming that leaching of mercury from amalgam restoration is much lower than the mercury consumption from distinct sources like water, seafood, and industry [12].

When restorative material implanted into the oral cavity, invariably, it bridges an active interface, through which restorative material influence the body and vice-versa. Regardless of the material placement, this synergy takes place based on the material, the interaction forces, the host response, and it's functioning [13, 14]. The endorsement for the quality of dental restoratives comprises *in vitro* (cell culture), *in vivo* condition (animal test), and clinical experiment of the restoratives. However, limitations with other factors like time, expenditure, and integrity have restrained the significance of this conventional biological testing procedure [15]. Therefore, commercial firms introduce restoratives with limited clinical experience and may depend on the *in vitro* and *in vivo* testing conditions [16]. The endorsement of these tests is not totally reliant on the tested biomaterial but also affected by the used testing schemes. Therefore, a strict evaluation of these dental restoratives will be judicious before the commercialization.

Numerous literature has been executed to recognize and enhance the physical and mechanical characteristics of dental restoratives [17–21], but comparatively fewer articles are available to consider the biocompatibility of dental implants or restoratives. Although physical and mechanical characteristics are significant in designing a biomaterial for dentistry, the biological attributes also have the same level of consideration with the selection and use of these biomaterials [22, 23]. This paper will be benefitted in accomplishing the better understanding for the biocompatibility of distinct metallic and polymeric dental materials as well as the further advancement in the biocompatibility evaluation system.

7.2 Detrimental Effect of Dental Restoratives: Irritation, Toxicity, Allergy, and Mutagenicity

There are various biotic outcomes that can transpire once restoratives are implanted in association with the active tissues that develop an active dynamic interface. These interface activities are dependent on the location of restoratives, its contact period with living tissues, properties of restorative materials, and health of the patients. The tissue interaction with non-biocompatible material may causes allergic reactions such as toxicity (release of toxic substances that can cause tissue necrosis and cell/tissue death), inflammation, and mutagenicity (direct or indirect destruction to DNA that leads to genetic alteration) [4, 5]. One of the biological consequences is inflammation that encompasses the stimulation of the immune system to protect it from hazards, and this outcome correspondingly results in the chronic toxic and allergic infections in the long term.

Generally, the allergic infections occur when a body identifies a foreign material and responds suspiciously, including the whole immune system that comprises lymphocytes and monocytes or macrophages. Mutagenic reactions take place when constituents of the restorative material affect the base pair of DNA cell, which adversely alters the cellular processes of the human body, called mutations. Numerous metal ions, as well as some resins used for dental applications, such as copper, nickel, and beryllium, etc., show mutagenic potential. However, in most cases, directly used dental restoratives were reported only local infections without any systemic problems [6].

7.3 Absorption Routes of Toxic Substances Released From Fental Restorations

The global normative access towards the biological importance of dental materials has led to the development of many inert biomaterials that claims to nil or nominal release of toxic substances from restorations [14]. However, all restorative material goes through degradation, some degree of dissolution, chemical erosion, or corrosion. Leachable constituents of matters are released due to the erosion or deterioration over time. If released constituents contain toxic agents and dissolved, may results into either local (may affect one area of the body for the very small duration) or systemic reactions (may affect to one or more organs of the human body on the long term) [24].

The probable routes of systemic ingestion of leachable chemical constituents from restoration can be through many ways such as diffusion to a pulp via dental tubules as shown in Figure 7.1, directly through oral

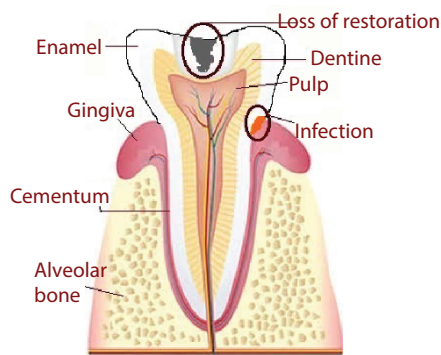


Figure 7.1 Cross-section view of tooth structure and restoration.

mucosa [25, 26], ingestion of released constituents in the gastrointestinal tract [27], or digestion of volatile matter in lungs [28, 29].

7.4 Toxicity of Frequently Used Dental Restoratives

There is a wide range of dental biomaterials used in dentistry, including irrigants, liners, prosthetics, cavity filling materials, intercanal medicaments, mouth rinses, and subgingival implants. The growing technological complications of novel synthetic materials has directed to enhanced knowledge regarding performance restrictions and biological influences of newly developed dental materials [30].

The various biomaterials used in dental restoration can be structurally categorized into the following classes: metals, ceramics, polymers, and composite-based restorations. These materials are categorized based on the nature and presence of predominant interatomic bonds [4, 6]. Metallic materials are characterized by metallic bonding; ceramics are organic compounds linked by ionic or covalent bonds, whereas polymers are formed by grouping monomers through the polymerization process [31]. Composites are designed by mixing two or more chemically distinct phases of distinct materials, leads to the formation of novel material having superior properties than that of original constituents [32, 33]. Some of the widely used materials in dentistry are briefly explained below.

7.4.1 Dental Silver Amalgams

Dental amalgam is an extensively used metallic restorative material in posterior teeth application. It comprises liquid and swarf mercury encompassing tin, silver, zinc, copper with other elements. It has certain disadvantages, i.e., unfavorable aesthetic properties, inadequate adhesiveness to the tooth structure, and free mercury contents [5, 30]. Free mercury content in dental amalgam is considered as the controversial point for many years being associated to the toxicity effect, and its contact with living tissues leads to the problem of contact dermatitis in workers and patients [5, 6]. Mercury exists in three forms, i.e., metals (Hg_0), inorganic ions (Hg^{2+}), or in the form of mercury ethyl or methyl. Metallic form of mercury ingests to the body by means of vapor through lungs or skin and the breathing process and enters to the bloodstream via alveoli, since circulated to the whole body, specifically affect the nervous system and tissues adipose [33, 34].

Literature studies have reported that based on the quantity of alloy present, the amalgams released by the vapor is enough source for 1–3 μg of

mercury absorption per day. Also, the wear of amalgam restoratives during various oral functioning promotes around 45 µg of mercury ingestion per day into the body (that can reach the gut) as amalgam particulates or by its dilution, that leads to the release of Hg^{2+} ions. The mercury content of about 3 µg/kg has been considered to show the toxic effect at its lowest level. Literature data reveals that severe symptoms were found as renal going paresthesia or neurological effects at the level ≥ 500 µg/kg, and ataxia at $\geq 1,000$ µg/kg, joint pain at $\geq 2,000$ µg/kg and if it going to increase at the level of $\geq 4,000$ µg/kg may even cause death of the patient [6, 34]. Over time, the chronic exposure leads to the symptoms, including weakness, anorexia, fatigue, insomnia, weight loss, dizziness, tremors, distrust, and irritation at the extreme level [5].

Fewer literature studies have reported that diffusion of mercury into enamel and dentine adversely affect the mineralization process of tooth structure, i.e., more prominent in older patients. However, it has been reported that mercury released from amalgam in dogs and humans do not reach the pulp. Hence, it can be hypothesized that mercury does not diffuse, but infiltrate back into the restorative materials and further reacts with unreacted alloy elements [35, 36]. Only tin and zinc with a high concentration in dentine is below the restorations by amalgam [37].

The toxicity of free mercury along with the copper in dental amalgams have been demonstrated by the cell culture screening tests. The implantation test result shows that the low copper-amalgam (2%–5% Cu) do not even impede the growth of cells, but the direct contact of high copper content amalgams (20%–40% Cu) originates the severe reaction issues [38]. However, the cavity preparation should be of foremost importance because it prevents the problem of thermal conductivity as well as micro-leakage. It has been found from studies that using amalgam without cavity preparation (for 0.5 mm of remaining dentine) arises the problem of pain and inflammatory response in next three days. However, many studies conducted professionally to the population exposed to the mercury, no information found regarding extensive harm due to mercury release from dental amalgam [4, 5, 39].

7.4.2 Glass Ionomer Cements

Glass ionomer cements (GICs) were used for dental restoration since 1969 and firstly introduced by Wilson and Kent [39]. The traditional GICs are available commercially in liquid and powder state. The powder form of traditional GICs consist of alumina (Al_2O_3), silica (SiO_2), aluminum fluoride

(AlF₃), calcium fluoride (CaF₂), sodium aluminum fluoride (Na₃AlF₆), and aluminum phosphate (Al PO₄), whereas its liquid form comprises polyacrylic acid (30%), alkenoic acid, tartaric acid (10%), itaconic acid (15%), and water (45%) [40, 41]. This traditional GICs have some limitations in clinical application, i.e., inferior mechanical properties than that of dental amalgam and resin-based composite restoratives and exhibits quite slow polymerization reaction process [42]. This traditional GICs undergone some modification in its composition, to promote its physical and mechanical characteristics such as addition of bis-phenol-A glycidyl methacrylate (bis-GMA) or some other hydrophilic monomers [i.e., 2-hydroxyethyl-methacrylate (HEMA)] which results in the formation of resin-modified GICs and polymerization initiators (i.e., light-cured glass ionomer system) to improve the efficacy of polymerization reaction process [17, 31].

The stability and biocompatibility of this restorative over time are one of the essential requirements to its utility in biomedical applications such as dentistry, neurological surgery, ossicular chain dislocation and prosthesis, rehabilitation of tegmen, and posterior canal wall injury, etc. These restorative materials show exclusive properties that encompasses the biological characteristics such as release of fluoride throughout the restoration period, capability to ion exchange with the restorative materials and preservation of tooth structure for longer period, presence of high molecular weight polyacrylic acid, fast pH neutralization, and nominal exothermic curing reactions [43, 44]. Primarily, pH of these materials varies in the range 1.6–3.7, i.e., very acidic in nature of GICs. However, it increases to 5.4–7.3 after the completion of the full polymerization process.

Freire *et al.* [6] have reported that changes in parameters, such as temperature during curing reactions, pH value, and leaching of ionic constituents (i.e., sodium, aluminum ions, calcium, fluoride, strontium, and zinc) leads to the mild cytotoxic effect. A large amount of HEMA monomer incorporation into resin-modified GICs were reported as a more cytotoxic effect than that of traditional GICs since the hydrophilic characteristics and low molecular weight, as well as the incomplete polymerization reaction, ends with residual monomers that can readily circulated through the dentine tubules and adversely affect the pulp bacterium. The screening tests for the cytotoxicity have shown that newly prepared GICs are slightly cytotoxic but it diminishes over time. The release of fluoride (shows therapeutic response) from the material results in *in vitro* cytotoxicity [45]. The results of the usage test after 4 weeks reported that these cements exhibit the mild reaction to dentine pulp and absence, or minimal inflammatory

infiltrate was observed from ionomer cement. This response may be due to the increased permeability of dentine after etching with orthophosphoric acid [6, 37].

These GICs are one of the best alternatives for being used as a liner substance around the pulp since the diffusion of polyacid by the dentinal tubules is limited because they are large sized molecules having high molecular weight (can't diffuse) and highly susceptible to adhere tooth structure [37, 40]. Just as the dental pulp, when it is utilized in subgingival restoration do not show inflammatory response to the soft tissues of the oral cavities and prove immense tolerance to the GICs [44].

7.4.3 Resin-Based Composites

The growing demand for direct restoration with good aesthetic properties has led to the development of resin-based composite materials. Composite resins are the advanced class of polymer-based dental restorative materials. It is a mixture of the organic matrix, inorganic filler, and coupling agent, which is formulated by free radical polymerization process and widely used as luting cement and restorative material for tooth restoration [46]. In dentistry, the biggest contribution in the field of composites was made by Bowen in 1963. He has evolved an innovative resin-based composite based on bis-phenol-A glycidyl methacrylate (Bis-GMA). It is an ester of an aromatic di methacrylate, which is sintered from methyl methacrylate and epoxy resin (ethylene glycol bis-phenol A) [47, 48].

Most of the resin composite used for dental applications is the mixture of monomers, i.e., Bis-GMA, 2-hydroxy ethyl methacrylate (HEMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA) [17]. Many types of the fillers (i.e., silica, quartz, glasses, and ceramics) have been incorporated into this resin-based matrix to improve the physicochemical and mechanical properties of dental material [32, 49].

In the early 1960s and 1970s, mineral-based filler materials were used in chemically cured resin composite for direct filling purpose and did not diminish their potential, causing serious pulp reaction. If not lined appropriately, it leads to chronic inflammation of dental pulp tissues that may continue for an unlimited time. Incomplete curing of the resin in the deep cavity increases the concentration of unpolymerized monomer, which reaches to the dentine pulp and creates the problem of hypersensitivity and cytotoxicity by these materials [50, 51]. The allergic reactions related to

the resin-based composites influences patients along with the dental staff working with these materials [52, 53].

The biocompatibility of these materials comprises toxicity of the luting cement and restoratives and their efficacy in avoiding fissure caries. Literature data reveals that newly developed; chemical/light-cured resin composites, when tested in cultured cell medium for 24–72 hours of exposure, it often leads to minimal to moderate cytotoxic infections and reduces significantly after 24–48 hours of setting and by the existence of dentine barrier [30]. The research outcomes demonstrate that light-cured composite shows mild toxic response than that of chemically cured composites, but this toxic influence of material is extremely dependent on the type of resin used and light-curing efficiency.

The biological tissue response of resin composite has been tested by *in vivo* usage test. Light and chemically cured restorative composite located in the tooth cavity (0.5 mm dentine remaining) represent low to modest pulpal inflammatory response after the 3 days of usage [54]. This response decreases as the postoperative duration increases (around 5–8 weeks), there is increased reparative dentine that has been noticed. The minimum adverse reaction of pulp to the restorative material was observed with the effective use of bonding agents and protective liners [55]. Some of the newly developed Bis-GMA free resin composite, polished composite materials exhibit significantly lower *in vitro* cytotoxicity due to the lower volume of leachable constituents, although some of the materials persist its toxic nature, even in the polished state [56]. However, no confirmation has been found that any commercially used resin originates xenoestrogenic influence or *in vivo* effects of leached constituents of resin composite on the soft oral tissues [55]. Some literatures through clinical trials have reported that methacrylate-based resin composites might be a source of hypersensitivity. Contrary, the problem of contact dermatitis has been associated with the allergic infections to acrylic resins [30].

However, the association of aesthetic characteristics with physical, chemical, and mechanical properties as well as affordable cost makes the resin composite materials significantly important for dental applications. Resin composites nowadays are predominantly preferred as the best material for occlusal loading conditions in dental applications such as posterior teeth applications. Their properties have significantly upgraded in this new era to enhance the stability of materials in different oral environments [57, 58]. There are some factors which show a detrimental effect on the resin-based composites which is discussed in next section.

7.5 Factors Affecting the Degradation Process of Resin-Based Dental Restoratives

In a harsh oral environment, detrimental effects of the biological system on dental restorative materials are termed as the biodegradation. It includes not only the destruction or dissolution of dental material in saliva but also demolition of physical and chemical properties along with the erosion and wears triggered by the food, mastication, and bacterial activities as represented in Figure 7.2 [59]. Therefore, it is essential to assess the reactivity of dental restoratives into the oral cavity, which is governed by saliva constituents, mastication forces, temperature variation, oral microbes, and chemical, nutritional changes, etc.

7.5.1 Saliva Constituents

Under the oral environment, resin composites are exposed to numerous physical and chemical agents present in drinks, saliva, food, and other oral hygiene routines. These composites should be resistant to different oral environments and show minimum diversity inside the mouth because the interaction between these agents may lead to degradation of restorative composites. In humans, saliva has 99.5% of water along with important constituents, including electrolytes, white blood cells, enzymes (i.e., lipase and amylase), mucus, epithelial cells (consist of DNA), and antimicrobial compounds (such as lysosome and IgA) [60]. Hence, the abundance of water in saliva prominently affect the degradation process of resin-based dental restoratives because these materials have polar characteristics and

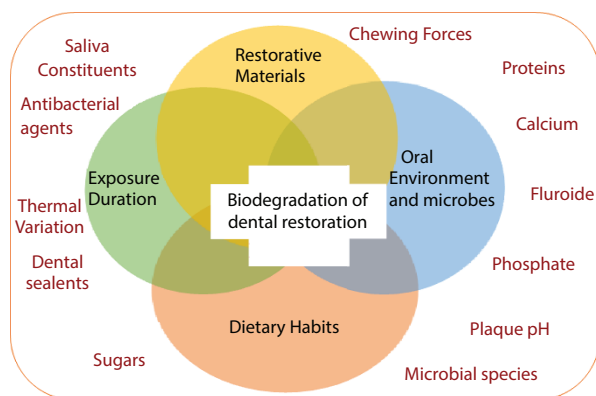


Figure 7.2 Major factors affecting biological properties of materials.

water molecules can readily infiltrate through the polymer network which allows the diffusion of unpolymerized/unbound monomers or additives from the composite material [61].

Literature has reported that in an aqueous environment, a typical resin composite becomes saturated within one or two months of placement [62, 63]. In polymer-based materials, this degradation phenomenon takes place through the enzymatic reaction and passive hydrolysis process [64]. However, the extent of the degradation process is significantly dependent on the degree of curing of resin (ester groups shows higher affinity to the loosely cross-linked network) and chemical composition of monomers, i.e., used for producing polymeric chain network, specifically, when enzymatic degradation phenomenon takes place [63].

7.5.2 Masticatory Forces

The biodegradation phenomenon of dental restoratives can also be encouraged by the fatigue and fracture that takes place due to the relatively unsteady repetitive loads, i.e., simple masticatory forces. During the masticatory functions, continuous application of dynamic mechanical and environmental loads causes the progressive deterioration of the material. Over a period, these forces cause the crack nucleation from microvoids and growing phenomenon, which further leads to the catastrophic failure of dental restoratives. This failure process is exclusively assisted by the pre-existence of residual stresses and microvoids into the resin composites that may be introduced into the material at the time of material processing [24, 65].

7.5.3 Thermal and Chemical Nutrient Variations

The wide range of thermal variation in the oral atmosphere originates from the dietary routine of a person. The consumption of hot food and drinks leads to the maximum surface temperature of the tooth around 47°C, but some literature has also reported unrealistic value, i.e., 0°C–67°C [60]. Such variation in temperature creates a hostile environment for the restorative material, which leads to inferior mechanical properties as well as volumetric expansion and contraction. Since thermal induced deformation is characterized by the coefficient of thermal expansion, it should be compared with the tooth substrate than the CTE value of the material itself [66]. The presence of continuous thermally induced loading to the restorative materials correspond to the high thermal gradient, and surface stresses cause microleakage and degradation of composite material [24].

The longevity of the restorations is also affected by the dietary habits. Daily intake of acidic foodstuff and beverages or other chemical contents like calcium, fluoride and phosphate content, lifestyle as well as biological aspect like saliva flow rate, dental, and soft tissue anatomy, etc., directly influence the Ph value of intraoral environment which in turn decide the lifespan of restorative materials [60]. The salivary fermentation boosts the sucrose level, causing enhance in the acidity and leads to potential caries development which corresponds to enamel/restorative dissolution. The cariogenic potential of edible items can be evaluated by several factors like salivary retention time, the extent of acid formation due to bacteria fermentation, condition of consumed food [24].

7.5.4 Oral Microorganism

The interaction between polymer network and oral pathogens form oral biofilm on the tooth surface that may cause multifactorial illness triggers from saliva, which corresponds to the imbalance between the process of demineralization (loss of minerals) and remineralization (mineral gain). These oral biofilms can deteriorate the resin material, thus negotiating the marginal integrity and cause recurrence of caries which promote failure of the restoration. The significant factors that are leading to remarkable continuous destruction of tooth structure or dental material are substrates, microorganism, acidic invasion from cariogenic bacteria at low pH, host/teeth, and time [67]. An *in vitro* investigation has reported that the colonization of oral bacteria on the composite surface leads to the increased surface roughness of material after incubation which causes surface deprivation [24]. In general, many factors such as saliva components, masticatory loading, oral microbes, and pH of oral environment are collectively responsible for the degradation of the polymer composite.

7.6 Conclusion

- In the current scenario, in the development of any type of dental material, one must give equal importance to the biological properties as aesthetics, strength, and functional characteristics of materials.
- The biocompatibility of dental restoratives significantly relies on its location, chemical composition, and synergy with the oral cavity. Diversified biological responses of

different dental restorative materials are characterized by the concentration of released substances that may show its immunogenic, toxic, or mutagenic nature.

- By thoroughly studying the literature data, it can be concluded that no material is altogether biocompatible, the location of restorative material in the oral cavity somewhat governs its biocompatibility.
- However, for small depth cavity (remaining dentine) resin composites and the modified glass ionomer cement with proper cavity preparation can be considered as a better substitute than dental alloys and amalgams that have improved biological responses, functional performance, and aesthetics as well.
- Further, *in vitro* investigations and meticulous clinical trials are necessary because of some probable exceptions.

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Technological Advances in Magnetic Abrasive Finishing for Surface Treatment of Alloys and Ceramics

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Abstract

Magnetic abrasive finishing process is super-finishing process which comes in class of magnetic assisted finishing process. This process is used to super finish advance material such as super-alloys, ceramics, and composites with tolerance in microns of surface roughness. This work will throw some light on the classification based on the magnetic field generated by magnets. This paper will give a detailed insight of experimental investigation on the co-relation existed between process parameters, i.e., machining gap, circumferential speed, vibration, and magnetic particles composition and performance responses, i.e., material removal, surface temperature, and surface roughness. The importance of analytical and mathematical modeling along with simulation based on finite element methods also discussed in this paper. The important response parameter which had been simulated was magnetic forces, surface temperature, and surface roughness. This paper will give better understanding of hybrid magnetic abrasive finishing process which had been created by fusion of different advance machining processes at last.

