SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Chapter 10
Role of Alloying Elements on Powder Metallurgy Steels and Spectroscopic Applications on Them

Sefa Celik
Istanbul University, Turkey

Nuray Bekoz Ullen
https://orcid.org/0000-0003-2705-2559
Istanbul University-Cerrahpasa, Turkey

Sevim Akyuz
Istanbul Kultur University, Turkey

Aysen E. Ozel
Istanbul University, Turkey

ABSTRACT

The powder metallurgy (PM) technique is suitable for mass production and is a well-established process for the low production costs of net-shaped products close to long series. The properties of the iron-based PM parts, such as strength, hardness, magnetic properties, impact, wear, and corrosion resistance, can be improved with adding various alloying elements. The desired surface performance can be achieved with various surface coating technologies. Recently, various coating techniques have been developed as discussed in the chapter. The alloying elements have a significant effect on the coating quality of the final product. Surface coating can be analyzed by examining the surface-coated powder metallurgy (PM) using infrared and Raman spectroscopy technique. This contribution focuses on the role of alloying elements on properties and coating technologies of powder metallurgy steels and Fourier transform infrared (FT-IR) and Raman spectroscopic applications on them.

DOI: 10.4018/978-1-7998-4870-7.ch010

Copyright © 2021, IGI Global. Copying or distributing in print or electronic forms without written permission of IGI Global is prohibited.

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

1. THE IMPORTANCE OF POWDER METALLURGY IN INDUSTRY

Powder metallurgy (PM) process is a near-net-shape production process that combines the properties of shape-making technology for powder compression with the improving of ultimate material and design properties (mechanical and physical) along with the subsequent densification or consolidation processes (e.g., sintering).

PM methods produce complicated components in a simple process, gas atomization, due to rapid solidification, easily and safely allows microstructural modifications such as grain refinement, reduced segregation, and increased solubility. Low cost and high quality in mass production, wide alloying probability and low-density part production are other advantages of PM technology (Angelo and Subramanian, 2008; Chawla et al., 1999; Lee et al., 1998). Nowadays lots of PM-products are used in various industries; these are automotive and off-highway vehicle applications, machinery, computers and fabric sector equipment, home appliances and biomedical device manufacturing sectors. PM products have high surface quality and their properties such as strength and wear resistance may be improved by applying heat treatment. PM methods ensure part-to-part reproducibility and are appropriated to medium-to-high volume manufacturing. If required, controlled microporosity may be supplied for self-lubrication or filtration. The advantage of the method is that the PM alloy can be exactly designed for environmental agents. Then, it may be applied in low amount to form a metallurgical bond with a low-cost substrate that will withstand application conditions (Samal, 2015; Lee et al., 1998). The desired surface performance can be achieved with various surface engineering technologies that can be applied to PM components. In recent times, many numbers of surface coating techniques have been developed such as organic coatings, ceramic coatings, metallic coatings, laser-based techniques, thermal spray coatings, chemical vapour deposition (CVD), physical vapour deposition (PVD) coatings, and other methods of surface modification, which help to improve the tribological properties of the PM materials (Boing et al., 2020; El-Eskandarany, 2015; Donghai et al., 2017; Lee at al., 1998).

PM technology combines different fields, such as polymer and chemical engineering, physical metallurgy and surface sciences. Advances in the field of PM in the last decade are the result of a method of a multi-disciplinary approach (Narasimhan, 1996; Klar and Samal, 2007; Dangsheng, 2002). An extensive range of engineering materials are available, and through proper material and method selection, the necessary microstructure may be created in the material with the addition of variety alloying elements. Alloying additives such as nickel, copper, molybdenum, graphite or carbon are added to the base iron powder to provide the desired performance characteristic of a PM product. A few alloying techniques are available to create PM-products from low alloy powders (Samal and Newkirk, 2015; Salgado et al., 2001; Klar and Samal, 2007). In this chapter; alloying techniques of PM steel products and the effects of alloying elements on PM steel parts, and their surface treatment are discussed. In recent years, surface the coating technologies used in coating of PM-products have been mentioned. Moreover Fourier Transform Infrared (FT-IR) and Raman spectroscopic studies on the alloy composition of PM steels will be discussed.

2. ALLOYING METHODS IN POWDER METALLURGY

The microstructure of PM materials, the size, morphology and distribution of the pores in it, directly affect the mechanical properties of the product. Alloy elements are added to increase material performance

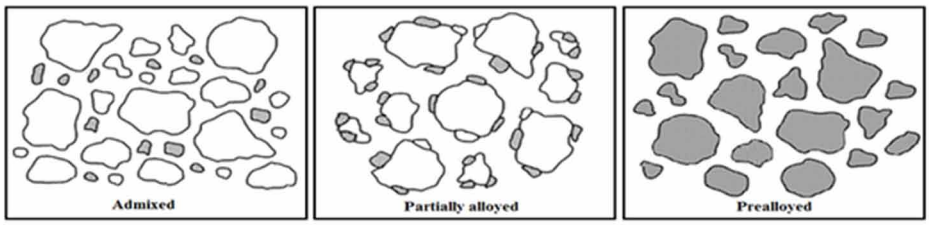
SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

characteristics. For example, it is very significant to add alloying elements to develop the mechanical properties of pure iron because it is essential for the production of components such as strength, hardness, ductility, impact resistance and fatigue strength. At the same time, the alloying technique has an important influence on the microstructure and porosity of the final product (Narasimhan, 2001; Dincer, 2014; Skoglund et al., 2013). Carbon is normally mixed into the iron powder in the form of graphite, but different metallic alloy elements are often admixed by various techniques (Narasimhan, 1996; Lee et al., 1998; Narasimhan, 2001). The methods used in the alloying of ferrous PM materials can be classified as follows; (Samal and Newkirk, 2015; James and West, 1998; Yu et al., 2004; Lee et al., 1998).

a) Admixed alloys
b) Partially alloys (diffusion alloys)
c) Pre-alloys
d) Hybrid alloys (mix of diffusion-alloyed powder with pre-alloyed powder)

The schematic representation of the above-mentioned different alloy methods is illustrated schematically in Figure 1.

Figure 1. Schematic representation of alloying methods (Lee et al., 1998; Yu et al., 2004).



Admixed Powders

Alloy additions may be mixed into iron powder in elemental form or as ferroalloys such as Fe_3P, FeCr or FeMn. This alloy method is the most common and cheapest method used in generally ferrous powder metallurgy. The additions are not alloyed with the iron powder when the mix is pressed, so, the admixed materials maintain most of the compressibility of the base iron powder. The diffusion of the alloying elements in iron at sintering temperature during sintering limits the degree of alloying. Therefore, the observed microstructures may be microstructurally and chemically heterogeneous. The density needed to obtain the requested mechanical properties usually determines which type of powder to use. Water atomized iron powders or directly reduced sponge iron may be used as the base powder for admixed structures (Yu et al., 2004; Lee et al., 1998; Bergman, 2011; El-Eskandarany, 2015). The benefits of admixed processing with binders can be listed as follows: (Lee et al., 1998; Yu et al., 2004; Angelo and Subramanian, 2008).

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

- Provides reduction of variability in sintered properties
- Opportunities for new alloy improvement,
- Developed (or consistent) flow rate and good die filling while maintaining same green strength,
- Potential for obtaining enhanced PM part weight and densities control without the require,
- Potential for developed efficiency,
- Use of fine particle additives.

Partially Alloyed (Diffusion Alloyed) Powders

The demand for making high ductility, high strength PM parts by only pressing and sintering has been influential in the development of various composite types of partially pre-alloyed steel powder containing molybdenum, nickel and copper. In partially alloyed powders, also known as diffusion alloyed powders; alloy additions are metallurgically bonded to either a pre-alloy powder base or an elemental iron powder. Since the compressibility of the base powder is not desired to be significantly reduced, the diffusion alloying of the additions is controlled to ensure sufficient bonding to the base powder while limiting the diffusion degree of the additives. Products made from partially alloyed powders have a complicated as sintered microstructure occurring of regions of martensite, fine unresolved pearlite, bainite, nickel-rich ferrite including blocky carbides, in addition, scattered nickel-rich areas of retained austenite. This complicated microstructure ensures a combination of better tensile ductility and tensile strength in addition to a material with great impact energy. Diffusion alloyed materials may be heat treated to developed for such as apparent hardness, strength, and wear resistance. Diffusion alloyed powders have also enabled the removal of double sintering-pressing and sizing because of the high hardness achieved in the sintered condition (Lee et al., 1998; Bergman, 2011; El-Eskandarany, 2015; Samal and Newkirk, 2015). The benefits of diffusion-alloyed steel powders are (Lee et al., 1998; Yu et al., 2004; Angelo and Subramanian, 2008):

- Enhanced green strength,
- Uniform distribution of alloying elements,
- Protection of high compressibility of the base iron,
- Less alloy separation and dusting risk when transporting the powder mixture,
- Excellent stability of this composite type base powder,
- Good sinterability.

Pre-alloyed Powders

Pre-alloyed low alloy steel powders are beneficial in the production of PM components manufactured for use in high performance applications. The amount and type of the alloy used may be controlled the hardenability of the pre-alloyed materials. For example, nickel, manganese and molybdenum compositions are added to the molten iron during the steel production process to produce a chemically consistent powder. During melting and atomization, applications are followed to ensure the production of powders that do not contain non-metallic inclusion and suitable for the most demanding requirements. The reactivity of carbon in graphite form is excellent with pre-alloyed powders, and it provides close control of the combined carbon content during sintering. These powders are utilized in a wide variety of applications. Changing performance requirements are met with a combination of alloy selection, carbon additions

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

and processing conditions. The compressibility of admixed or partially alloyed powders is generally higher than that of pre-alloyed powders. Generally, pre-alloyed powders are often used for parts that need heat treatment. The amount and type of the alloy used may be controlled the hardenability of the pre-alloyed materials. For example, the compressibility of pre-alloyed powders using only molybdenum as the main alloy material is higher than Nickel-Molybdenum pre-alloyed powders. Products made from pre-alloyed powders have a uniform microstructure and apparent hardness. Carbides formed in the as-sintered condition are not in lamellar in nature. The characteristic carbide morphology may be defined in the as-sintered condition with pre-alloyed materials (Yu et al., 2004; Lee et al., 1998; Bergman, 2011; El-Eskandarany, 2015; Samal and Newkirk, 2015; Angelo and Subramanian, 2008).

Hybrid Alloy Powders

Hybrid alloys are formed by adding elemental and ferroalloy additions to partial or pre-alloyed base powders to obtain the desired chemical composition. When added to nickel or copper pre-alloy powders, it can be highly compacted with molybdenum, which is the addition of the main alloy. It has become widespread with the use of pre-alloyed powders. It is particularly suitable for the addition of high-carbon ferroalloys to these pre-alloyed powders to produce chromium-molybdenum, manganese-molybdenum and chromium-molybdenum-manganese steels. Addition of elemental Ni to partially alloyed powders may be to provide greater impact properties. The compressibility and hardenability of hybrid alloy materials are mainly related to the properties of the base powder used. The general characteristics of hybrid materials are that it has heterogeneous microstructure and apparent hardness. Generally, higher sintering temperatures and longer sintering times caused to more diffusion of alloy additions and the formation of more homogeneous microstructures (Lee et al., 1998; Bergman, 2011; El-Eskandarany, 2015; Samal and Newkirk, 2015).

3. THE EFFECT OF ALLOYING ELEMENTS ON THE PROPERTIES OF POWDER METALLURGY PARTS

The addition of alloying elements (pre-alloyed, admixed, or diffusion-alloyed) is an important aspect of the design stage as the part of PM component manufacturing and has a marked effect on the mechanical properties of the final product. Alloyed PM steels are a particular group of PM materials, having various composition of alloying elements (Cr, Mo, Ni, Mn, V, Cu, Ti and W). Each alloy elements specifically affects the properties of the PM steel and additionally plays an essential role in heat treatment behavior. Strong bonding of alloy additions offers an economic advantage in terms of less green scrap, higher alloy efficiency and an easier maintenance environment. The amount of respirable dust in the immediate surrounding of the compaction press is decreased in order of magnitude and plant purity is significantly developed. Variety alloying system such as Fe-C, Fe-P, Fe-Cu, Fe-Mo-C, Fe-Cu-C, Fe-Ni-C, Fe-Cr-Mo-C, Fe-Ni-Cu-Mo -C, Fe-Mo-Cu-C have definition of ferrous materials (Lee et al., 1998; Angelo and Subramanian, 2008; Shanmugasundaram and Chandramouli, 2009; Yu et al., 1998).