Keywords: Alloys, ceramics, magnetic abrasive particles, magnetic field, finite element method, multi-objective optimization

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8.1 Introduction

Magnetic abrasive finishing (MAF) process was originally introduced in 1940s in USA for enhancing surface quality by removing material in micro-chips from the workpiece surface. But major development was done by Boron and his associates in USSR in 1950s-1960s. Initially, they used this process for critical applications in field of cutting tools, turbine blades, and airfoils. Shinmura and colleagues' findings had evolved MAF process such that, it became adaptive enough to finish bio-metallic body parts, surgical tools, aero-space machinery, too [1]. In MAF process, finishing is performed by inserting the magnetic abrasive particles (MAPs) in the machining gap/working gap present magnetic poles and target surface of workpiece. MAPs are created by mixing iron particles and abrasive particles (Al_2O_3 , SiC) in required proportion [2]. These MAPs align them to form a flexible magnetic abrasive brush (FMAB) under the influence of magnetic field when they are placed in specified working gap. This FMAB acts as multi-point cutting tool that removes material in forms of micro-chips from the target surface. Indentation and micro chipping are two mechanisms responsible for material removal in MAF process. Normal magnetic force creates the indentation in the surface by pressing abrasive particles of FMAB. Tangential cutting force created by rotational speed of FMAB responsible for the micro chipping at the workpiece surface. Normal force and cutting force are dependent on voltage, working gap, mesh size, and rotational speed [3].

The classification of MAF process is layout according to magnetic field used to energize the MAPs in the working gap; such as permanent magnetic field MAF, static-direct current (DC) magnetic field MAF, pulsed-direct current (DC) magnetic field MAF, and alternating current (AC) magnetic field MAF. This paper elaborates the findings of experimental investigation carried out by eminent researchers for the surface treatment of alloys and ceramics using the MAF process. The experimental investigations laid major emphasis to reveal the contribution of process parameters with respect to finishing performance via MAF process. The most influential are process parameters are voltage, magnetic flux density, mesh size, working gap, composition and type of MAPs, rotation speed that basically affect the finishing performance of the MAF. Contribution of MAPs has been also reported in this paper. The major emphasis had been given on the finite element modeling and simulation, multi-objective optimization, and at last importance of hybrid MAF process has been reported. Figure 8.1 summarizes the detail about major research areas and aspect of the MAF

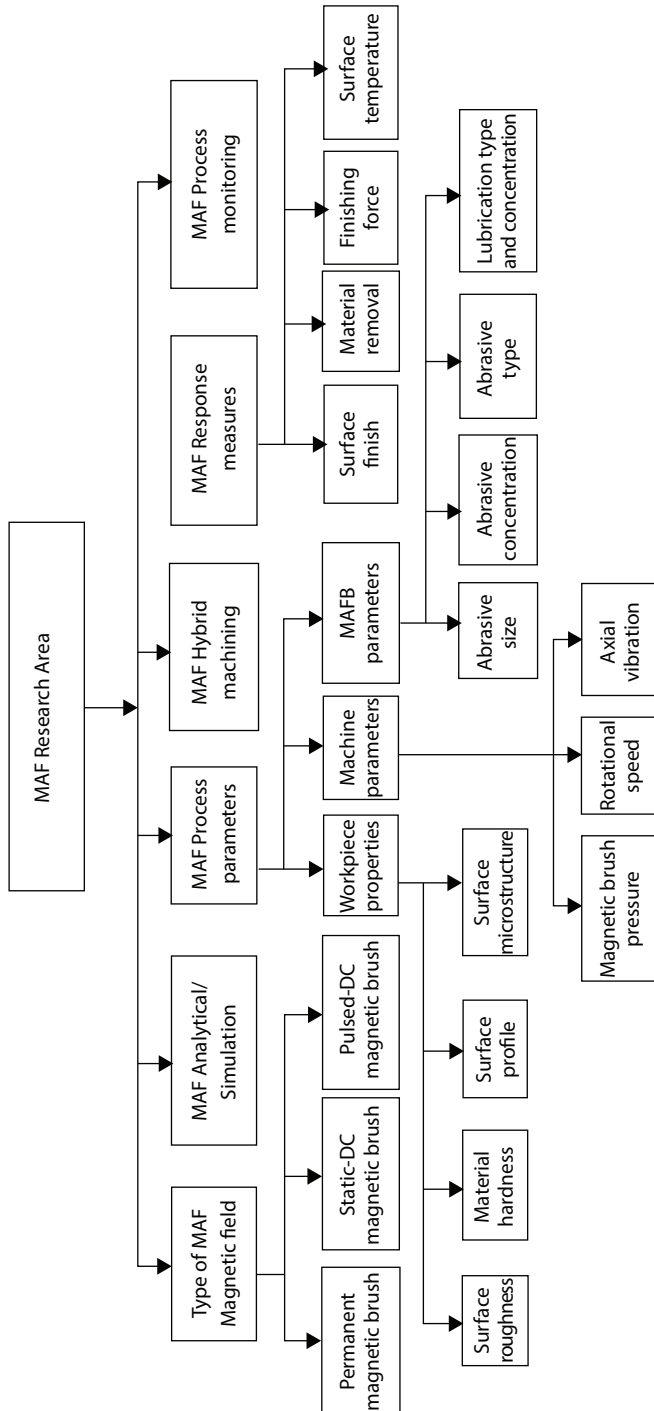


Figure 8.1 MAF process research areas.

process that were carried out. Tables 8.1 and 8.2 provide a major glimpse of researches carried to improve the surface texture and quality of different alloys and ceramics using MAF process.

8.2 Classification of Magnetic Abrasive Finishing Process

8.2.1 Magnetic Field Generated by Permanent Magnet

At first, rare earth permanent magnets were used to generate magnetic field in MAF process. When MAPs were placed in the machining gap due influence of magnetic flux, MAPs get aligned according to the magnetic lines of flux and formed a FMAB. Abrasive particles get stuck in between iron particles creating a chain in the FMAB. Advantage of using permanent magnet was that, it gave constant magnetic flux and limitation that the strength of magnetic brush could not vary according to need. Wang *et al.* [4] had constructed internal magnetic abrasive finishing setup by using four sets of permanent magnets made up of rare earth material for finishing inner parts of cylindrical workpiece. The magnets were placed on the internal surface of magnetic yoke, as shown in Figure 8.2. To divide abrasive particles into two equal portions in magnetic field, angle between two magnetic poles was kept at 60 degrees. The whole setup was mounted on the lathe cross slide and yoke was driven by gear drive electric motor assembly.

8.2.2 Magnetic Field Generated by Static-Direct Current

Initial studies conducted on MAF by using permanent magnetic field showed that it had certain limitations. To overcome the limitation, magnetic field generated by static-direct current was evolved which help in better controlling of magnetic flux and it enhanced the performance of MAF process. By using it, strength of magnetic flux could be regulated by current and voltage of electromagnet and helps in superior finishing of the surface of workpiece. For utilizing the advantageous feature of static-direct current magnetic field, Yamaguchi *et al.* [5] employed static direct current to generate magnetic field to finish internal cylindrical parts via MAF process. Figure 8.3a displays the graphic representation of direct current MAF setup with stationary magnetic pole arrangement. A stable magnetic field generated in the finishing zone when direct current was fed to electromagnet. This magnetic field formed the FMAB and material was eroded

Table 8.1 Major areas of experimental research in MAF process.

Approaches	Authors	Working material	Problem description	Methodology used
Experimental investigation:	Jain <i>et al.</i> [9]	Alloy steel	Effect of machining gap & circumferential speed of workpiece for cylindrical workpiece.	Static DC magnetic field and homogeneous mixture of semi-bounded particles
Material removal and Surface finish	Singh <i>et al.</i> [10]	Steel alloys	Parametric investigation of flat surface of workpiece	Static DC magnetic field
	Mori <i>et al.</i> [11]	SUS 304 stainless steel	Behavior of magnetic forces in FMAB	Static DC magnetic field
	Mulik <i>et al.</i> [12]	AISI 52100 Steel	Impact on surface roughness with interaction between rotational speed and voltage	Static DC magnetic field with alternate N-S poles four poles electromagnet.
	Girma <i>et al.</i> [13]	Stainless steel-SS304	Effect of mesh size of MAPs on the surface roughness and material removal	Static DC magnetic field, response surface methodology

(Continued)

Table 8.1 Major areas of experimental research in MAF process. (Continued)

Approaches	Authors	Working material	Problem description	Methodology used
<i>Material removal and Surface finish</i>	Singh <i>et al.</i> [14]	Steel alloys	Performance examination of flexible magnetic abrasive brush	Static DC magnetic field, response surface methodology and ANOVA
	Ahmad <i>et al.</i> [15]	Stainless Steel 202	Characteristics of sintered MAPs	Taguchi L9 orthogonal array
	Lin <i>et al.</i> [16]	stainless SUS304	Spherical magnetic poles with special troughs that form magnetic brush.	Static permanent magnetic field
	Im <i>et al.</i> [17]	STS 304 bar	Examination of micro-diameter & weight	Static permanent magnetic field, Unbounded magnetic abrasive composed of diamond paste, iron particles and grinding fluid
	Jiao <i>et al.</i> [19]	SUS304 stainless steel	Role of revolution radius of FMAB on surface roughness, 3D micro-morphology and cross-sectional shape	Static permanent magnetic field, combined revolution motion to magnetic abrasive particle brush

(Continued)

Table 8.1 Major areas of experimental research in MAF process. (Continued)

Approaches	Authors	Working material	Problem description	Methodology used
	Jain <i>et al.</i> [21]	Steel alloy	Analyzed the influence of pulse-on time and duty cycle on normal magnetic force, surface roughness reduction and force ratio.	Pulsed DC magnetic field, pulsating FMAB by using pulsed-direct current power source
	Zou <i>et al.</i> [22]	alumina ceramic	Micro-finishing mechanism of alternating MAF process on alumina ceramic plate	Alternating magnetic field with low frequency
	Xie <i>et al.</i> [23]	5052 aluminum alloy	Influence of magnetic force period acting on the magnetic particle	Alternating magnetic field
Experimental investigation:	Singh <i>et al.</i> [24]	Alloy steel	Investigation of forces responsible for the indentation and micro-chipping of workpiece surface	Static DC magnetic field, resistance type force dynamometer

(Continued)

Table 8.1 Major areas of experimental research in MAF process. (Continued)

Approaches	Authors	Working material	Problem description	Methodology used
<i>Finishing force</i>	Jain <i>et al.</i> [25]	Alloy steel	Force analysis between magnetic and non-magnetic material	
Experimental investigation: <i>surface temperature</i>	Mulik <i>et al.</i> [26]	Steel-AISI 52100	Influence on surface temperature due to process parameters such as abrasive particles weight, voltage and pulse on time.	Buckingham's dimensional model
Experimental investigation:	Chang <i>et al.</i> [27]	SKD11 steel	Basic principle & finishing characteristics of unbounded magnetic abrasive particles	Static DC magnetic field, Unbounded magnetic particles
<i>magnetic abrasive particles</i>	Yan <i>et al.</i> [28]	SKD11 tool steel	Role of unbounded magnetic abrasive in enhancing the surface quality of Electro-Discharge Machining machined surfaces.	Unbounded magnetic particles, Taguchi L_{18} orthogonal array

(Continued)

Table 8.1 Major areas of experimental research in MAF process. (Continued)

Approaches	Authors	Working material	Problem description	Methodology used
	Liu <i>et al.</i> [29]	SUS304 steel	Comparative study of behavior between the sintered abrasive particles and simply mixed abrasive particles.	Energy spectrum analysis using scan electron microscopy, superconducting quantum inter-device to compare M-H curves
	Wang <i>et al.</i> [30]	SKD11 tool steel	Effect of silicone gel mixed in MAPS on the finishing response in MAF process.	Blended the silicone gel with magnetic abrasive particles
	Wang <i>et al.</i> [31]	SKD11 tool steel	Role of temperature in self-sharpening effect of magnetic abrasive gel	Blended the silicone gel with magnetic abrasive particles
	Wu <i>et al.</i> [34]	SUS304 stainless steel	Comparative analysis on the role of different lubricants in magnetic abrasive brush such as neat oil, silicone fluid and water-soluble fluid	Low frequency alternating magnetic field

Table 8.2 Major areas of theoretical research, recent advancement, and hybrid machining in MAF process.

Approaches	Authors	Workpiece material	Problem description	Methodology used
Theoretical investigation:	Jayswal <i>et al.</i> [35]	Alloy steel	Investigation of distribution of magnetic force on workpiece surface	Galerkin's finite element methods
	Jain <i>et al.</i> [36]	Alloy steel	Prediction indentation and rotation of magnetic abrasive particles on finished surface	FEM model using Galerkin's method
Modeling and simulation	Yang <i>et al.</i> [37]	AISI304 stainless steel	Magnetic field characteristic of magnetic poles	Finite element method
	Kwak [38]	Magnesium	Enhancement of magnetic flux density of non-ferrous materials by placing permanent magnet (NdBF _e) behind workpiece	ANSYS software-based FEM
	Misra <i>et al.</i> [53]	AISI 52100	Theoretical modeling of finishing torque	Finite element method, ANSYS
	Misra <i>et al.</i> [54]	AISI 52100	Theoretical modeling of material removal mechanism	Finite element method, ANSYS

(Continued)

Table 8.2 Major areas of theoretical research, recent advancement, and hybrid machining in MAF process. (Continued)

Approaches	Authors	Workpiece material	Problem description	Methodology used
Thermal mathematical modeling	Misra <i>et al.</i> [55]	AISI 52100	Theoretical modeling of mechanism of surface roughness	Finite element method, ANSYS
	Komanduri <i>et al.</i> [39]	Si3N4 ceramics balls	Calculation of flash temperature generated during finishing and flash time at interface finishing surface	Classical moving heat theory of Jaeger
	Kumar <i>et al.</i> [40]	Si3N4 ceramics balls	Prediction of temperature rise in the workpiece	Finite element method (FEM), SIMU-MAF software
	Mishra <i>et al.</i> [41]	Steel-AISI 52100	FEM analysis of the magnetic distribution and temperature distribution	ANSYS software
	Singh <i>et al.</i> [42]	Aluminium 6060	Dimensional analysis of surface temperature	Buckingham - π theorem

(Continued)

Table 8.2 Major areas of theoretical research, recent advancement, and hybrid machining in MAF process. (Continued)

Approaches	Authors	Workpiece material	Problem description	Methodology used
Multi-objective optimization	Djavanrodi [43]	brass shaft CuZn37	Modeling of surface roughness for finishing brass	ANN, Levenberg-Marquardt algorithm
	Ngyen <i>et al.</i> [44]	SUS202 steel	Multi-objective optimization of MAF process using SUS2002 multi-curved surface material	Metamodel such as PRS, RBF, KRG AND SVR model, MOPSO algorithm
	Misra <i>et al.</i> [45]	AISI 52100	Optimization of material removal and surface roughness	Multi-objective genetic algorithm
	Singh <i>et al.</i> [46]	Aluminium 6060	Optimization of surface temperature, surface roughness and hardness	Hybrid multi-objective Moth fly- Artificial neural network

(Continued)

Table 8.2 Major areas of theoretical research, recent advancement, and hybrid machining in MAF process. (*Continued*)

Approaches	Authors	Workpiece material	Problem description	Methodology used
<i>Hybrid Magnetic Abrasive Finishing</i>	Judal <i>et al.</i> [47]	Aluminium	Examining the vibrational frequency and abrasive size in the enhancement of surface finish and material removal.	Vibration assisted cylindrical magnetic abrasive finishing process
	Mulik <i>et al.</i> [48]		Contribution of relative motion and rotary motion of FMAB in finishing of workpiece surface.	Ultrasonic assisted magnetic abrasive process
	Kala <i>et al.</i> [49]	copper alloy and stainless steel	Enhancement of magnetic flux density in working	Ultrasonic-assisted double-disk MAF process
	Yun <i>et al.</i> [50]	alumina ceramic tubes	Role of finishing trajectory of FMAB on the finishing quality of workpiece	Ultrasonic assisted magnetic abrasive process
	Judal <i>et al.</i> [56]	Stainless-Steel	Influence of electrolytic current on material removal and surface roughness	Electrochemical process with MAF- process

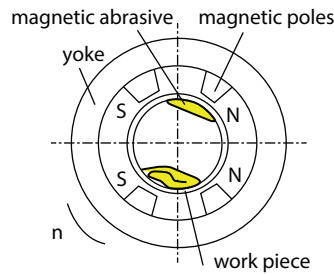


Figure 8.2 Permanent magnetic field MAF process setup [4].

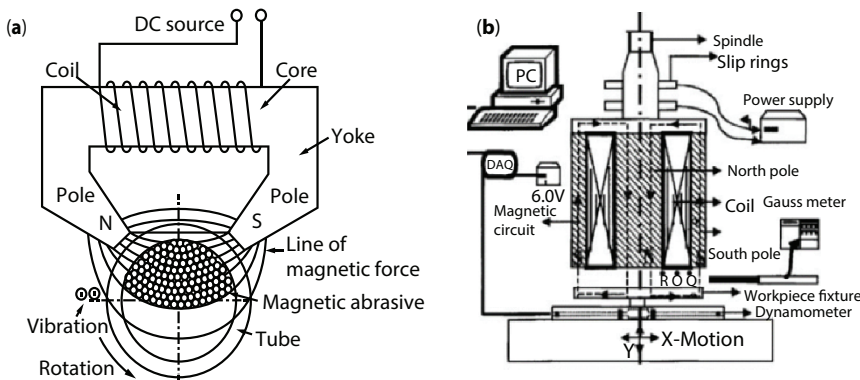


Figure 8.3 Graphical representation of static DC-MAF: (a) internal setup [5] and (b) plane setup [6].

from the surface of the workpiece by providing rotational to the cylindrical workpiece.

Further Singh *et al.* [6] modified the concept of inner static magnetic field to design and fabricate flat-faced electromagnetic tool to finish plane surfaces. Figure 8.3b shows the modified flat-faced MAF setup. This setup consisted of two poled magnet, external shell served as south pole, and central iron core served as north pole. When the electromagnet was energized with DC supply, magnetic flux generated between north and south poles into the machining gap without considerable magnetic flux leakage. This generates a stiff magnetic abrasive brush to finish plane workpiece surface.

8.2.3 Magnetic Field Generated by Pulsed-Direct Current

Both the magnetic field generated by permanent magnets and static-direct current which had a drawback that it diminishes the stirring effect. Due to

that, active abrasive particles were worn out very quickly that results inefficient finishing of workpiece. To overcome this major problem, Singh *et al.* [7] had developed pulsed-direct current MAF that shown in Figure 8.4. This new setup, flexible magnetic abrasive brush, was made pulsating by using pulsed-direct current power source. It was developed because it had string effect due to which fresh abrasive particles met the workpiece surface and creating good surface finish. For longer creation of FMAB, the electromagnet was fed with larger duty cycle pulsed current. This process had excellent stirring effect to produce high quality surfaces.

8.2.4 Magnetic Field Generated by Alternating Current

Recently, work had started to maximize the scattering effect of MAPs in the magnetic abrasive brush with assistance of alternating magnetic field, produced by feeding alternating current. This new mechanism provided reciprocating motion to the abrasive particles to enhance the utilization rate of MAPs that led to higher finishing efficiency of MAF process.

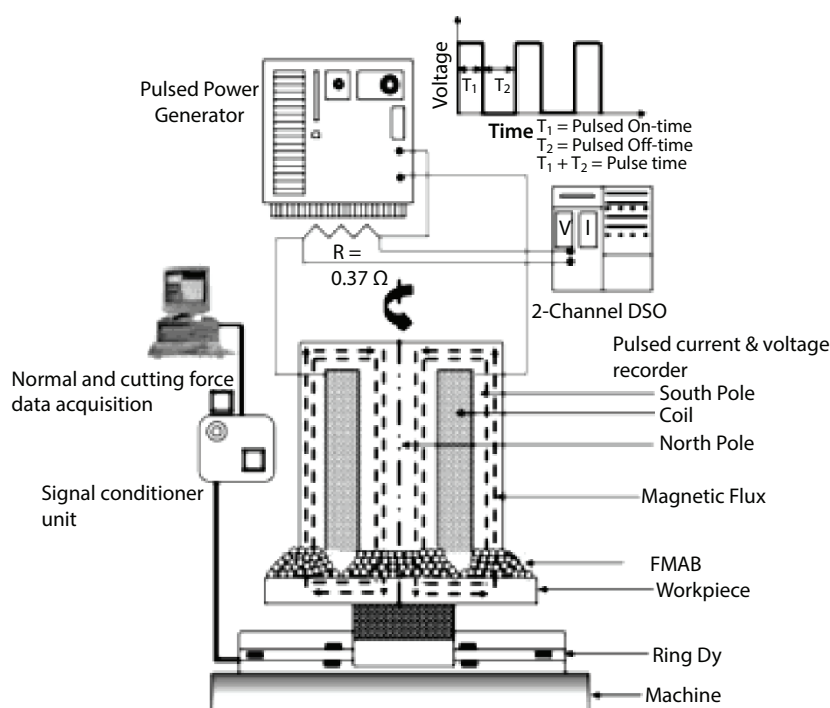


Figure 8.4 Graphical representation of pulsed DC-MAF setup [7].

Wu *et al.* [8] utilized the advantageous features of alternating current to develop an alternating field MAF process to finish a brass workpiece. Their MAF setup constructed by placing an electromagnet on motor to provide rotational motion. Magnetic abrasive particles were dispersed into a tray containing water-soluble fluid, adding fluid enhanced finishing quality of workpiece. This tray had placed over the electromagnet shown in Figure 8.5 and then workpiece was placed on the tray. Their mechanism provided good surface finish in the workpiece due to the excellent stirring effect of MAPs.