Carbon is the main element for PM steel and steel. Because of the increasing in temperature of the martensitic transformation, the carbon enhances the tensile strength and hardness but reduces the elongation. This is valid for wrought steel as well as for PM steels. In the components containing more than 0.8% carbon concentration, residual austenite formation takes place, which causes a decrease in tensile

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

strength. Carbon dissolves in austenite during heating. Subsequently, the transformation of austenite to ferrite-carbide aggregates results in changing strength levels after cooling from the austenitizing temperature. The porosity of sintered PM steels affects the properties that may be seen after heat treatment. As mentioned above, the properties depend on the processing conditions (Yu et al., 2004; Lee et al., 1998; Danninger and Gierl, 2008).

Nickel is added to enhance the strength, impact and abrasion resistance, and fatigue strength of steels. Shrinkage may occur during the sintering. Nickel steels are the most widespread high strength and heat treated materials. Usually 1-4% Ni alloy is added in PM steels. The addition of nickel does not enhance the sizes, but causes shrinkage and forms a solid solution with a limited solubility in iron. The impact of nickel on tensile strength is lower than copper. Because the solubility of nickel to iron is quite low, but it increases the hardening ability of the steel. Thus, it provides additional benefit to the parts to be heat treated to obtain enhanced mechanical properties (Lee et al., 1998; Danninger and Gierl, 2008; Angelo and Subramanian, 2008; Shanmugasundaram and Chandramouli, 2009).

Copper is added to steel for enhance strength, wear resistance, and apparent hardness. It is usually added in combination with other alloying elements. The addition of copper and graphite leads to growth in sintered compact. Copper is mostly added to iron because it melts and quickly dissolves, thereby significantly enhancing the strength of the iron. Copper melts (T_m=1083þC) at the sintering temperature normally used (1120þC). Liquid copper penetrates the spaces between the grain boundaries and the powder particles within single powder particles. After copper melts, it leaks along the grain boundaries of the structure during sintering, which explains the swelling behavior. For this reason it is difficult to separate grain boundaries from particle to particle contacts. Copper steels can be heat treated to enhance strength, wear resistance and apparent hardness (Angelo and Subramanian, 2008; Mocarski et al., 1996; Angel et al., 2014).

Chromium creates unsteady carbides in steel. But chromium is inexpensive and widespread. It enhances corrosion resistance, particularly to intercrystalline corrosion. Additionally, it can delay transformation throughout tempering. Cr is the most widely used alloying element in heat treated structural steel (Bergman, 2011; Wang, 2005; Angelo and Subramanian, 2008; Engström et al., 1992).

Molybdenum is generally used for nitriding, because the nitrides it forms strengthens the steel. Mo enhances creep resistance and hardenability. The prevalence area of austenite is narrowed with the addition of Mo. The steel containing 3% Mo has a ferritic structure. Molybdenum has a high affinity for carbon and creates carbides, for example Mo_6C. Molybdenum is an effective hardening agent and develops densification because it is a ferrite stabilizer (Mocarski et al., 1996; Bergman, 2011; Sułowski and Matusiewicz, 2013; Dincer, 2014).

Manganese provides enhanced strength and hardness in combination with molybdenum. Manganese is easily reachable and cheap, PM steels with this element have similar properties to Ni steels. On the other side, manganese has a high affinity for oxygen and causes problems during manufacture, therefore this element is added to powder mixtures as ferroalloy. Since manganese easily forms oxide, it is necessary to carefully select the sintering atmosphere. With the addition of sulfur, the workability of sintered iron and its alloys is developed. Also manganese sulfide particles have been added to iron to provide similar benefit. Recently days, the sulfur in the liquid melt is dissolved in the melt before being atomized (pre-alloyed sulfur) to create manganese sulfide (MnS) with carefully controlled amounts of manganese. If it was pre-alloyed, as a result of the addition of these particles of MnS causes as a gray phase in the pores or a MnS phase to form inside the iron particles (Wang, 1994; Lawley and Murphy, 2003; Šalak and Selecká, 2012; El-Eskandarany, 2015).

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Silicon has a positive effect on the magnetic properties of iron. Silicon reduces the saturation induction and enhances the resistivity. Liquid phase occurs during the sintering (Bergman, 2011; Danninger and Gierl, 2008).

Phosphorus has a positive effect on the soft magnetic features when it is added to iron. The phosphorus element stabilizes the alpha phase, which is more open, and creates the liquid phase at 1050°C. The sintering occurs at the mostly used temperature of 1120 °C. Phosphorus causes to enhance the resistivity and saturation induction and reduces the coercive area. Phosphorus forms a liquid phase, like copper, under the normal sintering conditions. However, the difference in microstructure is important. In contrast to the copper in low concentrations, it forms shrinkage because of the formation of phosphorus sintering in the ferrite phase. The diffusion rate of phosphorus is not as fast as a carbon, but it is fast enough to provide a good dispersion in the material at normal sintering times and temperatures (Bergman, 2011; Dobrzanski et al., 2007; Šalak et al., 2005).

The combination of alloying elements significantly affects the properties of steels. There are many studies in the literature about the effect of alloying elements on the microstructure and mechanical properties of PM steels. In the Continuous-Cooling-Transformation (CCT) and Time-Temperature-Transformation (TTT) diagrams, changes on the temperature and composition ratio of a dedicated alloy are observed. In these diagrams, the composition specified for an alloy is determined experimentally. The location and shape of the curves in the diagrams depend on the grain size of the austenite, the amount of alloying elements and according to the time axis. On the other hand, with some exceptions, an increase in the austenite grain size or alloy elements content leads to a reduction in the ratio of austenite-ferrite and austenite-perlite transformations. There are basically two ways alloying elements can decrease the austenite transformation rate: alloying elements can do this by reducing the nucleation and growth rates of bainite, pearlite and ferrite. The transformation of austenite is delayed, probably because of the fact that it is required to wait for the alloying elements to diffuse before the nuclei of new phases may form and grow. It is dependent on molybdenum, nickel and copper to provide the desired hardenability in most alloyed PM steels. As a consequence; alloy compositions in sintered steels for structural parts must be meticulously selected to achieve the required properties (Angelo and Subramanian, 2008; Baran et al., 1999; Kahraman and Gulenc, 2002; Warke et al., 2009; Hu and Tian, 2012; Park et al., 2015).