8.3 Major Areas of Experimental Research in Magnetic Abrasive Finishing

8.3.1 Process Parameters and Their Influence on Surface Roughness and Material Removal

At early stages of investigation, researchers performed experimental studies using static direct current to energized electromagnet to produce magnetic field in MAF. Most of the experimental studies had been done to explore the effect of input parameters, i.e., magnetic flux density, machining gap, type of abrasive, abrasive mesh size, circumferential speed and axial vibration on surface roughness (R_a), and material removal rate. Jain *et al.* [9] had worked on the effect of machining gap and circumferential speed of

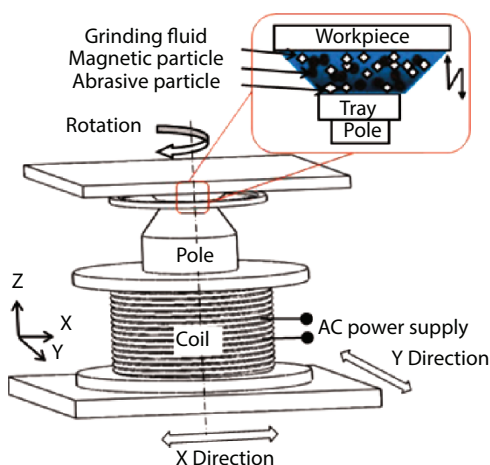


Figure 8.5 Graphical representation of alternating-MAF process setup [8].

workpiece for cylindrical workpiece. Experimentation was done by using homogeneous mixture of semi-bounded particles of ferrous powder of 300 mesh size, alumina of 600 mesh size, and servo pin 12 as lubricant. Material removal improved with rise in the rotational speed but in case of machining gap, it gave large removal at lower gap because magnetic abrasive brush becomes stiffer and deeper cutting of material was achieved. In case of surface roughness, it increased as the speed of workpiece increased because more number of grains met with the surface. Further, Singh *et al.* [10] had examined the surface texture produced FMAB in which magnetic forces play key part in creation of FMAB and generating abrasion pressure. They concluded that strength of FMAB must be adequate; that it could easily overcome resistance obtained by workpiece material to distort and strength of FMAB and indentation depth of abrasive particles in the workpiece could be control by regulatory the magnetic force for different working gap by varying supplied current of the electromagnet, as there was close relationship between current and magnetic force.

For better understanding the behavior of magnetic forces in magnetic abrasive finishing, Mori *et al.* [11] had studied the behavior of planer-type magnetic abrasive polishing for a magnetic neutral material, i.e., stainless steel. In their study, they found that FMAB formed among magnetic pole and workpiece material were the summation of three types of energy, namely, tension energy, magnetization energy, and repulsion energy. The magnetic field formed the normal force that hard-pressed abrasive of brush end to make indentation into material surface. Normal force was most important force that responsible for the material removal. For the enhancement of magnetic forces, Mulik *et al.* [12] designed and constructed a sophisticated four-pole electromagnet arrangement with alternative north and south poles for maximizing the surface finish in short processing time. Their investigation laid emphasis to reveal the effect of interaction among different process parameters on the surface roughness. They proposed that voltage in interaction with rotational speed impacted most the surface roughness. Surface finish was better at lower rpm because abrasive particle had greater indentation rate due to higher magnetic flux in working gap when voltage kept at high. But at higher rpm, there was reduction in the surface finish due to centripetal force becomes large enough to topple abrasive to indent in workpiece.

For the systematic conduction of experiments, design of experiment provided organized method to find out the proper interaction between input process parameter and output response parameters. Girma *et al.* [13] employed response surface methodology for conducting experimental analysis of material removal rate and surface roughness in MAF process.

In their finding, surface finish improved when bigger grain size of MAPs was used to finish plane surface, but it showed reverse trend in case of cylindrical surfaces. For bigger MAPs grain size, enhancement in surface roughness was affected by means of size ratio, current, and feed. Effect of size ratio was explained, when size of iron particle was larger to abrasive particles, then iron particle tends to cover abrasive particle which reduces the cutting edges for material removal. But when it was reversed, then magnetic force reduced that it may not be able to hold abrasive particles. Feed rate depends on the spindle speed and at lower speed feed rate increase because grains could remove surface peaks more efficiently.

Later, Singh *et al.* [14] had done the performance examination of flexible magnetic abrasive brush by means of response surface methodology and ANOVA. The experiment was performed on steel alloy workpiece using unbounded MAP and good surface finish in nanometer was achieved. It was concluded that machining gap and magnetic flux density were dominant parameters trailed by grain size and number of cycles. Feed was given to workpiece to get uniform surface finish over workpiece. Their study established a relation between number of cycles and surface roughness for different current value. Analysis of variance indicated a decent relation between the predicated and experimental data. Most recently, Ahmad *et al.* [15] applied Taguchi L_9 orthogonal array to reveal the impact of process parameters on the finishing quality of workpiece in the MAF process. Their study laid emphasis to retrieve the characteristics of sintered MAPs. Sintered MAPs were the bonded MAPs base (Fe) metal matrix surrounded by (Al_2O_3) abrasive particles. These sintered MAPs eventually enhanced the finishing performance of MAF process. They concluded that voltage was the most influential parameter affecting surface finish along with mesh size and working gap.

Permanent magnet made of rare earth metals gives excellent magnetic flux and their design and setup are compact and could be easily mounted on conventional machines that easily maintained. To tap above features, Lin *et al.* [16] had developed permanent magnetic finishing mechanism by modifying CNC machine to finish free flowing surface of stainless SUS304 material. In their investigation, conclusion was drawn that high efficiency could be achieved by using spherical magnetic poles with special troughs that form magnetic brush. The contribution of feed rate had been explained, as more number of magnetic abrasive particles would pass through working zone which improve the surface finish at lower value of feed rate. Further, to concentrate the magnetic flux density in working area, Im *et al.* [17] modified the design by adding yoke in permanent magnet. Experimentation was done using permanent magnets (Fe-Nd-B), yoke part

made of SS41 steel was added to stimulate seamless flow of magnetic field. Unbounded magnetic abrasive composed of diamond paste, iron particles, and grinding fluid used for the study. The investigation exhibited that it was conceivable to restrict the micro-diameter and weight of cylindrical STS 304 bar. However, roundness improved at initial processing stage as the original surface unevenness was swiftly removed during initial stages, which was similar to surface roughness. The intensification of magnetic flux in aluminum and other non-ferrous materials, Givi *et al.* [18] conceptualized new mechanism. In this mechanism, aluminum plate was placed between the permanent magnet and magnetic abrasive brush. The brush exerted pressure on the back side of the workpiece, and this increased the penetration rate of abrasive particles into workpiece surface. Experiments were done by three-level full factorial technique and ANOVA was applied to determine the contrition of process parameters. Their investigation revealed that the working gap and No of cycles were the most significant factors affect surface finish.

Further, the competence of permanent magnet assisted magnetic abrasive brush was enhanced by adding new mechanisms. Jiao *et al.* [19] combined revolution motion to magnetic abrasive particle brush in MAF process to enhance the surface finish. They took surface roughness, 3D micro-morphology, and cross-sectional shape as output response, measured during the ongoing experiments using measuring devices. They revealed that revolution radius had direct impact on the surface roughness. Greater the revolution radius greater was the reduction in the roughness. The maximum improvement in surface was registered for 6-mm revolution radius with 60% improvement to conventional MAF process. Recently, Verma *et al.* [20] designed and fabricated a novel magnetic tool to finish internal holes and tubes. The magnetic tool consisted of 2 NDFe35 permanent magnets with similar poles facing each other. To maximize the magnetic flux density on the edge of tool, ferromagnetic disc was between magnets shown in Figure 8.6. The magnetic flux variation was achieved by varying gap between two magnets. Their variable magnetic flux tool had achieved efficient finishing of stainless steel with 89.6% change Ra and 56 nm of surface finish.

Pulsed D.C. magnetic abrasive finishing had many advantages over the other two types of MAF. It had better control on magnetic flux and stirring effect that produces high quality surfaces. Jain *et al.* [21] developed the pulsating flexible magnetic abrasive brush (P-FMAB) by using pulsed DC power supply to overcome the demerits of S-FMAB. It was well-established fact that use of S-FMAB; lacked stirring effect which leads to early wear-out of abrasive cutting edges which result in lower finishing

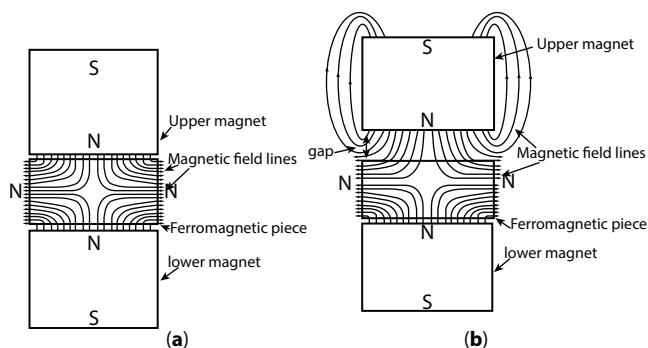


Figure 8.6 Movement of magnetic lines with alike poles. (a) without gap; (b) with gap [20].

rate. To study the effect of duty cycle and pulse-on time on, normal magnetic force, % reduction R_a value, and cutting force, author developed empirical models. Further, a correlation between magnetizing energy and surface finish was developed. It was observed that PC-MAF gave superior rate of surface finish to DC-MAF. The surface texture achieved by P-FMAB was more consistent than S-FMAB. The enhancement in surface finish was due to creation and demolition of FMAB during pulse on-time and pulse off-time of pulsed DC power supply. At last, it was found that current ratio played important role in mixing abrasive particles, and at higher value, a greater number of fresh particles interact with workpiece.

The advantageous scattering feature of alternating magnetic field MAF process was further tapped by Zou *et al.* [22], to investigate the complex micro-finishing mechanism of alternating MAF process on alumina ceramic plate. They employed alternating magnetic field with low frequency to form magnetic abrasive brush that had exerted greater finishing force to finish harder alumina ceramic. They established a relationship between the magnetic particle size and alternating magnetic field frequency with respect to finishing force. The experimental results proved that alternating magnetic field had better finishing performance in finishing harder ceramic material such as alumina plate and achieved surface improvement from 244.6 nm to 106.3 nm R_a in 80-min finishing time. Most recently, Xie *et al.* [23] investigated theoretically that magnetic force period acting on the magnetic particle was twice the magnetic field period in the alternating MAF process. They stated that change in finishing and magnetic forces were always lagged behind the change in magnetic field. Finishing force surges with surge in magnetic particle size and less affected by magnetic field frequency. Further, finishing proficiency rises with rise in

magnetic particle size in roughing stage but in contrast to finishing stage, surface quality increases with decrease in magnetic particle size. Finally, their experiment result showed that surface finish with 3 nm was achieved on the 5052 aluminium alloy plate.

8.3.2 Process Parameters and Their Influence on Finishing Forces and Surface Temperature

Finishing forces and surface temperature used as important response parameters that affect surface quality. Finishing forces had huge impact on surface texture and surface temperature had several impacts such as strain hardening, corrosion, etc. Experimental investigations had been done to investigate the effect of input process parameters on output responses, namely, finishing forces and surface temperature during MAF. For the data acquisition of magnetic forces, Singh *et al.* [6] constructed resistance type force dynamometer for the analysis of forces which are active during the finishing of workpiece. They implemented Taguchi design of experiment to find out the vital process parameters of MAF process that influenced surface quality. In their investigation, they found that magnetic forces and cutting forces were necessary process parameters that were affecting response parameters of MAF process. Through investigation, it was instigated that machining gap and voltage were most significant parameter because at higher voltage, electromagnet generate more magnetic flux density at lower gap; hence, there was increase in strength of magnetic brush which leads to more indentation which degrade surface quality, but the effect of grain mesh number and rotational speed was found irrelevant.

Again, Singh *et al.* [24] continued their investigation and their focus was on the forces which were responsible for the indentation and micro-chipping of workpiece surface in MAF process. It was found that normal force and cutting force were accountable for indentation and micro-chipping, respectively. The normal magnetic force was directly proportional to the current and inversely proportional to machining gap. Cutting force also rises with rise in current for specific gap because magnetic brush become stiffer and depth of indentation increases which offer more resistance to rotation of brush by workpiece therefore increase in cutting force. Later, Jain *et al.* [25] did comparative force analysis between magnetic and non-magnetic material for MAF process. They opted EN-8 ferromagnetic material and brass as non-ferromagnetic material for the experimental investigation. Their study concluded that for EN-8 and brass, current and working gap were the most significant factor that highly affect the generation of normal force and tangential cutting force. Substantially,

rotational speed also played an important role and had direct relation to both the forces. Whereas, abrasive mesh size didn't have substantial impact on the forces with respect to both the opted materials.

The experiment investigate on impact of surface temperature in MAF process was initiated by Mulik *et al.* [26]; their finding revealed that a relationship between the surface temperature and the output responses such as wear of surface, finishing accuracy, cutting mechanism, and surface integrity. The study was carried on ultrasonic-assisted magnetic abrasive finishing and the temperature study was performed for diverse processing conditions. Further, they developed temperature semi-empirical model using Buckingham's dimensional analysis for calculation of the coefficient which was based upon experimental data for the prediction of temperature. They concluded that the temperature rise directly depends on pulse on time, abrasive weight, and voltage. The higher voltage increases the magnetic flux density that led to stiffer magnetic brush that erode the surface more, results in higher temperature rise. The impact of weight of abrasive particle could be understood that with its increase, more cutting edges were available for cutting the surface which subsequently affects temperature. The effect of RPM of the electromagnet was inversely proportional to the temperature and it happens because at faster rpm; centripetal force becomes insufficient to grip MAPs and particles topples more than it indents into workpiece surface.

8.3.3 Study of Magnetic Abrasive Particles and Its Effect on Performance Parameters

Experimental investigations of magnetic abrasive particles were important because it had great impact on the performance of MAF. Literatures revealed that magnetic abrasive was basically three types: unbounded, semi-bounded, and bounded. But all had different characteristics and impact on the process parameters. Recent researches have been done to develop magnetic abrasive finishing with gel to boost the productivity of the MAF process. The foremost investigation had been carried out by Chang *et al.* [27]; in their study, basic principle and finishing characteristics of unbounded magnetic abrasive particles were examined. The unbounded magnetic abrasive was formed by mixing of Silicon carbide (SiC) abrasive and ferromagnetic particle with a SAE 30 lubricant. The experiment was done by using three distinct particle sizes of iron grit and steel grit, SiC abrasive of 1.2 μm and 5.5 μm was mixed with it. The major experimental finding was that by using large particle size of ferrous particles there was increase in magnetic force and more space available to carry more

abrasive particles in the magnetic brush due to which performance of process increased. SiC abrasive particles were added to steel grit for finishing harder material due to which better results were obtained.

One study on unbounded magnetic particles was done by Yan *et al.* [28]; in that, they had demonstrated for MAF process using unbounded magnetic abrasive that effectively enhanced the surface quality of Electro-Discharge Machining machined surfaces. For determining optimal process parameters, they applied Taguchi L_{18} orthogonal array to improve the surface finish. The optimum combination was 1-mm working gap, 3.0- μm particle size of SiC abrasive, 0.5-g weight of SiC abrasive within the UMA, 320- μm size of steel grit, 0.75T magnetic flux density, 5-Hz axial vibration frequency of workpiece, 0.6-m/s circumferential speed of workpiece and 15-min finishing time. Liu *et al.* [29] had done the comparative study of behavior between the sintered abrasive particles and simply mixed abrasive particles. To compare these two type abrasive media, the different sets of procedure and testing were opted to chalk out the difference in their performance. At first, the surface morphology was done to found out whether the abrasive particles had properly bound with the larger magnetic particles. For this, energy spectrum analysis had done by using scan electron microscopy. To compare the magnetization of two abrasive media, superconducting quantum inter-device used to compare M-H curves of two abrasive media. It was found that sintered abrasive media had higher magnetic flux density then simply mixed abrasive media.

Enhancement in semi-bounded was done by Wang *et al.* [30]; in their approach, they blended the silicone gel with magnetic abrasive particles to increase its efficiency and to achieve higher machining process performance. Silicone gel as a semi-solid polymer with deformable properties, this makes it easy to wrap and hold the abrasive particles in the finishing and it does not stick with workpiece. The result showed that using gel had increase the machining performance with great leap. This was achieved because the machining was performed not only by magnetic forces but was also done by viscous force of silicone gel. Further, silicone gel had better self-sharpening ability which contributes in great enhancement of the performance. Later, Wang *et al.* [31] extended their study on the silicone gel magnetic abrasive medium. In that, they gave detailed mechanism of MFGA, in that temperature played important role in the self-sharpening effect of magnetic abrasive gel. Figure 8.7 gives clear ideal about the magnetic abrasive particles which had been bounded by using silicone gel. Study revealed that temperature of the magnetic abrasive gel rose above the 110 C within 30 min during the finishing process. Due to which the

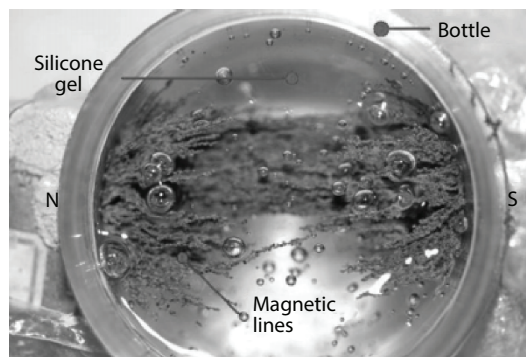


Figure 8.7 Magnetic lines of steel grits in the silicone gel [31].

abrasive gel becomes fluid gel which allows slow motion of MAPs and increase availability of fresh MAPs near workpiece surface.

Tsai *et al.* [32] applied grey relational method analysis (GRA) which was established upon Taguchi experimental data to acquire best process factors in the MAF process using gel abrasive. At first, GRA was done to assess the influence of process factors on responses that were surface roughness and material removal. Further, surface roughness and material removal were important for obtaining the optimal parameters; hence, their coefficients were averaged in equal weights of 0.5 to trace the grey relational grade. After that, the response of Taguchi was used to obtain the most influential parameter. Wang *et al.* [33] had extended their work on Gel abrasive; their experimental investigation revealed that generation of temperature in the silicone abrasive gel media was dependent on the plasticity of silicone gel. Temperature was inversely proportional to the plasticity of the silicone gel because low plasticity silicone gel had good circulating ability in the finishing area and it made easy for renewed abrasives to abrade the finishing surface; hence, there was rise in temperature in the finishing area. It was established that silicone gel abrasive media with low plasticity of 80 or 120 had produced better surface finish than the 160-plasticity silicone gel abrasive media.

Role of lubricant in the alternating MAF process was investigated by Wu *et al.* [34], they investigated the finishing characteristics of low frequency alternating magnetic field in the MAF process. They performed a comparative analysis on the role of different lubricants in magnetic abrasive brush such as neat oil, silicone fluid, and water-soluble fluid on the finishing performance of the process. They revealed that neat oil was most compatible with alternating magnetic field in order to achieve better surface quality

and larger material removal. Role of rotational speed was crucial in achieving better finishing force and material removal. Current frequency affects the finishing force and angle variation of magnetic particles. Greater angle variation facilitates better rolling of abrasive particles in the brush, hence improving the finishing.

Table 8.1 outlines the major research contribution carried out in the field of MAF process for processing the surface texture of different alloys and ceramics. The detailed description is done to give maximum information about the experimental researches in MAF process, comprised with investigation in surface roughness, material removal rate, magnetic finishing force, surface temperature, and magnetic abrasive particles.

8.4 Major Areas of Theoretical Research in Magnetic Abrasive Finishing

8.4.1 Finite Element Analysis of Magnetic Abrasive Finishing

Previous literature had reported about the use of finite element analysis (FEA) for the modeling and simulation of magnetic forces that had great impact on the surface finish. To study the theoretical aspects of magnetic abrasive process, Jayswal *et al.* [35] had established FEA model to investigate distribution of magnetic force on workpiece. In their approach, modeling of the surface roughness, material removal, and magnetic forces of workpiece were done by Galerkin's finite element methods. They predicted that indentation and rotation of FMAB removed a small quantity of material from workpiece surface. Edge effect was responsible for high magnitude of normal force near the magnetic pole edges. Later, Jain *et al.* [36] developed FEA model using Galerkin's method to analyze the irregular surface produced by MAF. Gaussian distribution function of surface profile was used to develop surface roughness model. They conducted a series of numerical experiment planned using FEM and surface roughness model to examine the effect of different process parameters. Further, it was realized that surface roughness prediction was much closer to experimental value in non-uniform surface to the uniform surface profile.

To boost the magnetic intensity in the machining gap, following investigation had been carried out using finite element method to develop new design and technique that enhanced the overall performance of magnetic abrasive finishing. First investigation in this area was done by Yang *et al.* [37]; they examined magnetic field characteristic of magnetic poles by applying finite element method. Further, it was observed that in case

of plane MAF, concentration of magnetic field distribution was not uniform in the machining gap. This happens due to uneven concentration of magnetic field of magnet and its strength was more at inner part than that of outer part of magnet. To make it uniform throughout, they proposed three distinct shapes of poles design and all three designs were examined using finite element method. At last, it was established that cylindrical magnetic poles with special grooves gave best results for proper distribution of magnetic field and generated good quality surface texture. After that, Kwak [38] had proposed a technique to enhance magnetic intensity of non-ferrous materials by placing permanent magnet (NdBFe) behind workpiece surface. He used ANSYS software to simulate the magnetic flux density and results showed that permanent magnet act as booster which rises the magnetic intensity in machining gap. The advantage of this technique was that, with rise in magnetic intensity lesser MAPs could be used for larger machining gap. At last, it was found the effectiveness of the system increased significantly.

To study the impact of heat on the machining surface, researchers developed mathematical modeling and used finite element method to establish a relationship between surface temperature and process parameters of MAF. Komanduri *et al.* [39] applied the Jaeger's thermal model of moving disk heat source to find thermal effect on ceramics rollers finished via MAF process. The main objective was to find the chemo-thermal effect between the interface surface magnetic brush and workpiece. They concluded that their investigation was that flash temperature was the function of scratch length, sliding speed, and polishing pressure of magnetic abrasive particles on workpiece surface. It was established that temperature rise was directly proportional to polishing pressure. Kumar *et al.* [40] had developed a mathematical formulation via FEM model to predict "rise in temperature" at the finished workpiece surface. Author implemented MATLAB based SIMU-MAF software for the forecasting of temperature rise at finished surface while conducting MAF operation. They concluded that temperature raised due to increase in MAPs velocity and magnetic flux. RPM of electromagnet plays direct role in the temperature rise. For lesser rise in temperature at the surface of workpiece, magnetic flux density and magnet rpm must be properly specified.

Further accuracy of simulation of surface temperature had increased using ANSYS modeling software and Mishra *et al.* [41] had used ANSYS software for the modeling and simulation of work-brush boundary temperature in MAF process. Simulation of the temperature distribution and magnetic distribution had done between the finished surface of workpiece and magnetic brush interface during the MAF process using unbounded

magnetic abrasive particle. Three-dimensional magneto static and axisymmetric transient heat conduction module were used for magnetic and temperature modeling. The predicted surface temperature was found in between 34°C and 51°C and there was negligible impact of temperature on surface finish and surface integrity of finished surface. Most recently, Singh *et al.* [42] developed predictive semi-empirical model to predict the raise in temperature on the aluminium 6060 surface. Their model was based on the Buckingham π theorem of dimensional analysis. The predictive model revealed the advantageous feature of dimensional modeling and the important characteristic of aluminium 6060 material properties along with the process parameters of the MAF process with respect to the surface temperature.

8.4.2 Process Optimization of Magnetic Abrasive Finishing

In recent years, the different multi-objective optimization techniques were employed to enhance the process performance of MAF process. For achieving this, Djavanrodi [43] applied the ANN for modeling of surface roughness for finishing brass via MAF process. He proposed that ANN a sophisticated technique that could simulate and predict the response such as surface roughness with an accuracy of 0.999 coefficient of determination (R^2) between simulated and experimental results. Levenberg-Marquardt algorithm was employed with back propagation to simulate the experimental results with excellent agreement. Ngygen *et al.* [44] did multi-objective optimization of MAF process using SUS2002 multi-curved surface material. They used ring magnetic field to assist the MAF process for multi-curved surface finish. Multi-metamodels such as PRS, RBF, KRG, AND SVR models were used to find the best solution and for better prediction MOPSO algorithm was employed. The best optimal result was predicted by the PRS metamodel coupled MOPSO. Recently, Misra *et al.* [45] did multi-objective optimization of ultrasonic-MAF process. They optimized the contrary responses, material removal, and surface roughness using multi-objective genetic algorithm (GA). Further, they combined the GA with fuzzy set to improve the optimum results. Their hybrid approach found in compliance with experimental results and achieved 68.5% improvement in R_a and 70.1% reduction in material removal. Most recently, Singh *et al.* [46] had developed a hybrid multi-objective optimization by merging moth fly optimization with the artificial neural network. The moth fly search algorithm was used to replace the search algorithm of artificial neural network in the developed MOO-ANN model. Their hybrid model had efficiently reduced the mean square error in the ANN and effectively optimized the

process parameters to find out the best responses such as surface temperature, hardness, and surface roughness.

8.5 Hybrid Magnetic Abrasive Finishing Process

To maximize the performance of the MAF process, new finishing process was developed by the combination of conventional and non-conventional finishing process with MAF. To incorporate benefits of vibration motion of workpiece, Judal *et al.* [47] developed vibration assisted cylindrical MAF process by modifying high speed lathe. Figure 8.8 shows schematic diagram of setup in which U-shaped electromagnet was placed on aluminum carrier plate mounted on sliding unit. Sliding unit was made to vibrate by using a spring return solenoid system in which pulsed current was feed. Frequency of vibration could be regulated by varying the frequency of pulsation. The experimental conclusions were drawn that vibrational frequency and abrasive size played a vital part in enhancement of surface finish and material removal. The material removal was enhanced with rise in vibrational frequency because vibration replaced the worn abrasive particles with fresh particles in the brush.

Merits of vibration were so high that it was thought that it would be good idea to combine magnetic abrasive finishing with ultrasonic machining to produce great results. Mulik *et al.* [48] were first to develop ultrasonic assisted MAF process (UAMAF) by combining ultrasonic vibration with MAF process. In that high frequency, electric signal of 20 kHz was

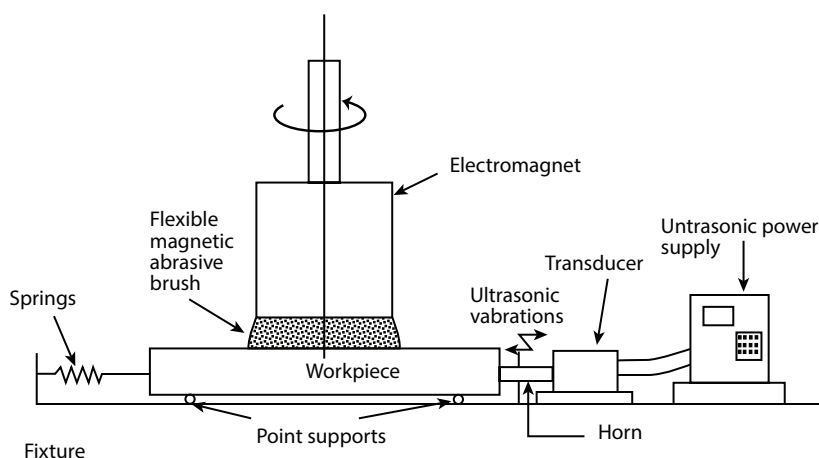


Figure 8.8 Schematic of UAMAF setup [45].

converted into vibration by using transducer. Due to which a longitudinal movement of workpiece was imparted by ultrasonic vibration that provide relative motion to abrasive particles against to workpiece surface. Both relative motion and rotary motion of FMAB contributes in finishing of workpiece surface. A high carbon bearing steel workpiece was effectively finished using unbounded magnetic abrasive particles. Further, Zhou *et al.* [49] concluded that when ultrasonic vibration and MAF process were simultaneously used, the finishing was done by mutual effect of high-speed rotation and high frequency vibration of FMAB. This process had easily penetrated hard material because of high frequency vibration generate instantaneous pulse pressure along with magnetic pressure. The result showed that surface texture and micro-crack were removed from workpiece and uniformed surface topology was generated. To develop a suitable finishing process for paramagnetic material, Kala *et al.* [50] used ultrasonic-assisted double-disk MAF process on para-magnetic metals, i.e., stainless steel and copper alloy. In their study, a number of magnetic disks were combined to form magnetic tool of four poles. Further, they observed that by splitting the assembly of magnetic disc into two parts and placing workpiece in between them increased the magnetic flux in machining gap, therefore enhancing the process performance.

Yun *et al.* [51] investigated the finishing mechanism of alumina ceramic tube by UAMAF process. Their study had enlightened the role of finishing trajectory of FMAB on the finishing quality of workpiece surface. The FMAB trajectory was depended on the frequency and rotational speed of workpiece. The removal of material and surface quality increased with increase in the frequency. With increase in rotational speed material removal increased but impact on the surface roughness was not significant. Their finishing mechanism achieved improvement in roughness from 1.1 μm to 0.3 μm and material removal of 485 mg with little brittle fracture on the finishing surface. Later, Amineh *et al.* [52] had proposed new finishing process by combining MAF with non-contact type ultrasonic machining. In this process, the cylindrical workpiece was finished by using a magnet which was moved inside workpiece and steel grits were used as abrasive particles. Whole finishing setup was submerged into water to use cavitation energy. The ultrasonic vibration created pressure difference in the liquid and cavitation collapse pressure was developed. The material removal took place by combined effect of ultrasonic vibration and cavitation energy. As a result, abrasive particles accelerated to the surface vertically and hammer it.

Theoretical modeling and investigation on the process mechanism of UAMAF had been most recently started by Misra *et al.* [53]; they did the

theoretical modeling of finishing torque in UAMAF. Simulation of magnetic flux density was done by finite element method to establish variation in the working gap. Their model established that the normal force was primarily responsible for finishing torque and higher voltage supply lead to higher finishing torque and normal force. Abrasive particle concentration directly influenced the finishing torque and normal force. Again, Misra *et al.* [54] continued the theoretical modeling to study the mechanism of material removal in UAMAF process. Their material removal model interpreted that total material removal was combination of steady state material removal and transient material removal in UAMAF process. They established that removal of material was direct function of initial surface roughness and asymptotically depended on workpiece hardness, but after a threshold value hardness didn't play any significant role. The steady state material removal was responsible for abrasion and transient material removal was responsible for shearing surface irregularities of workpiece. Recently, Misra *et al.* [55] did surface roughness modeling and simulation in UAMAF process. In that, they proposed the immediate surface roughness was function of immediate surface irregularities of the workpiece and material removal. Surface roughness reduction was inversely proportional to the workpiece surface hardness. Percentage change in roughness was asymptotically increased with surface hardness value and function of initial workpiece surface roughness. Greater the initial surface roughness greater would be reduction rate.

Electrochemical process used in combination with magnetic abrasive finishing made machining surface softer by etching process and material could be easily removed by using less magnetic force. Judal *et al.* [56] joined electrochemical process with MAF process for finishing cylindrical workpiece. In this process, the workpiece was coupled to anode and copper electrode to cathode. DC power supply feed to electrode with 0–3 A current and 0–33 V of voltage for forming a conductive layer between electrode and workpiece. Analysis shows that the electrolytic current had a significant influence on material removal and surface roughness, because surface irregularities were dissociated by using electrolytic current and hence easily removed by the FMAB. The main mechanism behind the finishing was abrasive assisted passivation. Sun *et al.* [57] developed plane electrolytic MAF process to finish SUS304 stainless steel. A new compound machining tool was designed and fabricated by combining the advantageous features of electrolytic and magnetic mechanism of electrolytic process and MAF process simultaneously. This new combined mechanism had tremendously reduced the finishing time from 75 min to 40 min for same process parameters and material removal was nearly six times greater than MAF

process. EMAF achieved about 50% higher surface quality and machining efficiency than MAF process.

Table 8.2 outlines the detailed description about the theoretical researches carried out in MAF process for processing the surface texture of different alloys and ceramics; along with recent advancement and hybrid machining MAF process. Table 8.2 provides the elaborated investigation done in field of modeling and simulation, thermal modeling, and multi-objective optimization.

8.6 Conclusion

MAF process had arisen as sophisticated super-finishing procedure that could easily improve the finished surface texture and quality of super alloys, ceramics, and biomaterials. Its application has expended to many critical and advanced industries, i.e., aero-space, defense, surgery, and medical sciences, etc., because critical parts manufactured in these industries need surface finish in microns. The performance measures such as surface roughness, hardness, temperature, and material removal rate depend on the voltage, rotational speed, working gap, and composition of magnetic abrasive particles. Stirring effect in flexible abrasive magnetic brush is important aspect in enhancing finishing performance and Alternating-MAF process along with Pulsed-MAF process provides excellent stirring effect. Use of gel as lubricant leads to better self-sharpening of magnetic abrasive particles. ANSYS and MATLAB software based on FEM were employed for better modeling and simulation of material removal, surface roughness, magnetic forces, and temperature of finished surface of workpiece. Efficiency of the MAF has increased by combining it with unconventional machining process such as ultrasonic machining and electrolytic polishing. Multi-objective optimization had been applied to boost the efficiency and effectiveness of magnetic abrasive process.

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Alloy Materials for Biomedical Applications

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Abstract

Metals and alloys have widespread use as biomedical materials for replacing dysfunctional hard tissues. The demand for development of alloy materials that fulfill all the requirements of biomedical alloys regarding mechanical, chemical, and biological characteristics is getting higher fast with increasing elderly population. Representative employed metallic materials are 316L stainless steel, cobalt (Co)-based alloys, and titanium (Ti) alloys. New nickel-free low modulus Ti alloys, zirconium alloys, biodegradable alloys, and niobium and tantalum alloys are proving very interesting to biomedical applications and are still under development nowadays. This chapter describes the commonly used biomedical alloys as well as the new metallic materials and the essential factors affecting their performance for clinical applications.

Keywords: Alloys, metals, implants, biomaterials, biocompatibility

9.1 Overview of Biomedical Alloys

Biomedical metals are usually used for the replacement of a lost or diseased biological structure of the human body [1]. The demand for biomedical material for replacing dysfunctional hard tissues is increasing rapidly with the growing aging world population and its higher risk to suffer diseases (e.g., arthritis and joint pain) and hard tissue failures [1, 2]. There is a wide

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application of biomedical materials, and it varies according to the human part to be replaced. Biomedical materials can be used as heart valves, intra-vascular stents, artificial ligaments, joint replacements, pins for fracture stabilization, dental implants, and removable partial denture frameworks (Figure 9.1) [3, 4].

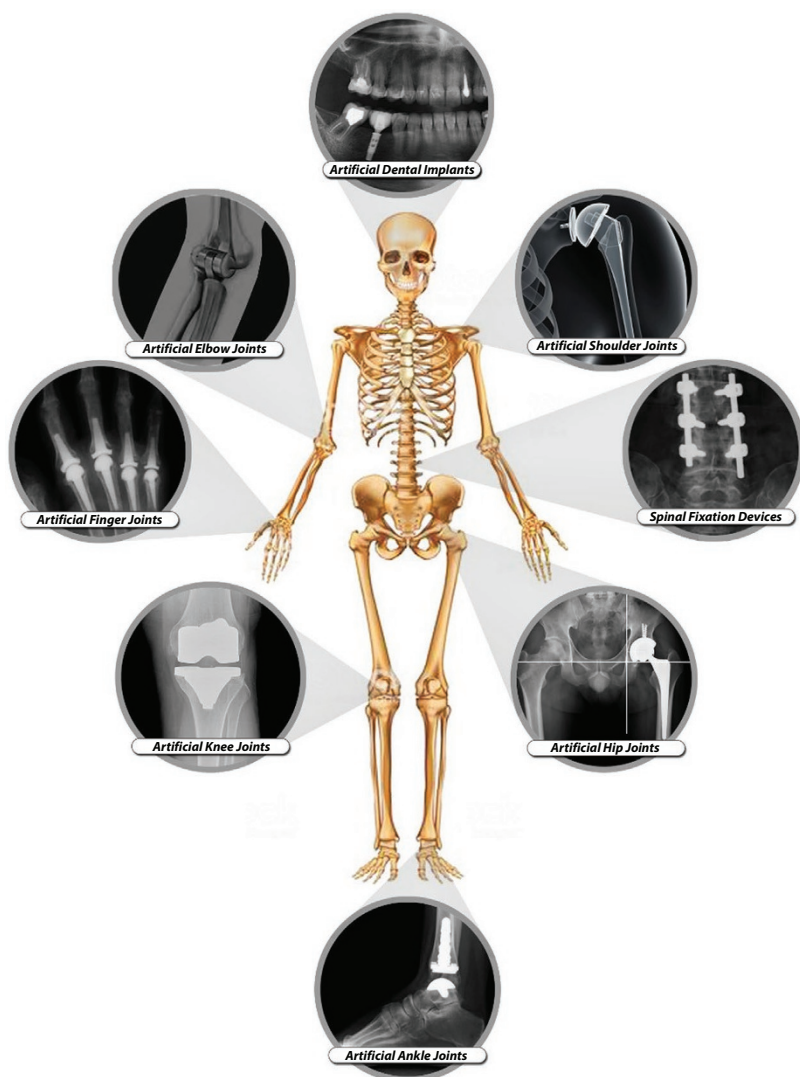


Figure 9.1 Application of biomedical materials according to the human part to be replaced.

An optimal biomedical alloy is predicted to present a combination of elastic modulus near to the bone, excellent corrosion and wear resistance, great strength, and high biocompatibility, including osseointegration and antibacterial ability [5, 6]. Based on these characteristics, metals and their alloys are suitable long-lasting materials for load-bearing applications [3]. Representative employed metallic materials are 316L stainless steel, cobalt (Co)-chromium (Cr)-based alloys, and titanium (Ti) and its alloys. However, the existent biomedical materials do not fulfill all the requirements for biomedical applications [1]. Nowadays, new concept biomedical alloys with other metallic materials [e.g., tantalum (Ta), zinc (Zn), niobium (Nb), zirconium (Zr), manganese (Mn), and molybdenum (Mo)] are being carried out and investigated to enhance mechanical, chemical, and biological properties of metals for biomedical applications [7–9].

9.2 The Key Properties Required for Biomedical Alloys

Biomaterials used for implantation applications in the medical and dental fields yield unique characteristics to satisfy the requirements demanded by the human body and to determine the success of the rehabilitation. Among biomaterials, metals have been used as material of choice in reconstructive surgery and in non-osseous tissues (e.g., blood vessels) due to their ability to alloy and, consequently, the possibility to alter extrinsic and intrinsic properties of the unalloyed metal to achieve suitable features for the required demands [9, 10]. In this context, biomedical alloys must exhibit satisfactory mechanical and chemical properties (strength, hardness, low elastic modulus, corrosion and wear resistance, fatigue resistance, percentage of elongation, and low density) and biological properties (biocompatibility, nontoxicity, hemo-capability, and osseointegration) (Figure 9.2) to extend their clinical application, since these properties are determinant factors for the failure or success of an implant [11–13].

9.2.1 Mechanical Properties

Biomedical metallic alloy materials implanted in the human body are primarily used for load-bearing applications and must present excellent mechanical reliability to tolerate the repeated cyclic loads usually applied on these implant devices as a result of daily activity (e.g., chewing, walking) [14]. In particular, these repeated cyclic loadings generates plastic

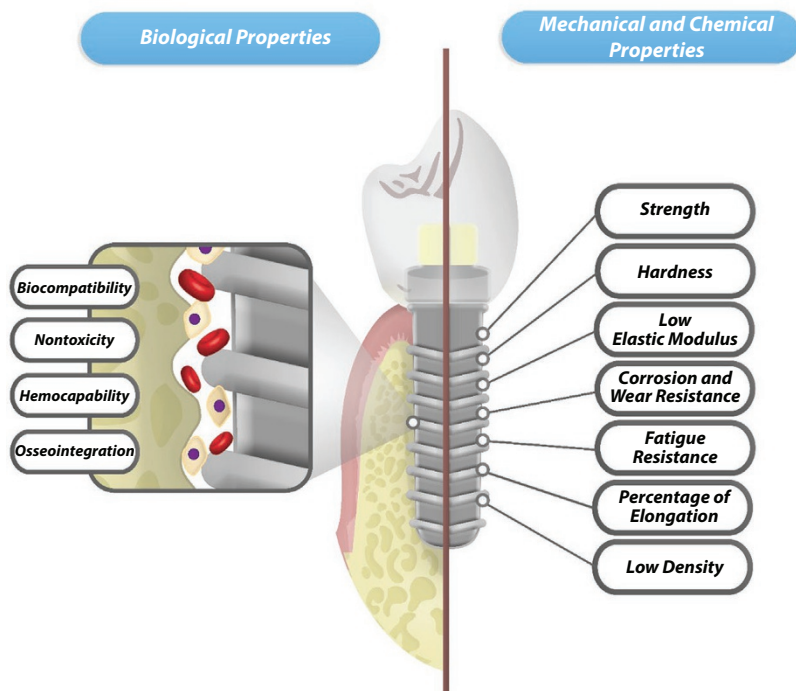


Figure 9.2 Biological, mechanical, and chemical properties required for implant alloys.

deformation characterized by small zones of stress concentration and, consequently, leading to fracture of the biomedical implant if the biomaterial has not sufficient fatigue resistance [1, 15]. Improved resistance against the initiation and propagation stages of small fatigue cracks can be achieved by the combination of strength and ductility using strengthening techniques, such as alloying, grain refinement and heat treatment [15–19].

Overall, alloying elements such as Ta, aluminum (Al), Zr, Mo, silicon (Si), and Fe tend to enhance alloy strength, which has been related to be higher for the $\alpha + \beta$ alloys [20–25]. In addition, it is worth mentioning that the concentration of β -stabilizers in the alloy must be drawn with caution, since the larger amounts of these elements can lead to a reduction of ductility and lower the tensile strength of the alloys [26]. Regarding the processing method, thermomechanical process of alloys is necessary to improve mechanical, physical, and chemical properties, since it affects the microstructure phases of the material [27]. Annealing, aging (heat) treatment and thermal treatments are examples of thermomechanical process capable to prevent or minimize unwanted grain growth and pore formation,

which has a positive effect in the mechanical characteristics of the alloy (e.g., hardness, strength, toughness, and elastic modulus) [18, 19, 28, 29].

An ideal biomedical alloy material should present excellent characteristics suitable for a desired application, such as great strength and hardness and low elastic modulus, in the case of implant application [9, 17, 30]. The biomaterial used as a substitute of the bone is preferably intended to have elastic modulus nearest to the bone, ranging from 10 to 30 GPa varying according to the bone type and the orientation of measurements [31]. One of the major issues related to biomedical materials is the stiffness mismatch of the biomaterial's elastic modulus with the adjacent bone, which cause "stress shielding" phenomenon related to bone resorption and failure of the implant [32, 33]. However, while low values of elastic modulus benefit the protection against the stress shielding effect, excessive lower values can result in micro-movements at the tissue-implant interface and lead to an unsuccessful rehabilitation treatment [34].