4. SURFACE TREATMENT OF POWDER METALLURGY PARTS

The majority of the parts produced by the powder metallurgy method are iron-based parts. Corrosion, like all other materials, is a major problem in sintered ferrous parts, and the porous structures of powder metallurgy parts make this problem even more important. PM metal parts in various structures are often subject to corrosion damage due to loss of functionality and size. The reduction of the corrosion resistance of the pores formed in the parts produced by powder metallurgy to environmental effects is explained by the fact that there is more surface area for corrosion and oxidation effects in a porous material. After sintering, many surface treatments are applied to improve the chemical, physical and mechanical properties of the powder metallurgy material and to increase the aesthetics of the product (Baran et al., 1999; Krishna and Patowari, 2013; Tian et al., 2006; Donghai et al., 2007). Steam treatment and phosphatizing processes are classical techniques that have been proven to protect ferrous PM materials from corrosion (Lee et al., 1998; Samal and Newkirk, 2015; Bergman, 2011; Danninger and Gierl, 2008; Konnov et al., 2019; Grimanelis and Eyre, 2007).

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Steam treatment is a frequently used to develop the wear properties and to increase the corrosion resistance of ferrous PM parts. On the treatment, all open surfaces (interior and exterior) are coated with Fe_3O_4, which is hard black magnetic iron oxide. Firstly; the materials are purified from oil or grease and then positioned in a forced convection furnace. Steam treating improves the properties of PM materials by: (Samal and Newkirk, 2015; James and West, 1998; Lee et al; 1998; Grimanelis and Eyre, 2007).

- Improving surface integrity
- Improving compressive strength
- Improving wear resistance
- Increasing surface hardness
- Increasing corrosion resistance

Phosphatizing is used to prevent rust by coating sintered iron materials with a thin film of iron phosphates. The materials are immersed in an aqueous solution consisting of primarily phosphoric acid (Chen et al., 2008; Konnov et al., 2019; Angelo and Subramanian, 2008).

Despite the mentioned surface protection processes; in many ways, surface coating treatments is a requirement for most PM metals. Because interconnected porosity in sintered parts causes surfaces to be exposed to the environment. For this reason, sintered parts are more sensitive to corrosion than their cast or machined counterparts. Because of that, the pores in the PM parts should be closed to prevent the coating solutions from being trapped in the pores. Copper, chromium, cadmium, nickel and zinc are widely used for coating. Additionally, electroless nickel plating can be used. Acid copper plating usually gives the best result on PM components because of its perfect throwing power. Nickel is used alone or on a copper, base to provide a bright corrosion-resistant surface and increase wear resistance. Chromium plating is applied to obtain decorative applications or wear-resistant parts. Cadmium plates have faster and better-throwing power than zinc. To plate a PM part with more than 10% porosity, it is important to fill the pores with a resin or to harden the surface so as not to pass the coating salts through the pores of the part. In addition, surface treatments such as ion implementation or anodization may be used to develop the corrosion properties of ferrous based PM parts. Since the powder metallurgy parts contain pores, corrosion resistance is not achieved, such as those obtained with wrought parts. This is probably due to the expansion of gases in the pores of the powder metallurgy parts when the material is heated to 300-400 ° C during the cooking process, which damages the coating. To avoid this, a pore-closing treatment is needed, which can withstand high-temperature heating, good economics and offers perfect dimensional tolerance (Krishna and Patowari, 2013; Tian et al., 2006; Donghai et al., 2007; Liu et al., 1994; Cameron, 2014; Attar, 1996; Tengzelius and Grinder, 2008; Xu et al., 2015).

The coatings act as a layer that protects the powder metal against corrosion. The coating is applied in order to harden the surfaces according to the effect of powder metals used in various areas; and if powder metal is used in an abrasive environment, coating processes are applied to prevent abrasion. All these features can be gained to powder metals during the production phase, but they are preferred because the coating process will provide better satisfaction and will also be more economical. There are two processes to improve existing materials by reducing corrosion: by adding alloy materials or using surface coating methods. Surface coatings are an applicable way to extend the life of metal components by increasing the corrosion resistance of metallic materials. In order to provide better tribological properties to the surface, a suitable coating strategy must be selected (Gill and Kumar, 2019; Boing et al., 2020). The coating techniques vary for different applications. So, the classification of the coating techniques

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

can be very confused. In recent times, numerous surface coating techniques have been developed to achieve the desired mechanical, physical and chemical properties, by means of thin and hard layers on PM structure, and these techniques are generally described below: (Angelo and Subramanian, 2008; Samal and Newkirk, 2015; Sundararajan and Sivakumar, 2005; Šolic et al.,2019; Gill and Kumar, 2019; Mahade et al.,2019; Ganesan et al.,2019; Boing et al., 2020; Cabezon at al., 2020; Konnov et al.,, 2019, Goldschmidt and Streitberger, 2003).