It is well established that the hardness and the elastic modulus of biomedical alloys are properties directly dependent on their constituent phases [30]. The addition of α -stabilizers has been related to be responsible for the hardening of the alloy [35]. However, solid-solution hardening decreases the bonding force among atoms responsible for the better performance of elastic modulus. Therefore, contrarily to hardness, the elastic modulus of an alloy could be lowered by suppressing the concentration of α -stabilizer and rising β content. In this context, β -type alloys are potential materials in terms of elastic modulus compared to unalloyed metals, α -type and two-phase $\alpha + \beta$ alloys [28]. It occurs because of the structural model of β phase in solid state, which is arranged in a body-centered cubic (bcc) crystal structure where the bonding force among atoms is higher than the α -hexagonal closed packed (HCP) crystal system (Figure 9.3), enhancing the mechanism of metal plastic forming [9]. However, β -type alloys are generally obtained by solution treatment, which decrease the strength characteristics of the material when compared to the mixed α and β phases [1]. To overcome this problem, for the purpose of enhancing the strength properties and maintaining elastic modulus at a level near to the bone, methods such as aging treatment and the introduction of small amounts of secondary particles (e.g., TiB and Y_2O_3) to the β -type alloys can be used [1, 19, 22, 36, 37]. These techniques reinforce the intrinsic properties of low elastic modulus β -type alloys, such as additional hardening, and also have good effects on the alloy's corrosion resistance by the refinement of its microstructure [1]. The solid-solution strengthening responsible for increased hardness of the alloy may favor the protection against oxidation by the existence of a thick and adherent oxide layer on the metal's surface [38].

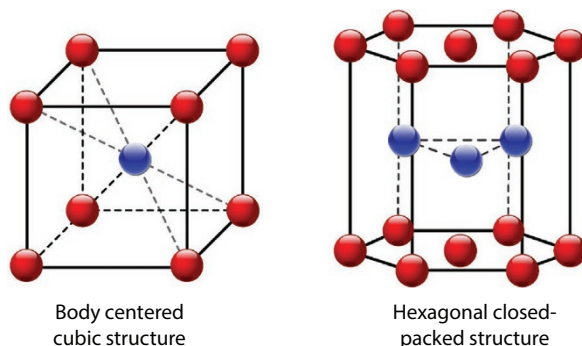


Figure 9.3 Representative body-centered cubic structure and hexagonal closed-packed structure of β and α alloys, respectively.

9.2.2 Corrosion Resistance

Corrosion resistance corresponds to the formation of a stable and resistant passive oxide layer against some adverse effects of physiological conditions of the body [39–41]. When metallic biomedical materials are exposed to cells, organic compounds, proteins, and body fluids, the oxide film naturally formed on the metal's surface is negatively affected by its destruction, leading to the release of ions and debris from the metal into the peri-implant tissues, which is associated to faster the corrosion process and, consequently, contribute to the infection of peri-implant tissues and the failure of the rehabilitation [42–44]. A convenient way to raise materials' corrosion resistance is to develop alloys with the addition of noble metals, such as β -stabilizer elements (e.g., Nb, Mo, Zr, and Ta), since with the presence of these elements the oxide film formed on the surface become thicker and nobler than the native passive film of unalloyed metal [9, 20, 34, 45–48]. Another way to develop oxide films with greater thickness is surface treatments such as plasma treatments, heat treatment, and magnetron sputtering deposition [21, 49, 50].

The protection of the surface against the diffusion of ions is of great concern, since some biomedical alloys have toxic elements in its composition, such as Al [51] and V [52], which could cause harmful effects on the human body. Therefore, future studies should be focused on the development of alloys that present in addition to good mechanical properties, an alloy composition free of toxic elements, or create surface treatments to diminish the ions release from the metal to the surrounding tissues.

The combination of all these properties could extend the long-term success of implant rehabilitation by increasing the biocompatibility and, consequently, the probability of occurring an adequate implant osseointegration process.

9.2.3 Biological Properties

9.2.3.1 *Biocompatibility*

When developing alloy materials for biomedical applications, an appropriate combination between the physical properties as close as possible to the tissue to be substituted with minimum toxicity to cause harmful effects when it is in contact with the body must be considered. According to Williams, whatever the required function, the biomaterials including alloy components should exhibit biocompatibility, which means not release any clinically significant toxic substances in the body to avoid adverse effects to the patient [43, 53]. Any biomaterial used as implants drives some sort of reaction, which is directly related to the oxide layer created on the implant surface, as these responses are more pronounced at the implant-tissue and/or biological environment interface surrounding the oxide film [8, 54].

In this context, biomaterials can be divided into four types of responses between implant and the surrounding tissues [8]:

1. *Toxic*. Toxic materials evoke the death of cells in peri-implant tissue, which can generate systemic damage to the host [55].
2. *Bioinert*. Bioinert materials have minimal interaction with the host tissue because of the development of a fibrous capsule around the implant isolating it from the surrounding tissue [56].
3. *Bioactive*. Bioactive materials connect to the host tissue at the interface by chemical bonds with tissues. When this interaction is related to bone tissue, occur deposition of collagen and minerals around the implant surface, which is a phenomenon defined as osseointegration [8, 57].
4. *Bioresorbable*. Bioresorbable materials resorb gradually into the human body by dissolution, hydrolysis, or corrosion and are superseded by a new bone tissue in its place [58].

9.2.3.2 *Osseointegration*

Once the biomedical alloys are considered as bone substitutes, they should have not only biocompatibility but also the ability to osseointegrate. After implantation, the implant surfaces are exposed to a complex physiological environment and it is conditioned by tissue fluids [59]. Therefore, the success of biomedical alloys implants depends on effective biomaterial-tissue interaction, in which the cellular attachment, proliferation, and differentiation, as well as the modulation of platelet activity, are affected by the alloys' chemistry and surface topography [59, 60]. There is considerable variation among biomedical implants with respect to design as well as elemental composition of the alloy [61]. Although the material composition have been advantageous to the mechanical properties of the implant, alloys exhibit biological behavior (e.g., osseointegration) comparable to that of unalloyed biomaterials (e.g., Ti-Zr vs. cpTi) [62, 63]. Therefore, the widespread of surface modification has been gained much attention of researchers to improve osseointegration ability to some metallic implants, including sol-gel modification, anodization, hydroxyapatite coating, and surface texturing and roughening [64–66]. Although it has been reported that these surface treatments improve or even accelerate the osseointegration process [64–66], some techniques create macro and micron scale features surface characteristics that have an indirect influence on cellular activity, which can compromise the long-term stability and performance of the implant [67]. Studies regarding new alloys with trace metals that are fundamental for bone metabolism [e.g., Tin (Sn), Si, and Zn], or the development of implant surfaces modified by the incorporation of these biocompatible elements, seem to be good alternatives for osseointegration improvement [68–71].

9.2.3.3 *Hemocompatibility and Antibacterial Activity*

Concomitant to biocompatibility and osseointegration ability, an ideal alloy material for biomedical application should exhibit hemocompatibility, with low thrombogenicity and anti-inflammatory properties [72, 73]. These properties are important factors to increase the rate of osseointegration, promote healing process, and avoid particle embolization, thrombus formation, and fibrin deposition, which are related to affect long-term implant stability [60, 74]. Additionally, it is interesting that the biomedical alloys used for implant applications be unfavorable to bacterial adhesion, since implant-related infections is a severe hidden problem that cause pain to the patient, risk of reoperation, and diminish the life-span of the

rehabilitation [75–77]. In addition, it should be noted the increase of antibiotic resistance bacterial strains, which can in turn lead to the requirement of the development of new strategy for an effective and prolonged antibacterial action [78, 79]. Therefore, several new alloy materials have been developed by the addition of antibacterial and anti-inflammatory elements in their composition, such as copper (Cu), silver (Ag), and Zn [76, 77, 80–83]. Notwithstanding, the ion release of these elements and their accumulation in peri-implant tissues would induce cytotoxic effects as well as reduction of workability in metals [76, 84]. Thus, an appropriate amount of antibacterial metal elements, respecting the acceptable limits for each specific metal ions in the body, is crucial for the development and the application of antibacterial alloys for clinical purpose [76].

9.2.3.4 *Biodegradability*

Another key factor for biomedical applications of alloy materials is the biodegradability. A metal is biodegradable when it has the ability to promote corrosion process but its products are non-toxic in a physiological environment [6]. However, biodegradable materials, such as iron (Fe), magnesium (Mg), Zn, and their alloys, do not have sufficient mechanical properties to endure load-bearing applications [85–87]. In light of the disadvantages of these poor mechanical properties, the addition of alloying elements such as Ag, Cu, and calcium (Ca) into biodegradable alloys emerges as a promising technique to solve these drawbacks while maintaining the implant's biocompatibility [5, 17, 82, 88].

9.3 Commonly Used Biomedical Alloys

Metals have been used as structural biomaterials for biomedical applications for centuries. Stainless steel (SS) was the earliest introduced metal used as biomaterial in the 1920s and it is still a commonly used alloy in all implant fields [89]. It attracted the interest of clinicians due to its outstanding corrosion resistance and good mechanical properties [89]. Cobalt-based alloys were first found in 1907 and have been used for decades in manufacturing of artificial hip and knee joints, dental implants, and prosthesis frameworks due to their great wear resistance, mechanical characteristics, and biological inertness [90]. Later on, Ti and its alloys have achieved much attention from researchers due to their superior biocompatibility compared to SS and cobalt-based alloys metallic biomaterials, as well as attractive mechanical properties, and wear and corrosion resistance

in physiological environment [1]. Nevertheless, sometimes, the implant fails in the long run of the rehabilitation, and a second surgery becomes necessary [49]. Recently, there is a growing interest to other metallic materials for biomedical implants development, such as Zr, Ta, Nb, and its alloys and biodegradable metals—Mg and Fe-based alloys—to overcome the issues of mechanical and biological properties of present implant biomaterials [1]. The development of new alloys is still under investigation to confirm their possible application on medical and dental fields. Hence, proper knowledge about the commonly used biomedical alloys and the factors affecting their performance on implant materials is essential.

9.3.1 Stainless Steel

Stainless steel is an iron-based alloy composed of at least 11 wt% Cr in order to impart “stainlessness” (i.e., absence of staining, rusting, or corrosion in relatively pure, dry air) to steels [91]. This level of Cr is needed to be incorporated within the metallic matrix to ensure the creation of an adherent, passivating oxide film on the steel surface in relatively unpolluted atmosphere, which allows a high corrosion resistance to the material [91, 92]. However, when elements like carbon (C) are present, or in moist atmospheres or polluted environments, the occurrence of pitting and rusting is increased, and a higher content of Cr is necessary to shield against these phenomena [91].

Modern SS, besides the basis Fe-Cr system, also contains several of other alloying elements which are able to strengthen specific characteristics (e.g., hardness and ductility) [91]. Besides Cr, these alloying elements include mainly C, nickel (Ni), Mo, Cu, and nitrogen (N). The role of each alloying element in SS complex is summarized in Table 9.1.

Among SS types, the 316L (316 low-carbon steel) is the surgical SS alloy normally used for biomedical implants, such as prosthetic joints, orthopedic plates and implants, dental implants, cranial implants, pacemaker, and bone fixation [12]. 316L SS typically contain 2–3 wt% Mo, 16–18 wt% Cr, 12–15 wt% Ni, and less than 2 wt% Mn and 0.03 wt% C [100, 101], which contributes to its reasonable corrosion resistance, ductility, and toughness properties [12]. However, although SS implants are still popular and have a considerable market share, the inflammatory and allergic reactions of Ni to patients rehabilitated with these implants has restricted its use [102]. To overcome this limitation, new types of SS alloys Ni-free have been developed for decades [103]. The development of Ni-free nitrogen containing SS seems to be a good alternative for the

Table 9.1 Main alloying elements of stainless steel (SS) alloys and their influence on SS matrix.

Element	Influence on stainless steel matrix	Reference
Chromium	Increases corrosion resistance and control the spread of stable pitting	[93]
Carbon	Increases hardness and strength; makes SS heat treatable to develop the martensite phase	[92, 94]
Nickel	Stabilizes the austenitic structure and improves toughness at low temperature	[95, 96]
Molybdenum	Stabilizes passive film and increases pitting and repassivation potentials	[97]
Copper	Increases pitting and protective potentials; provides antibacterial action	[98]
Nitrogen	Increases yield and ultimate tensile strengths; stabilizes the austenite; enhances corrosion resistance	[99]

conventionally used medical SS by presenting superior biocompatibility, and improved mechanical and corrosion resistance properties with increasing N content [104].

9.3.2 Cobalt Alloys

The cobalt-based alloys are alloys that contain a balance between biological and mechanical characteristics, with superior corrosion resistance and strength than SS, but more expensive to design [105]. Commonly used cobalt-based alloys in the biomedical area are:

1. *ASTM F75*: Widely applied to orthopedic and dental devices due to its excellent wear and corrosion resistance—mainly due to the protective Cr_2O_3 superficial oxide layer—and good mechanical properties. However, different microstructure of this alloy (Co-28Cr-6Mo) occurs according to the casting technique used, which can highly influence the mechanical behavior of F75 alloy implants [57, 106]. These microstructure features include: (1) enrichment of carbides and solutes (Mo, Cr, and Co) of interdendritic zones, while

dendrites have a reduce of Cr and an increase of Co; (2) dendrite creation of large grain size which diminish the tensile strength of the alloy; (3) casting defects with consequent implant fracture [106].

2. *ASTM F799*: Same as *ASTM F75* alloy composition (Co-28Cr-6Mo) but different in the processing methods, which provide different mechanical properties. Typically, a high temperature is used in initial steps of the thermodynamic process to increase deformability of the alloy, followed by using of low temperature in later stages to induce cold working, so achieving greater strengthening. As a result, the final, thermodynamically processed *ASTM F799* alloys shape presents yield and tensile strength twice higher than *F75* alloys [57].
3. *ASTM F90*: Different from *F75* and *F799*, *F90* is a wrought alloy with the addition of tungsten (W) and Ni in the alloy (Co-20Cr-15W-10Ni), which allows easier and enhanced machinability and fabrication process. In the annealed state, its mechanical properties are close to the as-cast *ASTM F75*, but when submitted to cold work, these properties are twice as high as those of *ASTM F75* [57, 106]. It is important to emphasize that in the last case, care must be taken in the manufacturing process to achieve homogeneity, to avoid stress concentrators and, consequently, undesirable failures [57, 106].
4. *ASTM F562*: Also known as MP-35N alloy (Co-35Ni-20Cr-10Mo), *F562* is a multiphase wrought alloy with excellent strength due to the multiple techniques involved in its processing [106, 107]. It demonstrates outstanding properties in terms of strength, corrosion behavior, and plastic deformation. The aging process of this alloy provides the highest tensile strength value (1,795 MPa) among the existent bio-medical metals [57, 106].

Among the four alloys aforementioned, the as-cast Co-28Cr-6Mo has wide application in removable prosthesis frameworks and orthopedic implants mainly due to its high wear resistance [57, 108]. The wrought Co-35Ni-20Cr-10Mo alloys are generally employed for fabrication of joint prostheses because of its long-term corrosion resistance along with strength [57]. However, the higher elasticity modulus of these materials (220 GPa), similar to that of SS (around 206 GPa), may be detrimental

to the use as bone substitutes, since it is susceptible to the occurrence of “stress shielding” and, consequently, fractures of the implant at load-bearing conditions [33, 106].

9.3.3 Titanium and Its Alloys

Among representative biomedical metals, Ti and its alloys have drawn great deal of interest for biomedical applications because they demonstrate the highest biocompatibility, chemical stability, and strength characteristics [1]. They are currently used in craniofacial and dental implants, orthopedic implants, and bone fixation materials [3].

Commercially pure titanium (cpTi) was first proposed as a substitute of SS and Co-based alloys due to its greater biocompatibility and chemical stability. However, in view of its poor mechanical properties (e.g., low deformability and wear resistance) to satisfy the requirements of biomaterials for biomedical applications, cpTi was replaced by the two-phase $\alpha + \beta$ Ti alloy, specifically the well-known Ti-6Al-4V alloy [109, 110]. Nevertheless, there are significant concerns on its long-term use, because of the cytotoxicity caused by Al and V once released inside human body [111, 112]. As alternative to V toxicity, novel V-free Ti alloys with a mixture of α and β phases were developed with Nb and Fe as substitutes of V [113, 114]. These metals present comparable mechanical performances to the Ti-6Al-4V apart from showing less toxicity [113–115]. However, in addition to Al has also been pointed out as a toxic element, the problem of stress shielding effect of α and $\alpha + \beta$ Ti alloys has also attracted lot of attention of several studies, mainly due to their superior elastic modulus compared to that of bone [20]. Therefore, low modulus β -type Ti alloys with non-toxic elements, such as Nb, Zr, Ta, and Mo, have been extensively developed for biomedical applications [1, 116–120]. Representative biomedical β -type Ti alloys and their elastic modulus in comparison to mostly used biomedical alloys (cpTi, Ti-6Al-4V, Co-Cr-Mo, SS 316L, Ti-5Al-2.5Fe, and Ti-6Al-7Nb) and bone are demonstrated in Figure 9.4.

Among β -type Ti alloys, Ti-23.7Nb-4.8Zr-1.7Ta-5Si and Ti-35Nb-4Sn can be highlighted, since they present the lowest elastic modulus values. However, conclusions from Figure 9.4 must be carefully interpreted, once it is an overview of representative β -type Ti alloys with methodologies not standardized. Alloy elastic modulus may vary according to the treatment and measuring methods. For example, the elastic modulus of water-quenched Ti-13Nb-13Zr is 63 GPa, whereas the same alloy when submitted to water quenching followed by aging treatment at 400°C for 3.6 ks present an elastic modulus of 97 GPa [121].

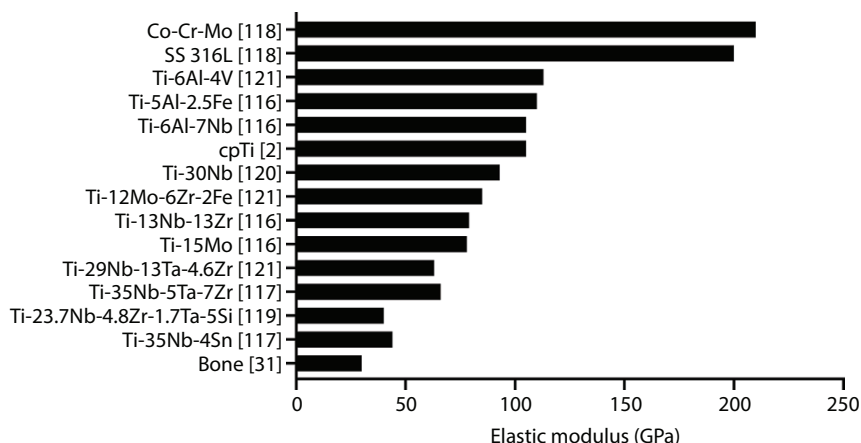


Figure 9.4 Elastic modulus (GPa) of representative β -type Ti alloys for biomedical applications in comparison to mostly used biomedical alloys (cpTi, Ti-6Al-4V, Co-Cr-Mo, SS 316L, Ti-5Al-2.5Fe, and Ti-6Al-7Nb) and bone.

It is important to emphasize that an ideal biomedical alloy should present not only low elastic modulus but also great hardness. For this, alloying cpTi with some elements (e.g., Al, Zr, and Fe) has been related to increase its hardness, in which Ti-Al-V, Ti-Ta-Fe, and Ti-Zr have the highest hardness values [9]. The implanted biomaterials must have sufficient properties to bear the physiological loads they are submitted and expected to long-last without the need of a second revision surgery [2]. An adequate equilibrium of mechanical and physical properties as close as possible to the bone is highly needed. In addition, to diminish the Ti alloys' elastic modulus, researchers are currently focusing on developing porous materials to reduce the stiffness [122–124]. Additionally, porous structures are related to enhance osseointegration since its structure facilitate the interposition and bone growth around the implant, allowing homogenous stress transfer between the biomedical implants and the bone [124, 125].

Novel Ti alloys are also necessary particularly in conditions of spine fixation, where the implants should present low elastic modulus adequate to prevent stress shielding, but sufficient high to prevent spring back effect [126]. Examples of such alloys are Ti-Cr and Ti-Mo [127, 128].

9.3.4 Zirconium Alloys

The favorable combination of excellent biocompatibility, chemical stability, and mechanical behavior is the main factor that makes Zr alloys desirable

for biomedical applications [129, 130]. Notwithstanding, for clinical applications, apart from these properties, the implants have other special requirements [131]. For example, magnetic resonance imaging (MRI) is extensively used to create a detailed diagnostic in medical surgery (e.g., brain disorders). However, when MRI is performed on a patient who has a metallic implant in the body, it can lead to image distortion because metallic implants interfere the magnetic field interactions [1, 132]. To decrease the defects and distortions, the development of devices and biomedical implants with low magnetic susceptibility are of great interest as MRI becomes gradually popular [132]. Compared with SS, Co-Cr alloys, and Ti, Zr has inferior magnetic susceptibility [1, 133]. However, unalloyed Zr has insufficient mechanical performance for using as structural biomedical materials [133]. Hence, Zr alloys have been designed mainly with Mo and Nb, since they are strengthening elements for Zr with low magnetic susceptibility [1, 134]. Studies have reported that the magnetic susceptibility of as-cast Zr-Mo and Zr-Nb alloys strongly depends on their phase constitution [132, 133].

Taking into consideration the chemical structure of Zr alloys, the equilibrium α and β phases are formed with intermediate α' and ω phases [133]. The magnetic susceptibility (χ) of each phase decreases in the following sequence: $\chi\beta > \chi\alpha' > \chi\omega$, suggesting that alloys with more ω phase should present lower magnetic susceptibility [133]. Among Zr alloys, it is highlighted the Zr-3Mo ($\omega+\beta$), which exhibit a quite small magnetic susceptibility (below $1.1 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) [1, 133]. However, as the amount of ω phase increases, the mechanical reliability (e.g., ductility and toughness) decreases [132]. Thus, the development of Zr alloys with low magnetic susceptibility without compromising the mechanical properties should be considered along with an ideal content of ω phase in the alloys. Recently, alloying Zr with some elements such as Ti, bismuth (Bi), Nb, and Mo has been explored to achieve enhanced mechanical characteristics and chemical stability, as well as lower magnetic susceptibility than unalloyed Zr and Ti alloys [135].

9.3.5 Tantalum and Niobium Alloys

Tantalum and niobium are safe metals found in the same natural source with almost identical physicochemical characteristics [136]. Because of their excellent biocompatibility, even better than Ti, these metals and their alloys are attractive alternatives for application in medicine and dentistry [137].

Tantalum is a notable ductile, chemically resistant and bioinert metal used in orthopedic implants, which exhibits exceptional *in vitro* and *in vivo* biocompatibility with excellent corrosion resistance [138, 139]. It has been used for plates and suture wires, as bulk implants or as surface coating for medical and dental implants [138–141]. However, the high cost of raw material, extremely high melting temperature (3,017°C), high elastic modulus (186 GPa), and density (16.6 g/cm³) have limited the widespread application of Ta as biomaterial on medicine and dentistry [138, 142]. To overcome these limitations, researchers have been focused on development of Ta alloys, since mixing Ta powder with other elements, such as Ti, to fabricate alloys for biomedical applications (e.g., Ti-25Ta and Ti-50Ta) is a powerful tool to reduce costs and improve mechanical characteristics, since Ta can act as a β stabilizer [143]. Other efficient way to enhance mechanical features (e.g., Young's modulus and stiffness) is the introduction of highly porous features, which is also beneficial for bone ingrowth and increase osseointegration [139, 144]. Pre-clinical and clinical results using various porous Ta implants have reported favorable bone-implant interface stability, supporting the application of porous metal implants made of Ta for biomedical applications [139, 144–146]. Ta-based coatings on Ti surfaces have also been related as a good alternative to achieve desirable properties for biomedical applications, with lower cost than bulk Ta implants, and combination of excellent Ta and Ti properties, which can produce a Ti-based implant with outstanding qualities [147, 148].

Recently, Nb alloys have been largely studied for implant applications since Nb is a non-toxic metal with excellent corrosion resistance and osteogenesis potential [149, 150]. It has been reported that Nb-2Zr is an attractive material since it presented good combination of mechanical, chemical, and biological properties compared to Ti-6Al-4V [151]. Furthermore, Nb-based alloys, such as the Nb-60Ta-2Zr and Nb-28Ta-3.5W-1.3Zr alloys, have been considered suitable materials for fabrication of stent materials, due to their remarkable lower χ_w values, which minimizes the image artifacts on MRI examination [152, 153].

9.3.6 Biodegradable Magnesium, Iron, and Zinc-Based Alloys

The study of biodegradable implant materials is considered a hot issue at the forefront in the biomedical field [154]. Particularly for short-term applications, such as bone fracture fixation or scaffolds, temporary biodegradable implants have become an attractive option to avoid disorders often related to long-term implantations of metallic devices in the human body [154, 155].

Magnesium-based alloys have attracted special interest due to their ability to biodegrade in physiological conditions, excellent biocompatibility, elastic modulus (40–45 GPa) close to the bone, and low density (1.74–2.0 g/cm³) [154]. However, despite many advantages, Mg-based alloys have high corrosion rate, which consequently reduces the mechanical strength as well as can result in the formation of H₂ gas, which can lead to balloon effect *in vivo* if rapidly absorbed by the organism [156]. Stress corrosion cracking and the fact that Mg is a common element in physiologic environment are the two reasons why Mg alloys have rapid degradation [7]. Alloying is a commonly used method to enhance Mg mechanical and chemical characteristics [7, 154]. Among Mg alloys, in the case of Mg-Al alloy, although the mechanical and corrosion resistance behavior are enhanced, the long-term biocompatibility of this alloy is questionable, since Al is a toxic element when in contact with tissues [7, 157]. Contrarily, the physiological compatibility of Mg-Zn and Mg-Ca alloys have been reported by a number of studies, mainly because zinc and calcium are elements required for the proper functioning of human metabolism [158–163], which make them attracting alloying elements for biomedical applications. The other alternative to hind deterioration of Mg implants is the surface treatment, by increasing the corrosion resistance with a non-harmful oxide coating [164]. Several coating methods have been related for this purpose, such as micro-arc oxidation, ion implantation, electrochemical deposition, and physical vapor deposition [7, 164]. However, once the coating suffer degradation, the Mg bulk material will be exposed to the physiological environment, which contributes to the problem of H₂ gas production remaining an important issue to be solved [7]. Future studies should focus on control H₂ gas production by alloying and associate it with surface treatment to control the degradation rate of the Mg implants for biomedical applications.

Contrarily to Mg-based alloys, the major disadvantage of Fe-based alloys is its very low degradation rate [155]. To accelerate the degradation of the Fe whereas maintaining enough strength, alloying Fe with noble and biocompatible metals becomes necessary. Among Fe-based alloys, Fe-Mn alloy family and Fe-5%Pt present the highest degradation rates [155]. Nevertheless, an *in vivo* study showed that after 52 weeks of follow-up, pins of pure Fe and Fe alloys containing Mn and Pd implanted in rat femurs demonstrated similar degradation rates [87]. In addition, Fe ions resulting of corrosion may be retained in surrounding tissues and cause complications [165], yielding the use of Fe-based alloys as temporary implants in biomedical applications questionable.

To overcome the limitations of Mg and Fe, Zn has been studied as an alternative for temporary implant applications, particularly attributable

to its moderate degradation properties [166]. However, since pure Zn does not present adequate mechanical properties for absorbable implant applications, the association of designing Zn alloys with a controlled thermomechanical treatment is of great interest [6]. Among Zn-based alloys, Zn-Mg, Zn-Ca, and Zn-Sr have been highlighted as alloys with promising results by *in vitro* and *in vivo* studies [167, 168]. Despite exhibiting favorable characteristics suggesting that Zn-based alloys are a potential biomaterial of next-generation temporary implants, it is worthwhile to note that many uncertainties still exist and there is a need to evaluate the corrosion dynamic properties, and the capabilities of non-traditional processing techniques to achieve better mechanical properties and the real performance of these alloys *in vivo* are extremely needed to confirm that fulfill all the requirements to be used as absorbable materials for biomedical applications [6].

9.4 Conclusions

There has been a constant concern of innovative alloy materials for biomedical applications that fulfill all the requirements of good mechanical properties, biodegradation behavior, biocompatibility, osseointegration ability, and antibacterial activity. The diversity of metals and alloys with these properties has experienced substantial growth with the advance of technology. Novel approaches of biomedical metals such as low modulus β -type Ti alloys, Zr alloys, and Zn-based alloys as biodegradable implants have appeared to be the next generation of biomedical alloys. Furthermore, surface treatment of such metallic alloys is becoming of great interest to improve key properties of biomaterials and enhance their performance for clinical applications. However, it is essential to highlight the importance of further researches, both *in vitro* and *in vivo* tests, to support the new alloy materials and surface treatments are effective and viable substitutes for the commercially available biomedical materials.

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Alloys for K-Ion Batteries

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Abstract

In the recharge battery area, potassium ion batteries attracted incredible attention in the electronic market owing to its fast-ionic conductivity, inexpensive, higher natural abundance, and a higher range of operating voltage. The area of research on potassium ion batteries is still in growing stage; in the market, PIBs replace lithium and sodium-ion batteries in electronic devices and vehicles. Although, PIBs technology is still under working for further developments. Despite continuous growth in finding conceivable material for anode and cathode, the progress of potassium ion batteries has faced different problems, such as low charging and discharging capacity, insufficient cycling stability, including low reversible capacities, and unsatisfactory energy density, which must be a severe concern for the commercialization of KIBs. In this chapter, we have discussed the alloys of different elements for cathode and anode material with emphasized their structural-performance relationship.

Keywords: Charge capacity, discharge capacity, stationary energy storing, potassium ion batteries, energy density

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10.1 Introduction

Lithium-ion batteries (LIBs) as resourceful electrical energy storage technology has been efficaciously developed and extensively utilized in numerous kinds of electronic devices and vehicles [1, 2]. The excess and continuous utilization of traditional nonrenewable energy sources have put these sources as well as the global environment both in danger [3, 4]. In the past decades, numerous attempts have been made to develop substitute batteries using earth-abundant and inexpensive materials. So, presently, the development of renewable and efficient energy storage technologies has become the prime importance. In this regard, the RBs are key the sources of power for global stationary energy storage like off-grid housing, home storage, and confined energy storage at solar and wind farms locations. Among all these, presently, the lithium-ion batteries with nonaqueous properties have been extensively utilized. But the element, i.e., Li used in these batteries is low abundant which may increase their cost in future. So, the development of low-cost batteries by using more abundant elements is important despite the use of lithium-ion batteries [5, 6]. Currently, the scientists are more focused on the development of sodium and potassium-ion batteries considering the future cost of lithium element used in the batteries [7, 8] Though the abundancy of Na is higher than the K in the Earth's crust, yet it is considered as poor potential ion for RBs. Hence, the state of this new area is quickly altering, and, recently, the significant advances in cathode and anode materials for full cell prototyping as well as PIBs have been reported [9, 10].

In comparison to sodium ion, the potassium ion is a potential ion for the RBs; hence, it is preferred over the sodium ion. Hence, the PIBs have attracted more researchers due to their inexpensive, high abundance (2.09 wt.%), and a potential ion for RBs. The low redox potential (-2.93 V) for K/K^+ assures high energy density and high operation voltage, which make it an auspicious candidate for low-cost electrical energy storage and high-energy-density applications. These batteries may have various advantages over the SIBs. Specifically, it is found that the redox potential for potassium plating/dissolution in a propylene carbonate solvent is lower than the sodium and lithium, which shows that its practical voltage is like high voltage batteries like LIBs and it is superior over the SIBs [9, 10]. Additionally, there are some well-developed electrode materials (graphite 10–12), which is not appropriate for the sodium-ion batteries, but it can be used in PIBs to improve this new technology at least in a practical point of view.

From 1980, the studies carried out on the electrochemical behavior of potassium ion, these studies close to the studies of lithium and sodium ion, but due to its large size and heavy atomic mass, limited researches had been conducted on the PIBs. After 2015, the studies of PIBs accelerated when a report found on accommodation of graphite into potassium reversibly and electrochemically at the RT. After this, number of studies has been conducted on it, for the application of large-scale energy storing and electric vehicles. Several cathodes and anode alloy materials were produced to enhance the features of the potassium ion batteries. The insertion potential of potassium in mostly carbon and non-carbon anodes found higher than sodium, such as for carbon approximately 2.2 V and non-carbon like $S_{n4}P_3$ is 0.1 V insertion potential (K/K^+). Researches carried out for the cathode materials are more challenging as compared to the anode for PIBs. As we know, cathode materials play important role in studying power, cycle, energy, cost, and safety [11–16].

The huge attention in looking for the most suitable materials for PIB is inspiring the researchers for the development of deeper understanding and advancement in techniques. Until now, three foremost types of Na/K storing mechanisms have been discovered: (1) the desertion/insertion reaction, (2) the conversion reaction, and (3) the alloying reaction. Discovery of phosphorus-based composites, titanium-based oxides, and some organic compounds revealed the more potential applications in this field, though some of the core issues have not been well addressed yet. The drawback of the P/Sn-based materials is its high discharge capacity (DCC), which suffers from high volume contraction. Organic molecules have advantages like high electrochemical performance and relative stability over the phosphorous/tin-based materials, but easy electrolyte solubility and poor electronic conductivity are their drawbacks, which is still needed improvement. Several anode/cathode materials have been synthesized for the solution of similar problems. Another serious problem is the low Coulombic efficiency (CE) of anodes, which is the common problem of almost all the anodes.

10.2 Anodes

10.2.1 Titanium-Based Alloy

Currently, the Ti-based materials such as anatase TiO_2 have been utilizing in PIBs as a new anode material. The pristine CNTs are incorporated on the titanium oxide for the improvement of electronic conductivity of

host. In the first cycle of insertion/de-insertion of K^+ , the TiO_2 anatase altered into Magneli phase Ti_6O_{11} . A reversible charge/discharge profiles obtained, by the newly formed composite, i.e., Magneli phase Ti_6O_{11}/CNT , is ~ 150 mA.h/g at 0.05 A/g, in 2nd cycle. *Ex situ* TEM and XRD analyses exhibit the process of charge storage in Magneli phase Ti_6O_{11} which occurs due to the conversion reaction during the insertion/de-insertion of K^+ . The electrode of Ti_6O_{11}/CNT composite has high CE (99.9%), cycling life of 500 cycles at 200 mA/g, and high capacity retention (CR), i.e., (76%). These prominent features offer great knowledge for better knowledge of the K^+ storage mechanism [17].

The $K_2Ti_8O_{17}$ is fruitfully synthesized by the hydrothermal method followed by annealing treatment and then used as anode material for PIBs [18]. For K^+ storage reaction, $K_2Ti_8O_{17}$ provides a promising host structure.

10.2.2 Niobium-Based Alloy

Niobium (Nb)-based material, nanostructured T-Nb₂O₅, has been explored as excellent anode material for PIBs. The T-Nb₂O₅ nanomaterial has expressed excellent cycling performance and rate, because of their hierarchical nanostructure and intercalation-pseudocapacitive hybrid mechanisms with fast kinetics. Additionally, the performance capacity and the current density of the material were found as 104 mA.h/g and 0.4 A/g, respectively. The decay percentage for 400 cycles observed as 0.068% per cycle. Another additional advantage of the T-Nb₂O₅ nanowires material is its utilization in the fabrication of anode for potassium dual-ion battery, which shows high performance rate, i.e., 81 mA.h/g even at 30°C. Furthermore, after 1,000 cycles at 20°C, it also reveals exceptional cycling stability with 86.2% CR [19].

10.2.3 Manganese-Based Alloy

Sun *et al.* synthesized material, i.e., high-performance K-Mn PB/graphene (KPB/G) composite by using the ball-milling method. The composite particles were shattered into small grains, and these grains were consistently loaded onto the few-layered graphene, which was used as an electrode for PIBs. This composite material revealed CC of 100.2 and 108.8 mA.h/g at 10 and 5°C, respectively, high average working potential (~ 4 V at 0.1°C), high initial DCC (131.4 mA.hg⁻¹ at 0.1°C), and cycle life (CL) of 82.4% after 300 cycles at 10°C, 89.3% after 500 cycles at 5°C, and 96.9% after 120 cycles at 0.5°C. Some specific properties of composite like the protective and conductive effects of graphene enhanced its electrochemical performance [20].

10.2.4 Tungsten-Based Alloy

Zhang reported a new host material, i.e., tungsten disulfide (WS_2), for the electrochemical intercalation of K^+ , and this material offers a reversible capacity (RC) of 67 mA.h/g and it can store up to 0.62 K^+ per formula unit. *Ex situ* electron microscopy and *in situ* XRD analysis exposed the high reversibility, the basic mechanism of intercalation of battery chemistry, and a comparatively small cell volume change (37.81%) in battery. These properties of the material (WS_2) convey its long lifespan and ultra-high structural stability, irrespective of fast or deep charging. The tungsten-based material (WS_2) revealed an unexpected average CE of 99.90% at 2.2C, high cyclability up to 600, and 1,000 cycles with 89.2 and 96.3% CR at 0.3°C. The electrochemistry of intercalation may open new opportunities for the development of high-safety and long CL for potassium ion batteries [21].

10.2.5 Iron-Based Alloy

Recently, Cho *et al.* and Zhang *et al.* [22, 23] produced a β -FeOOH material and explored the potential mechanisms of potassium and sodium storage, and its electrochemical performance as well. The special structural designs of material like adhesion of β -FeOOH on CNTs and 3D tetsubo-like β -FeOOH nanocuboids, significantly enhanced the electrical conductivity of the material. Additionally, its high Coloumbic efficiency, attained in the first cycle, revealed its potential for large-scale applications. Later, Li *et al.* developed a FeP/C composite. The material was synthesized by using the high-energy ball-milling method. This material offers a CC and discharge rate of 288.9 mA.h/g and 50 mA/g, respectively, which can fulfill the needs of future energy storage [24].

10.2.6 Nickel-Based Alloy

The electrical power grid lacks the technology for large-scale energy storage for a long period owing to load balancing, frequency regulation, and costly short-term transients. The robustness, low cost, energy efficiency, and high power required for grid-scale storage, which has significant trials for conventional battery technology. The researchers used nickel hexacyanoferrate (low strain) electrode material, which revealed the insertion/extraction of potassium and sodium ions in material, at high current densities, for almost 5,000 deep cycles in aqueous electrolytes of low cost. Its open-framework structure offers

CR of 66% of the initial capacity at a very high rate, and its round-trip energy efficiency reaches 99% at low current densities [25].

10.2.7 Zinc-Based Alloy

Potassium-zinc hexacyanoferrate produced by precipitation method in rhombohedral structure and was used as a cathode material. This material shows an initial DCC of 55.6 mA.h/g with a 3.9 V of discharge voltage and ~95% CR after 100 cycles. All K ions release from the structure at the initial charge process. During the discharge process, only 1.61 gets back into the fabric, out of 1.88 K ions per formula unit. This material shows a lattice-volume change (~3%) during a cycle, despite the sizeable ionic size of K and this lattice-volume change is extremely small. This unique property of the material is due to its exceptionally porous framework of FeCN_6 polyhedra and ZnN_4 bridged through cyanide ligand, with 3/2 atomic ratio of Zn/Fe, which supports its high structural stability and cycle performance [26].

Sulfides of transition metal show striking features to act as anode material for the PIBs owing to its higher theoretical capacities based on alloying reaction and conversion. Here, ZnS is used as an anode material for PIBs in which dendrites of material are extremely nested in the tertiary hierarchical structure. This structure is formed by the carbon nanosphere, the ultrafine ZnS nanorods, and the carbon encapsulated zinc sulfide subunits nanosphere structure. A stable specific capacity of 208 mA.h/g at 500 mA/g over 300 cycles and 330 mA.h/g is attained after 100 cycles at the current density of 50 mA/g. From DFT calculations, it was found that the interactions between carbon interface and ZnS can efficiently decrease the potassium ions diffusion barrier, and hence, it enhances the reversibility of potassium ions storing [27].

10.2.8 Lead-Based Alloy

The Pb-based electrodes alloyed electrochemically with K and analyzed by XRD as well as galvanostatic measurements. An initial high current pulse applied for the electrochemical reduction which protects the lead electrode from passivation. The crystalline KPb is produced due to alloying process. K_4Pb_9 and $\text{K}_{10}\text{Pb}_{48}$ are the two intermediate phases that appeared during the discharge, while only K_4Pb_9 appeared during the charging process.

Lead potassiated by the electrochemical method using precise cycling conditions. During the discharge process, three distinct steps appeared in

galvanostatic profile whereas only two steps appeared during the charge. The XRD analysis revealed the reaction mechanism, the formation of KPb, K_4Pb_9 , and $K_{10}Pb_{48}$ during the discharge, while only K_4Pb_9 is formed on going from KPb to Pb [28].

10.2.9 Tin-Based Alloy

Sn-based materials have shown the high capacity, though they have expressed the severe volume expansion also during the alloying. Mainly, the anodes for PIBs show larger volume change than that of SIBs and LIBs because of the larger radius of K and this significantly affects the capacity [29–32]. Hence, the Sn-based anode materials need more strategic improvement to enhance their performance, which mostly focuses on the use of conductive carbon substrate or host and development of efficient nanostructures. The conductive carbon substrate or host both can successfully improve the cyclic stability, buffer large volume change, and accelerate the reaction kinetics.

Sultana *et al.* [33] reported that the solid phase method used in the synthesis of Sn-C composite synthesized. The *ex situ* XRD analysis revealed the manifold alloying/dealloying reactions between K and Sn. The carbon substrate applied on Sn surface improves the conductivity on the surface and promoted the electron transfer among Sn particles. Additionally, it also reduced the strain effectively which developed during the alloying/dealloying. Though this technique has a drawback also, i.e., due to the slow reaction between K and Sn, the Sn element is unable to produce the Sn-K alloy phase. This limitation also controlled the Sn-C composite capacity, i.e., the predictable capacity of Sn-C composite was 590 mA.h/g while it showed below 170 mA.h/g due to such limitations.

Another Sn-based material, i.e., Sn-C composite, has been synthesized by mechanical ball milling method using 30 wt.% graphite with 70 wt.% Sn powder in which the nanoparticles of Sn dispersed on carbon (no longer graphitic). Sn-C composite act as a cathode in KIBs under the potential range of 2.00–0.01 V vs. K/K^+ , observed by the electrochemical experiment. The RC was also measured as about 150 mA h/g. XRD analysis showed the crystalline phase formed due to the DCC of K-half-cells and intensity decreased due to the charge. This shows that an alloying process occurred on the Sn electrode. The results shown, expanded the materials range, potential suitability for the anodes of PIBs and advocate for additional studies of the materials which can electrochemically from alloy with K.

In this regard, a 3D hierarchically carbon/Sn network was developed fruitfully, where a homogeneous layer of Sn nanoparticles was incorporated

in the porous carbon shells [34]. During the discharge process, they may improve the alloying reaction between K and Sn and suppress the change in volume changes. Moreover, the structural collapse was also minimized due to the porous carbon shells by an additional buffering effect. Hence, at the current density of 50 mA/g, the electrode reveals a high initial CC of 384.5 mA.h/g, which sustained up to 276.4 mA.h/g after 100 cycles.

Later, Zhang *et al.* [35] developed a sandwich-like $\text{MoS}_2@\text{SnO}_2@\text{C}$ anode material. In this material, the SnO_2 nanosheets shield the exfoliated MoS_2 nanosheets so that the restacking process can be avoided during the process of charge/discharge. The role of carbon in the material is to maintain the structural stability which is coated on $\text{MoS}_2@\text{SnO}_2$. After 25 cycles at 0.05 A g⁻¹, the sandwich-like $\text{MoS}_2@\text{SnO}_2@\text{C}$ nanosheets have shown the highest DCC of 312 mA.h/g and the best electrochemical performance in comparison with $\text{MoS}_2@\text{SnO}_2$, $\text{MoS}_2@\text{C}$, MoS_2 , and SnO_2 .