- **The thermal spray coating process** is commonly applied to protect PM alloys. The thermal spray coating is by far the most versatile modern surfacing method with regard to economics, range of materials, and scope of applications. Thermal spraying reduces wear and corrosion and greatly prolongs part service life by allowing the use of high-performance coating material over a low-cost base metal. Among the commercially available thermal spray coating techniques, detonation spray (DS), high-velocity oxy-fuel (HVOF) powder spray, plasma arc (PA) powder spray, oxyfuel powder (OFP) spray and electric arc wire (EAW) spray are the best choices to get hard, dense and consequently wear-resistant coatings are desired. The purpose of the coating process can be categorized as wear resistance, electrical conductivity or resistivity, oxidation resistance, corrosion resistance, thermal barriers restoration of dimension (Kahraman and Gulenc, 2002; Mahade et al.; 2019; Sundararajan et al., 2005).
- **The physical vapour deposition (PVD) coatings** have become a widespread practice nowadays. Multilayer coatings exhibit increased fracture resistance, adhesion and improved wear resistance. Chemical inertness and low friction coefficient can be realized by combining distinctive properties of various monolayers in a multilayer coating. High wear resistance can be achieved by thin and hard coatings particularly with PVD / Especially with PVD coating, thin and hard coatings with high wear resistance can be achieved (Goldschmidt and Streitberger, 2003; Boing et al., 2020; Šolic et al., 2019).
- **The chemical vapour deposition (CVD) coatings** are widely used in industry because of their versatility for depositing a very large variety of elements and compounds covering a wide range of materials from amorphous deposits to epitaxial layers having a high degree of perfection and purity. Chemical vapour deposition can be defined as a process in which the gaseous chemical reactants are transported to the reaction chamber, activated thermally (conventional CVD) or by other means (plasma-assisted CVD or laser-induced CVD) in the vicinity of the substrate, and made to react to form a solid deposit on the substrate surface. It is possible to deposit films of uniform thickness and low porosity even on substrates of complicated shape with this process. If a metalorganic or organic-metallic precursor species is used in a CVD process, the process is designated MOCVD or OMCVD. A large percentage of hard metals cutting tool inserts and sintered high-speed steel tools are now coated using CVD and PVD. The lower temperature PVD process also allows steels to be given a wear-resistant layer of titanium carbide, titanium nitride, alumina or a combination of these materials (Goldschmidt and Streitberger, 2003; Boing et al., 2020; Angelo and Subramanian, 2008).
- **Plasma-assisted chemical vapour deposition (PACVD),** known as plasma-enhanced CVD, is an important technique used for depositing films of cutting tools. The area of application for these types of coated materials is expanding with the development and application of ultra-fine powder grain sizes, as well as the advancements in technology. One method of coating hard metals is

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

PACVD technique rarely used for coating hard metals with ultrafine grain size (Boing et al., 2020; Angelo and Subramanian, 2008).

- In recent times, **laser-based techniques** such as laser cladding and laser deposition have made headway in the area of surface modification. These techniques can quickly melt the metal surface and then the metal solidifies rapidly, which helps to improve the surface properties of the materials. Laser deposition techniques have attracted great interest in the synthesis of semiconducting and insulating thin films in recent years. Additionally, these techniques have been successfully applied to the deposition of high critical temperature superconducting films. In the laser ablation technique, the material is vaporized and ejected from the surface of a target as it is irradiated by a laser beam. Films are formed by condensing material ablated from the target onto a solid substrate (Angelo and Subramanian, 2008; Mirzaali et al., 2019; Goldschmidt and Streitberger, 2003).
- **Ion implantation** is one of a number of surface modification processes that are emerging as an economical and viable process for improving the near-surface tribological properties of engineering components. The microstructural and chemical changes caused by ion implantation can significantly affect the surface performance of PM components (Angelo and Subramanian, 2008; Kolawole et al., 2019).

Apart from these coating techniques; there are various surface modifying techniques such as plasma spraying, biomimetic mineralization, electrophoretic deposition and sol–gel method (Boing et al., 2020; Cabezon at al., 2020; Konnov et al.,, 2019, Chen et al., 2008; Goldschmidt and Streitberger, 2003).

5. THE EFFECT OF ALLOYING ELEMENTS ON THE SURFACE COATING

PM structural parts can be covered with many coating techniques as mentioned in the previous section. Copper, nickel, cadmium, zinc and coating can be made for PM parts. However, porous parts must be filled with resin before coating so as to avoid penetration and entrapment of coating solutions in the pores (Attar, 1996; Angelo, 2008; Cameron, 2014). The coating properties of PM parts are dependent not only on the nature and distribution of phases present in the coating but also on a host of other properties like materials microstructure (largely determined by powder composition), porosity, the nature of residual stress and its magnitude within the coating and finally the coating-substrate adhesion (Link, 1998; Dangsheng, 2002; El-Eskandarany, 2015; Samal and Newkirk, 2015; Danninger and Gierl, 2008; Wang, 2005; Shanmugasundaram and Chandramouli, 2009; Mocarski et al., 1996; Wang, 1994; Angel et al., 2014; Engström et al., 1992; Mitchell et al., 2005; Hu and Tian, 2012; Park et al., 2015; Xu et al., 2015). The factors affecting the coating processes largely depend on understanding the properties of the material that changes with the alloying elements. There are many scientific studies on PM in the literature due to the wide usage area of PM-products and their superior properties. However, there are few studies on the effect of alloying elements of PM parts on the coating. In some of these studies, the following information is given about the effect of alloying elements on the coating. (Link, 1998; Dangsheng, 2002; El-Eskandarany, 2015; Samal and Newkirk, 2015; Danninger and Gierl, 2008; Wang, 2005; Shanmugasundaram and Chandramouli, 2009; Mocarski et al., 1996; Wang, 1994; Angel et al., 2014; Engström et al., 1992; Mitchell et al., 2005; Hu and Tian, 2012; Park et al., 2015; Xu et al., 2015).

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

- Copper increases the performance of the coating due to closing the pores with liquid phase sintering.
- Carbon has no significant effect on the coating appearance and thickness. Increasing C ratio causes an increase in coating hardness value. However, in PM steels with high carbon content, when the product is taken into the acid bath for surface cleaning, it can capture hydrogen and cause hydrogen brittleness.
- The high manganese content in PM steels can form a thick, low-impact coating. This creates a negative situation both in terms of aesthetics and coating quality.
- Silicon content in PM steels has a negative effect on thickness and appearance. If the Si content is high, a thick and matt coating is obtained.
- The high phosphorus content in PM steels forms a coating with a high tendency to break.

An ideal surface coating is directly related to the content of the alloying elements in the material. Residual stress formed by the microstructure that changes depending on the alloy element is among the most important factors affecting coating integrity. Besides the composition and properties of the PM part, the working conditions and design of the spray and curing equipment are the key factors affecting coating quality and process performance. This brief survey of the relationship between PM material coating technology and alloy elements will enable researchers interested in the subject to better to understand the coating process.