Guo *et al.* fabricated $\text{Sn}_4\text{P}_3/\text{C}$ composite, which was as anode material for PIBs. During the removal processes of K from K-P and K-Sn, this material revealed two oxidation signals at about 1.15 as well as 0.8 V. To alleviate the volume expansion, the K-storage mechanism of K-P and K-Sn alloy acted like a mutual buffer. Consequently, at 50 mA/g, the material unveiled an RC of 588.7 mA.h/g and maintained as 307.2 mA.h/g after 50 cycles, whereas after 20 cycles, the Sn/C and P/C materials merely remained 20% and 9% of their RC, respectively.

Tin oxides were examined as an anode material to know the electrochemical behavior of the electrode material and for the improvement in energy density of PIBs. XRD and XPS analysis supports the following characteristics: At the first charge (reduction) process, the phase separation of SnO occurred, which produced KOH and metallic Sn followed by the formation of KSn through the reversible alloying reactions occurred between the K and Sn. In contrast, SnO_2 is electrochemically reactive toward the potassium. Remarkably, at the initial cycle, the RC of SnO electrode is equivalent to the Sn electrode, which showed a RC of 183 mA.h/g with an 80% CR at the 30th cycle, while Sn electrode revealed rapid decrease incapacity due to the electrode disintegration encouraged by the substantial volume change during K-Sn alloying/dealloying reactions. No peeling off and crack sign appeared in SnO electrode material layer. The dispersion of Sn nanoparticles in amorphous-like K_2O matrices is confirmed by SEM image of the SnO. The cycle stability of SnO electrode enhanced due to the aggregation of Sn curbed by K_2O . The elemental substitution of part of oxygen, particle size optimization, an electrolyte solution would be very useful tools to improve the life cycle of SnO electrode [36–38].

10.2.10 Antimony-Based Alloy

A cubic K_3Sb alloy electrode exhibits an RC of 650 mA.h/g and theoretical capacity of 98%. The cycling performance and alloy structure were analyzed by galvanostatic and XRD techniques. The thermodynamics and kinetics of the K-Sb alloying reaction was studied by CV and electrochemical impedance spectroscopy. To end, this anode material was applied in the form of a K_3Sb-O_2 cell which shows low overpotentials, increased safety, relatively high operating voltages, and interfacial stability.

The electrochemical behavior of Sb-C composite was examined by McCulloch *et al.* The research group showed that the Sb-C material could form alloy with K, i.e., cubic phase K_3Sb alloy which shows around 98% RC of theoretical capacity, i.e., 650 mA.h/g. Though, this material also suffers from a drawback, i.e., during cycling, the expansion of volume becomes very high, and hence, structure damage is inevitable.

A 3D antimony@carbon (Sb@C-3DP) composite electrode was synthesized by a simple potassium chloride template method. The synthesized electrode offers an outstanding RC (516 mA.h/g at 0.05 A/g current density) and an exceptional rate capability (286 mA.h/g at 1 A/g). Additionally, it has excellent long cyclic stability (97% CR after 260 cycles) and exceptional microstructure, which can compensate the great volumetric change of Sb during potassiation and depotassiation processes. A battery produced by coupling Sb@C-3DP anode and PB cathode shows power density and energy density of 2,067.9 W/kg and 197.6 Wh/kg, respectively [39, 40].

A porous lead Sb on MXene was synthesized as the flexible, robust, and binder-free anodes for PIBs. It was developed as a versatile and facile electrodeposition approach. This approach conveys electrochemical strength, structural stability, and electrical conductivity to electrodes and successfully addressed the problem of Sb anode during cycling. This material can promote buffer volume expansion and ions diffusion during the process. Highly flexible and conductive MXene paper acts as an elastic current collector to accommodate volume change and ions transport during cycling. Anodes show unusually strong K storage performance, 270 mAh/g rate capability at 500 mA/g, a high RC of 516.8 mAh/g at 50 mA/g, and a stable CR of 79.1435%. Additionally, the facile and versatile electrodeposition tactic can be stretched to obtain several free-standing and flexible MXene@Metal [41].

Nanoporous antimony (Sb) (NP-Sb) was developed by a vacuum-distillation method by the evaporating low-boiling-point zinc (Zn), which was recycled. Its porosity and morphology were controlled by adjusting distillation temperature and Zn-Sb composition. The nanoporous structure has ability to facilitate ion transport and compensate the volume

expansion. The NP-Sb anode offers an enhanced electrochemical performance [42].

The Sn-based material electrode and its performance and electrochemical mechanism have been studied systematically for PIBs. Formation of poorly crystalline and/or nanosized KSn at the end of the potassiation of b-Sn and their electrochemical mechanism temperature were studied by *ex situ* ^{119}Sn MS combined with first-principles calculations. MS analysis and DFT calculations have supported the formation of the intermediate phase K_4Sn_9 during depotassiation. The combination of antimony and tin showed a diverse potassiation path for Sn, which affect the overall performance also. Whereas, Sb conquers the decay of the electrolyte triggered by Sn. This positive impact of the combination of Sb with Sn offered a stable high specific capacity of $>300 \text{ mA.h/g}$ and reduced electrochemical degradation of electrode.

The performance and electrochemical mechanisms of SnSb and b-Sn electrodes in PIBs were examined by ^{119}Sn MS, electrochemical measurements SEM, and XRD. The b-Sn electrode displays lower CR than the SnSb, which tolerates 75% of its initial RC after 40 cycles. After the potassiation of both SnSb and Sn electrodes, the development of KSn was examined by ^{119}Sn MS. Whereas, an intermediate phase, i.e., K_4Sn_9 formed during the charging process in b-Sn pristine electrode, which is confirmed by first-principles calculations and MS. The existing amount of Sn in the electrode decreases sharply after few cycles. Most of the b-Sn particles become inactive, whereas in SnSb material, a better reversible mechanism is found for the insertion/de-insertion. The morphology of the electrode is protected during cycling, which leads to the enhanced CR. Despite of the volume expansion, the potassiation of SnSb is produce in amorphous phases which protect the electrode from disintegration. Additional efforts can be made in search of appropriate salt/solvent couples or operative additives, which can balance the performance of negative electrodes [43].

Another Sn-based material, i.e., SnP_3/C alloying composite, was developed by ball-milling method, as anode for PIBs, with greater performance rate and cyclability. This electrode offers first RC of 410 mA.h/g and maintained 408 mA.h/g after 50 cycles at a specific current (SC) of 50 mA.g^{-1} . After 80 cycles, the high capacity remained as 225 mA.h/g at a high SC of 500 mA/g . The crystallographic analysis of the electrode showed a reversible and sequential conversion and alloying reactions as well. The carbon buffer layer and nanosized SnP_3 particles of the electrode are responsible for the exceptional cycling stability and rate capability of electrode. The SnP_3 particles as well as carbon buffer layer provide channels for K^+ migration and alleviate the strain caused by enough change in volume

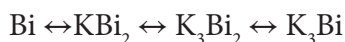
change during insertion/de-insertion. Additionally, the full cell composed of the potassium Prussian blue (PB) cathode and SnP_3/C nanocomposite anode displayed an RC of 305 mA.h/g at an SC of 30 mA/g, and after 30 cycles, it remained 71.7% of the original capacity [44]. The Sb@CSN composite material was synthesized by encapsulating the Sb nanoparticles on a carbon sphere network (CSN) and used as anode for PIBs. The electrochemical characterization and first-principles computations authorize sequential and reversible phase transformation of KSb , K_5Sb_4 , KSb_2 , and K_3Sb during process. This electrode shows 551 mA.h/g RC of at 100 mA/g after 100 cycles with an enormously slow capacity decay from 10th to 100th cycle by the rate of 0.06% per cycle. Whereas, at 200 mA/g current density, it controls the capacity up to 504 mA.h/g after 220 cycles.

An Sb-based anode material with high stability, i.e., $\text{Sb@graphene@carbon}$ (Sb@G@C) was synthesized and used to increase the performance of PIBs. The Sb@G@C anode show very good long CL over 800 cycles with 72.3% CR, for second cycle at 100 mA/g, RC was found 474 mA.h/g and exceptional rate performance.

In this electrode, Sb NPs are consistently confined by a carbon layer. This type of structure can suppress the buffer volume changes of Sb NPs during the charge/discharge and inhibit the self-aggregation of Sb particles successfully. Additionally, it can improve the redox reactions and ion/electron transportation as well [45, 46].

10.2.11 Bismuth-Based Electrode

Bismuth (Bi) shows exceptional interlayered spacing ($d(003) = 3.95 \text{ \AA}$) along c axis, which has unique physical properties such as less expansion in volume as compared to others. Thus, it can be an excellent alloy-based anode material for PIBs. Three different redox peaks at 1.15, 0.45, and 0.30 at 0.93, 0.67, and 0.57 V, respectively, i.e., three two-phase reactions. In the meantime, the CV traces of overlapping showed highly reversible alloying/dealloying reactions between K and Bi. The XRD of the intermediates showed a continuous phase change from the pristine Bi to K_3Bi , K_3Bi_2 , and KBi_2 which verified the reversible three distinct two-phase reactions given as equation.



Bi electrode with unique structure with electrolyte systems can compensate for the expansion of volume. According to Zhang *et al.*, an

electrolyte containing 1 M KPF₆ in diglyme with Bi anode produces an elastic oligomer that includes solid electrolyte interface during the first charge/discharge process. This SEI covered the electrode surfaces consistently which can tolerate the high-volume expansion also. This electrode exhibited a high initial CE of about 83% among alloy anodes for KIBs. Zhang *et al.* also offered a “concentrated electrolyte” method to attain significantly enhanced electrochemical storage performance for bismuth-potassium batteries [47–53].

10.2.11.1 Bismuth Oxychloride Nanoflake Assemblies

The electrochemical cyclability of Bi is very low in conventional electrolytes. Hence, 5 molar (M) ether-based electrolytes are utilized, which can successfully passivate the bismuth surface minimize the decay of electrode. BiOCl is a potential material that is used anode in PIBs. Its electrochemical performance and electrochemical mechanism of K-ions storage have been evaluated which showed high rate capability and great cyclability of BiOCl. The K-Bi alloy is formed at the early stage of potassiation. The mechanism study exposed that the potassiation of BiOCl occurred due to the conversion of BiOCl to Bi and the alloying reactions of forming K₃Bi, KBi, and K₃Bi₂. This anode material has shown the high capacities of 367 mA.h/gat 50 mA/g and 175 mAh/g at 1 A/g [30].

10.2.12 Phosphorus-Based Alloy

Recently, a novel nanocomposite based on black phosphorus has been developed as anode for PIBs with a very high capacity. This electrode has shown the first cycle capacity as high as 617 mA.h/g, which is much higher than the graphite in PIBs. The depotassiation is very fast, under certain conditions, in the electrodes [54].

Another phosphorus-based material, i.e., phosphorus (P)/activated carbon (AC) composite, has been reported, which is prepared by a vaporization-condensation-conversion approach. The capacity of the P/AC composite is higher on high P loadings, while, the cyclic performance is high at relatively lower P loadings, e.g., the P/AC composite with 45 wt.% of P (named PAC-50) showed a maximum capacity of 430 mAh g⁻¹ while with 32 wt.% of P (named PAC-35) exhibited 70% CR after 500 cycles. Additionally, the initial CE (ICE) can also be enhanced by controlling the P content, which gives the highest value of 84% at 45 wt.% of the P content (named PAC-50). The less oxygen-containing groups and low surface area are responsible for the high ICEs [55].

10.2.13 Germanium-Based Alloy

GeSe/black phosphorus (BP) heterostructures are very auspicious anodic materials for PIBs, and it has been inspected by first-principles calculations. After incorporation of K atoms, these materials show a semiconductor-to-metal transition, which improved the conductivity as well. The energy barrier for K atom diffusion on GeSe/BP surface is relatively lower than that on monolayer GeSe. Additionally, the GeSe/BP heterostructure can keep up to five layers of K atoms with negative adsorption energy, which enhanced the storage capacity. Hence, the GeSe/BP heterostructure has excellent potential for application in advanced electrode materials in PIBs [56].

10.3 Alloys for Cathode

10.3.1 Cobalt-Based Alloy

The Co-based oxide material has reflective properties to use in PIBs. Co-based electrode material was synthesized as exclusive P2-type $K_{0.6}CoO_2$ microspheres. These unique microspheres structure minimized the parasitic reactions between the $K_{0.6}CoO_2$ and electrolyte in its aggregated form. This also improved the rate of the intercalation/deintercalation K^+ . This electrode material shows high rate capability of 65 mA.h/gat 100 mA/g, high RC of 82 mA.h/gat 10 mA/g, and long CL, i.e., 87% CR over 300 cycles. The carbon anode coupled with high reversibility of the P2- $K_{0.6}CoO_2$ full cell further revealed the viability of PIBs [57].

10.3.2 Vanadium-Based Alloy

A xerogel of reticular $V_2O_{5.0} \cdot 6H_2O$ has been considered as a very good source of cathode material for rechargeable PIBs. The $V_2O_{5.0} \cdot 6H_2O$ could accommodate the larger K^+ in comparison to the orthorhombic crystalline V_2O_5 . Because the interlayer of $V_2O_{5.0} \cdot 6H_2O$ contains enlarged layer space of structural H_2O molecules. And the intercalation of H_2O molecules into the V_2O_5 layers enhances the electrochemical activity of potassium ion significantly. Owing to this, the initial DCC improves up to ~ 224.4 mA.h/g, which remains up to ~ 103.5 mA.h/g. Hence, the DCC of $V_2O_{5.0} \cdot 6H_2O$ observed is much better than the V_2O_5 electrode. In the meantime, the XPS combined with EDX and XRD techniques can be beneficial to explore the process of potassiation/depotassiation of electrodes, and it also illuminates the mechanism of potassium intercalation storage of $V_2O_{5.0} \cdot 6H_2O$ [58–64].

10.3.3 Iron-Based Alloy

Generally, for the selection of cathode with iron allot, PB and its derivatives are utilized, where $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox process is responsible for the energy-storing mechanisms. General formula for PB is $\text{K}_x\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6]$, and it has MOF-type structure where Fe^{2+} and Fe^{3+} are bridged together by cyanide ligand (CN), and forms 3D structure which is providing channel for the fast intercalation and de-intercalation, which representing that PB analogs are capable for K^+ storage. Here, $1e^-$ transfer is occurring between the Fe^{2+} and Fe^{3+} due to which CC of 80 mA.h/g was reported. The CC after 500 cycles was reported approximately 68 mA.h/g

This good CC retention rates and high-voltage profiles validate that PB is a capable cathode material for potassium ion batteries. Several reports found on Fe based cathode material. Moreover, Li utilized inexpensive potassium hexacyanoferrate(II) ($\text{K}_4\text{Fe}(\text{CN})_6$) and examine electrochemical properties. Here, to enhance the conductivity, researchers mixed Phosphorus with hexacyanoferrate and found in the CV curves a pair of strong peaks, which positioned at 3.67/3.5 V, conforming extraction/insertion of potassium ion. To compare CC with theoretical CC values, it was found that the hexacyanoferrate/carbon composite possess 0.9 potassium ion extraction/insertion per formula unit. XRD analysis of the cathode reveals that the one-electron transfer process occurs between $\text{K}_3\text{Fe}(\text{CN})_6$ ($\text{Fe}^{2+}/\text{Fe}^{3+}$) to $\text{K}_4\text{Fe}(\text{CN})_6$. This cathode material has DCC of around 70 mA.h/g according to the mechanism.

Though $1e^-$ transfer between redox couple of $\text{Fe}^{2+}/\text{Fe}^{3+}$ shows good results but their CC are low for potassium ion batteries. If we increase the number of electron transfer involved in the process might be a good option for the enhanced cathode capacities. For this, we have increased the potassium material on the electrode, can be useful in enhancing cathode capacity. In this direction, Chen developed $\text{K}_{1.92}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.94} \cdot 0.5\text{H}_2\text{O}$ as a cathode material for potassium ion batteries and found CC and DCC of 170 and 128 mA.h/g, respectively. Here more than one type of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple was responsible for charge/discharge, due to its different structure of $\text{K}_{1.92}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.94} \cdot 0.5\text{H}_2\text{O}$, here the N-coordinated to Fe^{3+} relative to Fe^{2+} . During CV analysis, two redox peaks found at $\sim 4.3/3.95$ and $\sim 3.6/3.4$ V due to redox peak LS and HS $\text{Fe}^{2+}/\text{Fe}^{3+}$, respectively. Further, $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ nanocubes was developed by Wang for aqueous potassium ion batteries, here all iron present in +2 state. In the CV analysis curve two redox peaks at 0.95/0.8 and 0.4/0.1 V for $\text{Fe}^{2+}/\text{Fe}^{3+}$ due to N and C-coordinated Fe of cyanide bridge ligand. The DCC

of nanocubes at 200 and 3 A/g current density was 140 and 93 mA.h/g, respectively. By the EELS analysis spectra, it was confirmed that during charging Fe^{+2} oxides into Fe^{3+} , while discharging Fe^{3+} reduces into Fe^{2+} [59–64].

10.3.4 Manganese-Based Alloy

The derivatives of manganese oxide with potassium are good candidates for the cathode material of potassium ion batteries. Vaalma first reported the utilization of birnessite K/Mn compound ($\text{K}_{0.3}\text{MnO}_2$) as cathode material for PIBs. This compound has two-layered orthorhombic-type unit cell structure with Ccmm space group in which the compound present in P2-type structure where ABBA-type oxygen packing in which octahedral sites occupied by Fe while Mn occupied trigonal prismatic sites. The DCC of the compound was found 136 mA.h/g at 1.5~4.0 V range with 0.55 potassium ion per unit formula. The layered compound has CC of 100 mA.h/g at 2.0~4.0 V range and after 50 cycles, CR was around 73%. If the voltage range were decreased up to 1.5~3.5 V, then cycling stabilities increase, but CC decreases up to 70 mA.h/g. In the CV spectra, two plateaus found at 3.9 and 3.7 V in the voltage range of 1.5~4.0, which indicates two-phase reactions. Another successfully developed K/Mn cathode material was $\text{K}_{0.5}\text{MnO}_2$ by Kim. XRD analysis signified that the compound exists in two phases of R3m and Cmcmm-type space groups. The major phase occurred in R3m-type space group, in which Potassium found in P-3-type structure while manganese oxide form stacked layer in ABBCCA-type arrangement. CV studies examined among 1.5–4.2 V potential range and found two oxidation peaks, in the CV spectra, no reduction peaks observed might be due no reversed reaction. The first CC and DCC were found 93 and 140 mA.h/g, observed, respectively, at approximately 0.39 and 0.57 potassium ion transport among 1.5–4. V. The degradation of CC after 20 cycles was 47 mA.h/g. While at around 0.22/0.44, potassium ion transported among 1.5 and 3.9 V and resulted in CC of 53 and 106 mA.h/g during first charging and discharging. Despite the enhancements in electrochemical performance in the cathode materials, for enhancing CC and cycling stability for potassium ion batteries are not enough competitive with the lithium and sodium-ion batteries. In the area of Mn-based material for cathode in potassium, ion batteries have needed more research for better understanding of the mechanism and improving CC and cycling stability [65–67].

10.4 Conclusion

Great attention in PIBs has grown up significantly in recent years after 2015. The PIBs are not likely to replace lithium-ion in the electronics devices and vehicles, where higher energy density is must requirement. They can compete with lithium and sodium-ion batteries for the application of stationary energy-storing applications, owing to the inexpensive and higher natural abundance of potassium. Owing to the similarities between potassium and lithium/sodium-ion batteries, results of this literature on LIBs/SIBs help to investigate the mechanism and other properties of PIBs. Because of large potassium ion radii, all results of other batteries are not completely suitable for studies on PIBs. So, detailed researches are required for potassium ion intercalation mechanism. In this chapter, a brief introduction of different alloys for the anode and cathode materials of different elements is reported. The area of research on potassium ion batteries is in immature stage; some models of PIBs have already shown good results and reveal potential applications for practical use. In future research, not only enhancing the cycle stability, stationary energy storing, and CC but also worked on safety parameters.

Abbreviations

EELS	<i>Ex situ</i> electron energy loss spectroscopy
CC	Charge capacity
DCC	Discharge capacity
PIBs	Potassium ion batteries
LIBs	Lithium-ion batteries
SIBs	Sodium-ion batteries

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Shape Memory Alloys

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Abstract

Shape memory alloys (SMA) are metal alloy materials that have been receiving increasingly more attention and study in recent years. These materials exhibit solid-state phase transformation by temperature between two different phase variants martensite and austenite under shape memory effect (SME). Upon heating, the material is in the high strength austenite state, and on cooling, the material changes to the low strength martensite state. This chapter of the book displays the basic feature, the character that made shape memory alloy a smart material.

Keywords: Shape memory alloy, actuator, martensite, austenite, phase transition, shape memory effect, superelasticity

11.1 Introduction

A shape memory alloy (SMA) is a class of smart material that has been receiving increasing attention in recent years owing to its ability “to remember” its original shape when subjected to thermal, mechanical, or magnetic variations. This property of shape memory effect (SME) is harnessed as motion or force in electromechanical devices and micro-machines. This lightweight, solid-state material is used as a substitute for conventional actuators such as hydraulic, pneumatic, and motor-based systems. SMA has the ability to “restore” to its parent shape when deformed by certain external stimuli. This property is caused by a reversible crystalline solid-solid phase transformation.

When compared with:

- The piezoelectric, SMA offers the salient advantage of being able to generate large strains, though at a lower frequency.
- The electric motor, SMA has got a high force to weight ratio, i.e., when the motor is scaled down that is not able to generate forces as SMA wires.