Techniques like Energy Dispersive Spectroscopy (EDS) and X-ray diffraction (XRD) are used to analyze the change in composition of alloying elements and phases of the coated PM material surface. Surface coating can be analyzed by examining surface coated powder metallurgy (PM) with Raman and FT-IR spectrometry.

6. FT-IR AND RAMAN SPECTROSCOPIC APPLICATIONS ON THEM

FT-IR spectroscopy is one of the important techniques in which the vibrations and structures of molecules are defined (Christy et al., 2001; Smith, 2011; Ciurczak and Igne, 2015; Ordonez and Prieto, 2012; Stuart, 2004). Once the molecule is irradiated by infrared light, which includes all IR wavelengths, the molecules absorb characteristic wavelengths for themselfs, which equal to the difference in their vibrational energy levels. Using IR spectroscopy, the recognition of the molecular structure is performed by the identification of functional groups and chemical bonds. In the industry loss of time is very important and it is desirable to check the product quality quickly. It is important that FT-IR spectroscopy performs this analysis in a few minutes (Celik et al., 2020).

Raman scattering is inelastic scattering of the laser light by the molecules. The energy of scattered photon is increased (Stokes Raman scattering) or reduced (anti-Stokes Raman scattering) during the scattering. The energy difference between the incident electromagnetic radiation (laser light) and the scattered light, gives information about the vibrational energy levels of the molecule and therefore the vibrational frequencies. The vibrational frequencies are characteristic for the molecular structure.(Jacob et al., 2018).

In many studies it was shown that specific characterization of all kind of materials, amorphous or crystalline, can be determined by means of Raman spectroscopy. This is possible, even though the crys-

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

tal or polycrystal insulators that are composed of several layers of material, or though they are metals (Cantarero, 2015).

Numerous defects and damages can occur in crystals during myco / nano-processing and crystal growth. These have a major effect on the mechanical, optical or electronic efficiency and sustainability of the machined workpiece, such as microstructural alteration, residual stress, phase transition, etc., Such defects and damages can be determined by means of Raman spectroscopy. Raman spectroscopy is significantly sensitive to the microstructural changes, impurities, residual stress, is a good technique for evaluating depth and dimension of these defects or damages It is an easy-to-use, non-destructive method of analysis. Raman spectra provides structural fingerprints and for this reason it is used for molecular recognition and verification within a wide range of scientific disciplines (Xu et al., 2018). Raman spectroscopy also allows detection of complex structural changes, sample mapping and depth scanning. It has important applications in material sciences including semiconductor industry, nanotechnology, solid state physics, synthetic polymer materials and has importance for identifiying all kinds of materials. Raman and FT-IR spectroscopy are known as complementary techniques. Both methods, which have difference in its principles, are good tools for material identification (Vaskova, 2011).

The studies of FT- IR and Raman spectroscopic applications in this field are given below:

In the study performed by Bach et al. in 2019, group theory in a combination with DFT+ U simulation was applied to crystalline materials to predict Raman spectra of anatase and rutile phases of TiO_2. Simulated Raman spectra were calculated and compared to the experimental spectrum and the coatings have been observed to have polycrystalline structures, contain anatase and rutile phases (Bach et al., 2019).

Micro-Raman spectroscopic analysis of different copper sulfate species was performed in a study conducted by Hayez et al (2004). Products such as antlerite, brochantite, posnjakite, langite and chalcanthite, which are likely to occur as a result of atmospheric corrosion of copper alloys, have been investigated. They developed a database of the characteristic Raman spectra of alloys (Hayez et al., 2004).

The interfaces of two diamond/metal composites with high thermal conductivity were analyzed by Raman spectroscopy (Makino et al., 2016).

In 1989, Yang et al., applied Raman spectroscopy to characterize the microscopic bond structure of a-SiGe: H alloys. The correlation between the degree of clustering of Ge-Ge and the transport properties of alloys is shown. Experimental results have been discussed due to an improvement in the quality of the alloy materials (Yang et al., 1989).

In a work performed by Rath *et al*. in 2003, the Raman spectrum of bulk and $Si_{1-x}Ge_x$ epitaxial alloys was investigated to create a metrology for evaluating alloy compositions from the first order Si-Si, Ge-Ge, and Si-Ge optical phonon Raman modes (Rath *et al*., 2003).

In 2019, Hashemi and his team also created an effective method for simulating the Raman spectra of alloys, comparing them with density-functional theory calculation, and applying to several bidimensional (2D) transition metal dichalcogenides (Hashemi et al., 2019).

In 2018, Rana et al., recorded the Raman spectrum of the Ge-S-Ga chalcogenide glassy alloy and analyzed it for diverse compounds compositions to investigate both high-frequency molecular-like modes and low-frequency acoustic zones. The addition of Ga has been observed to cause the formation of Ga-S bonds responsible for the formation of the tetrahedral device in the glassy network. Besides that, there are some homopolar S-S and Ge-Ge bonds that are characteristic of glasses for the basic GeS_4 structural tetrahedra groups. The addition of Ga also leads to replacement of S - S bonds with Ga - Ga bonds and has been found to shift to a slightly lower wavelength side in the Raman spectrum (Rana et al., 2018).

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

In a research conducted by Lara et al. in 2017, the phase transition of Gd^{3+}-doped $BaTiO_3$ ceramics was investigated by means of Raman spectroscopy. The Raman peaks, characteristic tetragonal ferroelectric phase of $BaTiO_3$, were determined as 205 cm^{-1} {E(TO +LO), A_1(LO)}, 265 cm^{-1} {A_1(TO)}, 304 cm^{-1} {B_1, E(TO +LO)}, 513 cm^{-1} {A_1(TO), E(TO)}, and 717 cm^{-1} {A_1(LO), E(LO)}. Raman peak, around 304 cm^{-1}, showed a decrease in intensity by increasing Gd^{3+}content, as a result of the decrease of tetragonality of $BaTiO_3$ ceramics (Lara et al., 2017).

In a report by Goff et al., on Raman spectroscopic investigation of crevice corrosion in Beryllium-containing nickel-chrome dental alloys, a simple design to model and classify products of corrosion likely to occur, using Raman spectroscopy, was suggested (Goff et al., 1998).