This is different from all other alloys, while heating, all metals will expand but whereas this will contract by generating an opposing force when loaded. The phase transition temperature is the boiling point temperature, at which change in phase occurs. For example, say in water, at boiling temperature it starts to change from liquid to vapor state; on the contrary in SMA at that phase transition temperature, it undergoes a solid-solid phase with the same chemical composition and atomic number but different crystallographic structures.

11.2 Evolution of Shape Memory Alloy

In 1932, Arne Ölander, a Swedish physicist observed: “rubber effect” in samples of gold-cadmium (Au-Cd) for the first time. Greninger and Mooradian (1938) observed SME in copper-zinc (Cu-Zn) alloys and copper-tin (Cu-Sn) alloys and by 1941, Vernon made use of this effect for his polymeric dental material. The significant existence of the memory effect determined by the thermoelastic behavior of the martensite phase broadly testified by Kurdjumov and Khandros in 1949. In 1951, Chang and Read first observed the “shape recovery effect” in gold-cadmium alloys. Similar effects were also observed in the 1950s in other alloys such as in In-Ti and Cu-Al-Ni. These led to many reports and findings by researchers and inventors, but commercialization as a product has been restrained due to their material high costs, manufacturing complexity, and unattractive mechanical properties. In 1962, William J. Buehler and his co-workers at Naval Ordnance Laboratory revealed the importance of SME in an alloy of nickel and titanium called NiTiNOL (for nickel-titanium Naval Ordnance Laboratory). Subsequently, the need for SMAs in engineering and technical uses has been in demand for as consumer products, industrial applications, structures and composites, automation, aerospace applications [1–5], mini-actuators, Micro Electro Mechanical Systems (MEMS), robotics, biomedical applications [1–5], and even in the fashion world. With wide areas of

application and the availability of the number of products on the market using SMAs continually growing, the use of SMA is advancing to a great extent. SMA is a transducer that converts the heat energy to a displacement/force energy in which it is extracted to be used. Heat energy can be brought out by the natural heat of the sun or any other thermal source by which it can be seen as a passive actuator. The distinctive characteristics of the SMA actuators prove to be excellent alternatives to conventional actuators; thereby increasing the progress of further innovative and inexpensive actuators with a substantial decrease in mechanical complexity and size. The statistical growth on SMA is shown in Figure 11.1.

With the high intrinsic strength of the SMA actuators, there is the advantage of being able to employ direct drive devices with smooth and noiseless operation. Direct drive devices eradicate the use of gears with their inherent problems of backlash and wear. SMA actuated systems are made “intelligent” and their shape or stiffness is actively modified by embedded/bonded SMA; this helps shock absorption, which had been the primary weakness of traditional actuators. For instance, the Nickel-Titanium (NiTi) SMA exhibits one of the maximum work densities of actuator systems at 10 J cm, which is capable to lift 100 times more than its weight and the work density is 25 times greater than that of the electric motors. The NiTi SMA is also bio-friendly and exhibits high wear resistance. Due to greater demands, the commercial application of NiTi alloys has established in many areas for lighter and more compact actuators.

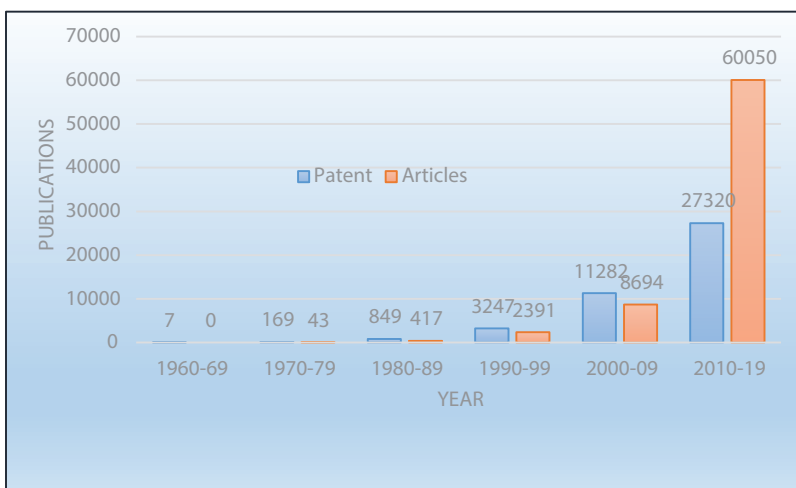


Figure 11.1 Statistical growth on SMA accessible publications.

11.3 Classification of SMA

The three main types of shape-memory alloys based on the chemical composition are copper-based, iron-based, and the equiatomic nickel-titanium (NiTi) alloys but SMAs can also be the product of a different combination of alloys like zinc, copper, gold, and iron. Although iron-based and copper-based SMAs (Fe-Mn-Si, Cu-Zn-Al, and Cu-Al-Ni) are commercially accessible and inexpensive than NiTi. Due to their stability, feasibility, and greater thermo-mechanic performance NiTi-based SMAs are desirable for most applications. Cu-Al-Ni SMAs are popular due to their wide range of useful transformation temperatures and small hysteresis. The thermal stability of copper-based alloys is inadequate by the decomposition kinetics and for this reason, sustained exposure of Cu-Zn-Al and Cu-Al-Ni alloys at temperatures above 150°C (300 F) and 200°C (390 F), respectively, should be avoided. The transformation temperatures may also shift due to aging at lower temperatures. The addition of Ferrous helps to bring down the transformation temperature and introduces hysteresis. Iron-based SMAs (SMAs), especially Fe-Mn-Si alloys, are materials that have great potential damping/absorber applications. Due to their low-cost constituent elements and accessibility of the mass-production facilities that are readily exploited for the manufacture of stainless steel, these alloys find advantages in commercial production. Yet, the production cost may not be lowered in practice unless the amount of the needs reaches that of the usual steels. However, each material has its own advantages for certain requirements or applications. The advantages of NiTi SMA, when compared to other SMAs, are its greater shape memory strain, thermal stability, high ductility, and excellent corrosion resistance. Wires of Flexinol® (the trade name for NiTi actuator wires specifically manufactured by Dynalloy Inc.,) are treated to contract like muscles when electrically heated and stretch as they cool back to ambient temperature.

A ferromagnetic shape memory alloy (FSMA) is another class of SMA, that changes/contracts shape under strong magnetic fields. Since the magnetic response is faster and more effective than temperature-induced response these materials are gaining a lot of interest. Under the influence of a magnetic field, alloys that exhibit shape change characteristics similar to SMAs have lately been under investigation. The large strains caused in magnetic SMAs (MSMAs) and high actuation frequencies have made these materials a strong candidate for high-frequency actuation devices. Metal alloys and shape memory polymers which are thermally-responsive materials have been established and became commercially accessible in the late 1990s.

SMA wire is initially at the low temperature (room temperature) which is now in the detwinned variant of martensite. Upon heating, it will experience a phase change to a stronger austenite cubic structure. At higher temperatures, the austenite structure is stable and at lower temperatures the martensite structure is stable. The temperature where the transformation starts and complete is called the austenite start temperature (A_s) and austenite finish temperature (A_f), respectively. Once SMA is heated beyond A_s , it contracts and transforms into the austenite structure, i.e., it memorizes its parent form. On the elimination of heating, at M_s , SMA will start to transfer from austenite and at M_f , it reaches the weaker twinned variant of the martensite phase. At this stage, the crystal structure of the SMA in the twinned form, in terms of strength, the young's modulus is six times less than the austenite phase. On the application of external tension stress, the twinned martensite becomes a detwinned variant of martensite phase M_d . Obviously, this gives rise to the SMA hysteric effect wherein the heating and cooling paths do not overlap. This effect occurs in the material at the pseudo-plasticity region.

The high actuation energy density results due to the possibility of phase transformation under high applied loads. On cooling, at a martensite start temperature (M_s), the transformation starts to return to the martensite state and is completed at martensite finish temperature (M_f) and this process is shown in Figure 11.2. M_d (detwinned martensite) is defined as the state of

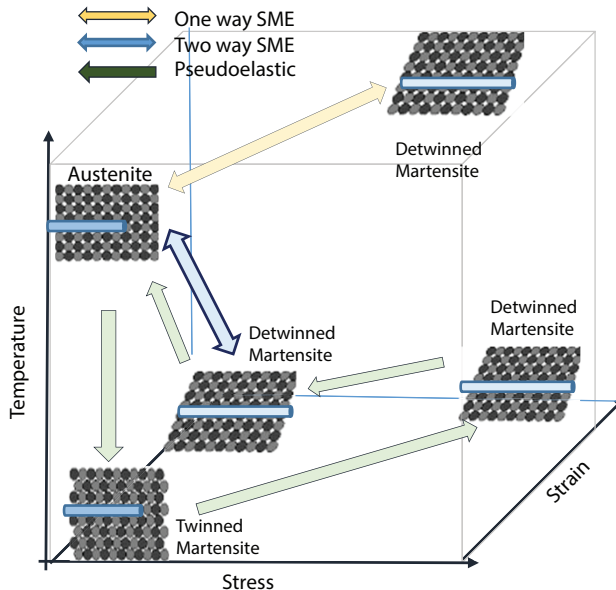


Figure 11.2 Overview on three-phase transformations.

the martensite at maximum temperature. The SMA will be deformed permanently like any ordinary metallic material when any stress above this temperature is applied. The SME is a diffusionless solid phase transition between martensitic and austenitic crystal structures. The generated motion or force in this process harnessed to drive any electromechanical device as an actuator.

11.3.1 One-Way Shape Memory Effect (OWSME)

Upon heating the one-way SMA (OWSMA) restores to its original shape but retains a deformed state (prestrain) on the removal of an external force. Unless it is stressed again subsequent cooling does not transform its shape. The OWSME forms the basis of SMA actuators.

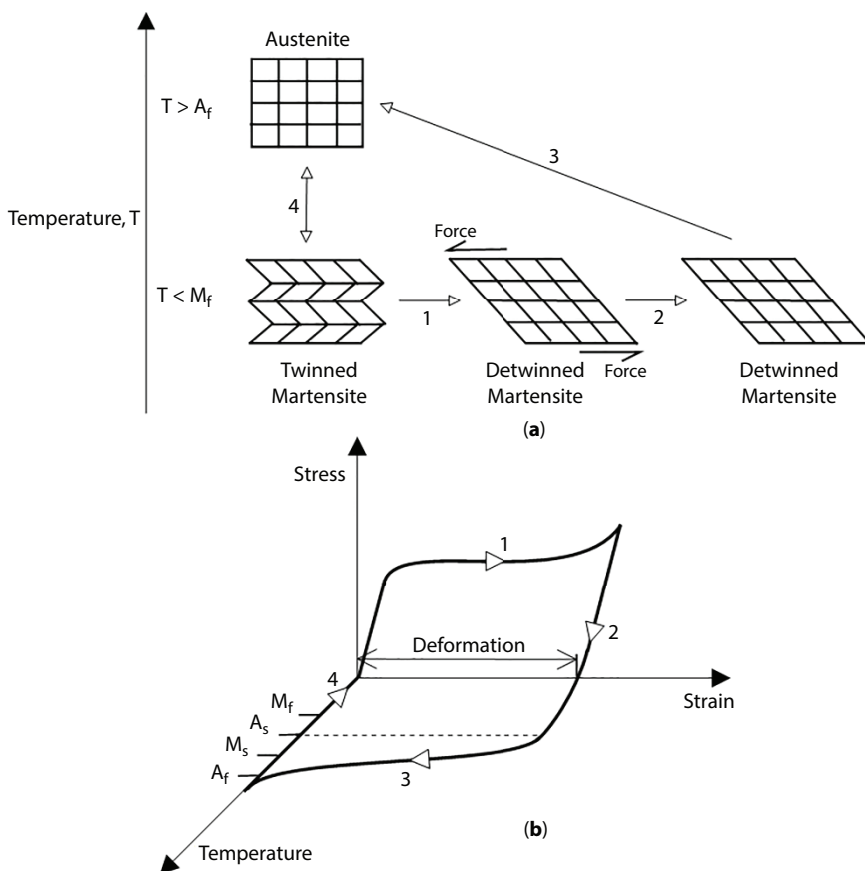


Figure 11.3 One-way shape memory effect [6]. (a) 2D crystal structure model of SMA; (b) stress-strain-temperature curve.

Continuous actuation to perform work can be achieved when the shape recovery and the high forces created as an effect of the phase transformation to the austenite state. The one-way effect of SMAs is depicted in Figures 11.3a and b.

11.3.2 Two-Way Shape Memory Effect (TWSME)

Two-way shape memory alloy (TWSMA) can recall its different shape at both heating and on cooling, and shape change occurs without any external stress. This has got the property of memorizing two shapes within its material and so-called as intrinsic/material TWSMA. However, TWSMA isn't used widely due to the "training" necessities and the fact that it usually yields about half the recovery strain delivered by OWSMA for similar

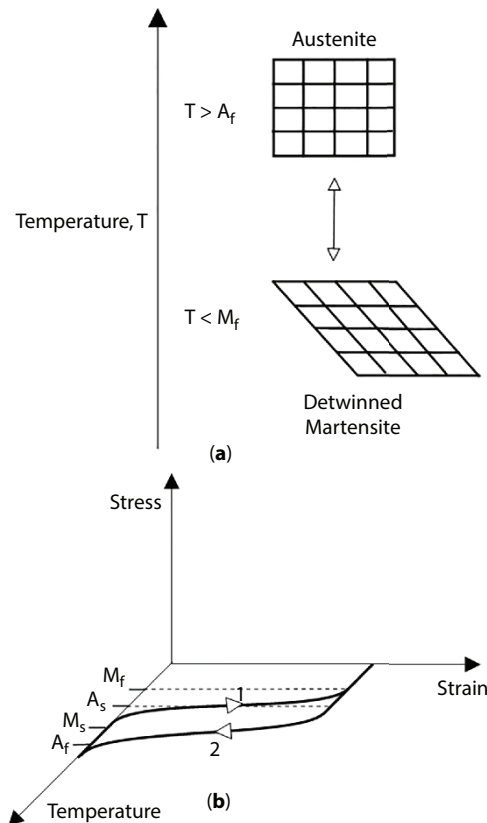


Figure 11.4 Two-way shape memory effect [6]. (a) 2D crystal structure model of SMA; (b) stress-strain-temperature curve.

material. Its strain deteriorate quickly, especially at high temperatures. Therefore, OWSMA provides a more consistent and cost-effective solution.

TWSME characterized ten times lesser strain than the conventional OWSME and can restore only approximately 0.6%–1% strain. The TWSME is shown in Figures 11.4a and b.

11.4 Pseudo-Elasticity or Super-Elasticity (SE)

At the application of mechanical force at temperatures between A_f and $M_{d\max}$, the SMA restores to its original shape, without the need for any thermal activation. This is due to the fact that the austenite crystal is not stable when the load is removed and it gets back to the martensite form. The cycle of the loading-unloading isn't similar to the ones in non-linear

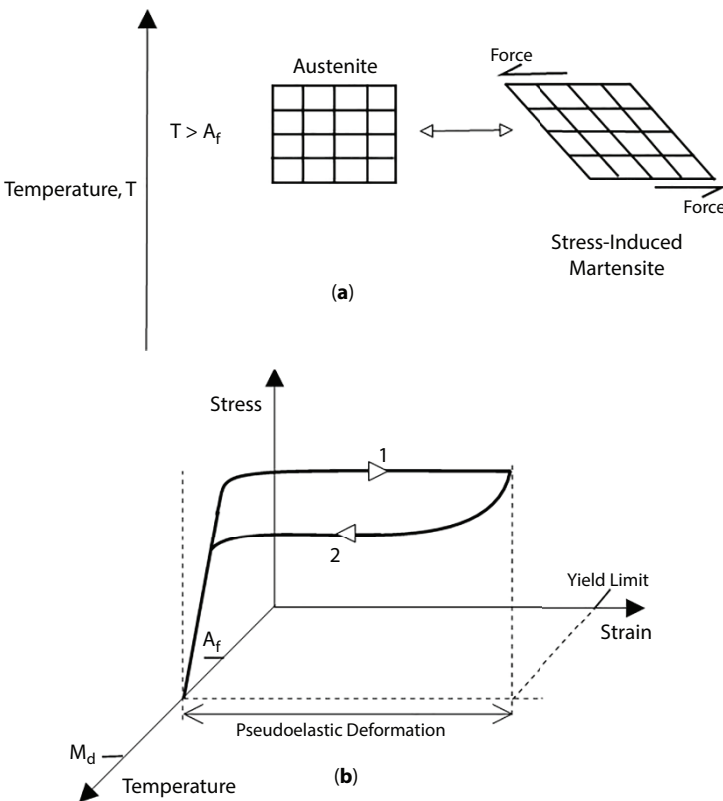


Figure 11.5 Pseudoelastic effect [6]. (a) 2D crystal structure model of SMA; (b) stress-strain-temperature curve.

elastic materials as it shows a hysteresis loop which is uncontrollable, thus making it unsuitable for control applications. This property is predominantly exploited in biomedical fields in designing SMA-based dampers, absorbers, and stents which dissipate energy and suppress the vibration of smart structures. The applications are like eyeglass frames and orthodontic archwires. The pseudoelastic effect is shown in Figures 11.5a and b.

Under certain conditions, SMAs display a two-way-effect, which makes it recall two different shapes, a low-temperature shape, and a high-temperature shape, even without external force [1]. Though it is less significant and its repeated behavior is not as well reported as that of the one-way effect. Because the repeated use of the one-way effect with outward reset force in many cases is the more profitable solution. A wire is loaded at temperatures above A_f but below M_d experiences superelasticity/pseudoelastic behavior. After the attainment of the first yield point, it can be stretched out to approximately 8% strain with no substantial stress increase. The wire returns to its original length elastically upon unloading, although with a stress hysteresis.

11.5 Biasing Configurations

The biasing element plays a vital part in any SMA wire employed system. The main functionality is to restore the martensite state of the SMA wire after the actuation thereby it enables repetitive operations. There are few combinations of SMA along with the biasing element that can be instrumented as classified in Figure 11.6.

The active biasing element is the one that needs to be energized to operate, in that case, there are two modes of achieving the motion. To create mechanical two-way performance, the potential key is to put two

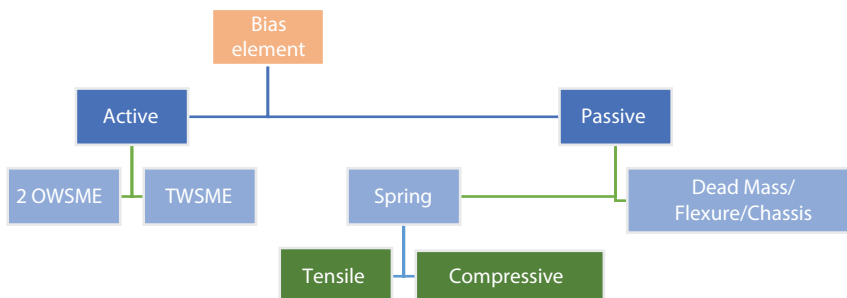


Figure 11.6 Classification on biasing.

OWSMA-based actuators one against another, i.e., heating one SMA to generate forward motion and heating another SMA for reverse and vice versa. TWSMA can realize in two modes due to its two-way shape memory property; in OWSMA, the transformation strain accompanied is only half of that when compared with that in TWSMA. The benefits of mechanical two-way actuators are higher motion and higher force than that in material two-way actuators, whereas the advantage of the material two-way actuator is the design of a simple, compact system with much fewer elements involved. The passive mode of the biasing element can be done by using a spring or a dead mass which can be a flexural cantilever beam or the chassis. The advantage of the active over the passive is that its bidirectional control, whereas passive can be controlled only with the actuation of SMA wire.

Figure 11.7 shows types of SMA configurations with OWSMAs.

- Figure 11.7a shows a one-way dead mass influenced actuator. The SMA element at its product phase at low temperature, and then, when it is heated, it gets contracted and moves element W upwards.
- Figure 11.7b shows a spring-biased actuator, which makes to move the slider back and forth. On heating, the SMA wires contracts pull the spring thus accumulating energy in it. When the SMA element is cooled, the energy accumulated in the spring is released and the SMA element

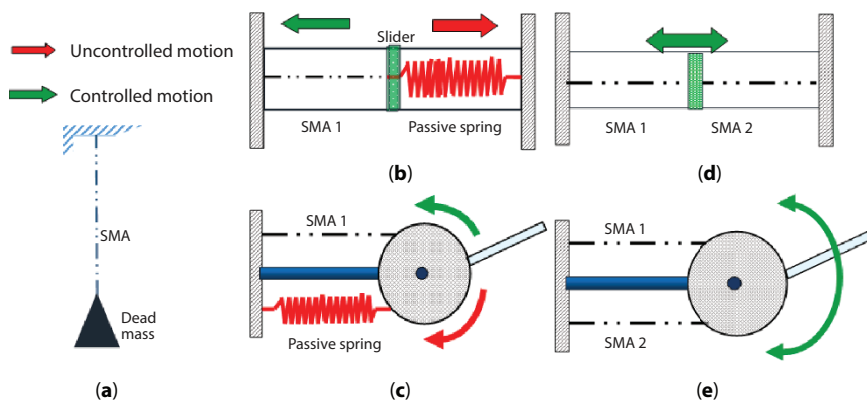


Figure 11.7 Types of SMA actuator configurations using one-way SMA wire. (a) one-way actuator; (b) biased linear actuator; (c) biased rotary actuator; (d) two-way linear actuator; (e) two-way rotary actuator.

deforms back, thus completing the operating cycle. This type is configured in the rotary mode in Figure 11.5c.

Both dead mass and spring are passive biased actuator and this can be controlled only in its heating path and the biasing element stiffness influences the cooling path. This type of configuration is applied for unidirectional control systems

- Figures 11.7d and e show two SMA elements to form a mechanical two-way actuator. Two opposing SMA elements are used, actuated alternatively to bring out the rotating oscillatory motion.

The bi-directional control is achieved by using a mechanical based two-way actuator in which both heating and cooling paths are controlled.

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