The role of molybdenum in the passivation and corrosion of nickel alloys has been investigated by Raman spectroscopy (Delichere et al., 1988).

In the work done by Reis and his team, 304L alloy stainless steel powder and multi-walled carbon nanotubes were mixed under the ambient atmosphere with ball milling and for a long grinding time ranging from 0 to 120 min. The morphological and structural changes related to the crystallinity of the samples due to doping process were investigated by the Lorentzian deconvolution from the Raman spectrum. In this study they provided Raman spectroscopic signatures for produced several distinct composites. It was shown that Raman spectra of nanocomposites based on SS 304L alloy metal nanoparticles and MWCNTs present multiple splits in the D, G and 2D-bands region as fingerprints (Reis et al., 2018).

Wu and his team's research in 2020 examined the tribological properties of the Ni_3Si alloy at high temperatures. The effect of adding Ti was investigated by means of Raman spectroscopy. The results showed that the coefficient of friction decreased as the temperature goes up, and the wear rate ranged marginally from 25 to 400 °C (Wu et al., 2020).

Raman scattering experiments were performed in a bulk $Si_{1-x}Ge_x$ single crystal with compositional gradient, which can be used as an X-ray monochromator for focusing and diffraction, to determine both residual strain and alloy composition. Both the residual strain and alloy composition are evaluated by analyzing strain effect on RS in conjunction with a strain model developed for bulk mixed crystals. It is found that the alloy composition evaluated from the RS results is in good agreement with that measured by the standard chemical analysis (Islam et al., 2004).

In the study of Kim at al., Raman spectroscopy was used when examining the effects of chromium and manganese as alloying elements on the corrosion resistance of carbon steel (Kim et al., 2018).

Nouicer et al. studied Ti_6Al_4V alloy by Raman spectroscopy in order to characterize titanium alloy surface in a biological medium (Nouicer et al., 2017). The effect of a biological medium simulated body fluid, on surface modification of titanium alloy Ti_6Al_4V, was investigated and depending on the Raman spectroscopy it was found that titanium dioxide consisted of rutile phase.

In a study conducted in 2017, tribofilms of carbon steel were analyzed by Raman spectroscopy and the technique proved to be effective in direct observation of films with lubricating oil in ambient air (Miyajima et al., 2017).

In 2011, Fernandes et al. was reported that zinc phosphate coatings modified with manganese and nickel were isomorphic with hopeite mineral (hydrated zinc phosphate) which was difficult to identify using X-ray diffraction, for this reason the phosphate coatings were determined using FTIR (Fernandes et al., 2011)

In the study conducted in 1988 (Jasinski et al., 1988), it was stated that by means of FT-IR spectroscopy, iron oxide and iron carbonate corrosion scales could be easily determined and the spectra were related to the chemical history of the corrosion process. In this study, it was found that the IR absorption

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

bands of most of the 11 crystalline iron oxides and iron carbonates were sufficiently separated from each other. However, it was also reported that vacuum exposure of some of these films, or preparation of KBr pellets made band shifts depending on the special oxide composition (Jasinski et al., 1988).

In a study conducted in 1992, oxide films formed on stainless steel SUS430 under different conditions were studied using infrared reflection spectroscopy, using a FT-IR spectrometer equipped with a polarized reflectance attachment and a wire grid polarizer. Comparison of the FTIR spectra of oxidized samples in a humid atmosphere and oxidized samples in a dry atmosphere showed the importance of water vapor at 873 and 973 K. The abnormal rapid oxidation at 873 K in a humid atmosphere with low oxygen pressure was characterized by a rapid increase in the intensity of the *ca.* 550 cm^{-1} IR band, depending on the increasing oxidation time (Honda et al., 1992).

Swiech et al. (Swięch et al., 2018) analyzed the corrosion products, that formed on the surfaces of Fe and Cu metal after being left in solution containing chloride, by means of FT-IR absorption and Raman spectroscopy. Depending on the spectral analysis, it was found that the main component types of corrosion products for Fe metal sample were lepidocrocite and paratacamide for Cu surface. The findings indicated that applying vibrational spectroscopic methods is a precise tool for recognizing and evaluating the products of corrosion.

In the 2012 report, comprehensive study was conducted on improving the corrosion properties of AISI D3 steel surfaces coated with multi-layer $(CrN/AlN)_n$ framework, which is accumulated by spraying with magnetron over various periods. For practical effects, the properties of CrN and AIN single layers accumulated under the same conditions as multi-layer systems were compared. Coatings were examined by various methods, especially by FT-IR spectroscopy. Depending on FTIR results it was reported that identification of the characteristic bonding in single layer coatings was possible (Cabrera et al., 2012).

Ti-6Al-4V-4B_4C metal matrix composite covering were coated on AISI 1040 steel using magnetron spraying in the 2020 study and the dry slippery wear behavior at room temperature was investigated. FT-IR and some other methods were applied on the investigation of coating morphology. The vibrational frequencies of Ti-6Al-4V-4B_4C coating are determined and the presence of B_4C in the coating confirmed by FT-IR spectroscopy (Prince et al., 2020).

The goal of the 2007 research, conducted by Sheban and her team, was to establish corrosion protection systems for chloride attacking concrete structures. Benzotriazole (BTA) and BTA derivatives were used as the steel corrosion protection product and it has been found that the BTA derivatives in simulated concrete pore solutions have good steel protection. The formation of either mono-or bi-dentate bonds between the triazolic nitrogen ring and the steel surface was shown by the FTIR (Sheban et al., 2007).

The effect of green lubrication on the tribological and mechanical properties of AISI 4140 steel was explored in the study conducted in 2019 and performance of three bio-based lubricants was examined, compared to five of the lubricants, and lubricants were chemically characterized using FT-IR spectroscopy (Sierra et al., 2019).

CONCLUSION

PM products are used in variety applications in many sectors. High surface quality of the products produced by powder metallurgy method and their mechanical and physical properties can be adjusted according to the working conditions are important aspects of the method. Properties of the iron-based PM parts such as strength, hardness, impact resistance, corrosion properties, wear resistance and mag-

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

netic properties can be improved with adding various alloying elements. Corrosion is a major problem due to the pore content in the iron-based PM product. Surface treatments can be applied to improve the corrosion properties of these parts. As mentioned in this chapter, besides the classical methods, the latest technology surface coating processes are used to improve the surface properties of PM products. The alloying elements have an effect on the thickness, bonding properties, appearance and brittleness of the coating. With using FT-IR and Raman spectroscopic techniques, the early detection of defects and impurity in the manufacturing process can be obtained quickly, that is very useful for controlling the production process and taking action.

REFERENCES

Anderson, A. (1995). *ASM Metals Handbook* (Vol. 18). Friction, Lubrication and Wear.

Angel, W. D. W., Jurado, L. T., Alcalá, J. F. C., Martínez, E. C., & Cedeño, V. F. V. (2014). Effect of copper on the mechanical properties of alloys formed by powder metallurgy. *Materials & Design*, *58*, 12–18. doi:10.1016/j.matdes.2014.02.002

Angelo, P. C., & Subramanian, R. (2008). *Powder metallurgy: science, technology and applications*. PHI Learning Pvt. Ltd.

Attar, F. (1996). Hardness evaluation of thin ceramic coatings on tool steel. *Surface and Coatings Technology*, *78*(1-3), 78–86. doi:10.1016/0257-8972(94)02395-6

Bach, L. X., Thuan, D. V., Thu, V. T. H., Phan, T. B., Vu, N. S. H., & Nam, N. D. (2019). An investigation on titania multilayer coatings for enhanced corrosion resistance of carbon steel in simulated seawater by sol–gel dip coating. *Journal of Materials Research and Technology*, *8*(6), 6400–6406. doi:10.1016/j.jmrt.2019.09.061

Baran, M. C., Graham, A. H., Davala, A. B., Causton, R. J., & Schade, C. (1999). A superior sinter-hardenable material. *Advances in Powder Metallurgy & Particulate Materials*, *2*(Part 7), 185–203.

Bergman, O. (2011). *Key aspects of sintering powder metallurgy steel prealloyed with chromium and manganese*. Chalmers University of Technology.

Boing, D., Oliveira, A. J. D., & Schroeter, R. B. (2020). Evaluation of wear mechanisms of PVD and CVD coatings deposited on cemented carbide substrates applied to hard turning. *International Journal of Advanced Manufacturing Technology*, *106*(11), 5441–5451. doi:10.100700170-020-05000-x

Cabezon, C. G., Hernandez, C. G., Mendez, M. L. R., Herranz, G., & Pedrosa, F. M. (2020). Role of carbon and nitrogen in the improvement of corrosion resistance of new powder metallurgy Co-Cr-Mo alloys. *Corrosion Reviews*. Advance online publication. doi:10.1515/corrrev-2019-0109

Cabrera, G., Torres, F., Caicedo, J. C., Aperador, W., Amaya, C., & Prieto, P. (2012). Improvement of electrochemical surface properties in steel substrates using a nanostructured CrN/AlN multilayer coating. *Journal of Materials Engineering and Performance*, *21*(1), 128–136. doi:10.100711665-010-9798-7

Cameron, D. (2014). Introduction to Films and Coatings: Technology and Recent Development. In Comprehensive Materials Processing (Volume 4.01, pp. 1-2). Elsevier.

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Cantarero, A. (2015). Raman scattering applied to materials science. *Procedia Mater. Sci.*, *9*, 113–122. doi:10.1016/j.mspro.2015.04.014

Capus, J. (2013). PM light alloys gaining applications in automotive sector. *Metal Powder Report*, *68*(6), 12–15. doi:10.1016/S0026-0657(13)70210-8

Celik, S., Albayrak, A. T., Akyuz, S., & Ozel, A. E. (2020). The Role of Multivariant Analysis on the Interpretation of FTIR and Raman Spectra. In Design of Experiments for Chemical, Pharmaceutical, Food, and Industrial Applications (pp. 104-129). IGI Global. doi:10.4018/978-1-7998-1518-1.ch005

Chawla, N., Fillari, G., & Narasimham, K. S. (1999). Recent advances in ferrous powder metallurgy. In Powder Materials: Current Research and Industrial Practices(as held at the 1999 TMS Fall Meeting) (pp. 247-255). Academic Press.

Chen, W. G., Duan, X. M., Dong, T., Gao, L. N., Chen, M. Z., & Ye, H. (2008). Study on Steam Treatment Process for Steel. *Surface Technology*, *37*(6), 57–60.

Christy, A. A., Ozaki, Y., & Gregoriou, V. G. (2001). *Modern Fourier transform infrared spectroscopy*. Elsevier.

Ciurczak, E. W., & Igne, B. (2015). *Pharmaceutical and medical applications of near-infrared spectroscopy*. CRC Press.

Dangsheng, X. (2002). The Effect of Rare Earth Compounds on the Friction and Wear Properties of PM Ni-based Alloy. *PM Technology-China, 20*(82), 67-70.

Danninger, H., & Gierl, C. (2008). New alloying systems for ferrous powder metallurgy precision parts. *Science of Sintering*, *40*(1), 33–46. doi:10.2298/SOS0801033D

Delichere, P., Goff, A. H., & Joiret, S. (1988). Study of thin corrosion films by in situ Raman spectroscopy combined with direct observation of nuclear reactions. *Surface and Interface Analysis*, *12*(7), 419–423. doi:10.1002ia.740120710

Dincer, M. (2014). *Sinter hardening studies of ASTALOY 85 Mo powder with varying copper contents* (Master's thesis). Middle East Technical University.

Dobrzanski, L. A., Brytan, Z., Grande, M. A., & Rosso, M. (2007). Properties of duplex stainless steels made by powder metallurgy. *Archives of Materials Science and Engineering*, *28*(4), 217–223.

Donghai, Y., Chengyong, W., & Fenglin, Z. (2007). Development of Cutting Tool Coating Material. *Tool Engineering*, *41*(6), 25–32.

El-Eskandarany, M. S. (2015). *Mechanical alloying: nanotechnology, materials science and powder metallurgy* (Vol. 2). Elsevier.

Engström, U., Lindberg, C., & Tengzelius, J. (1992). Powders and processes for high performance PM steels. *Powder Metallurgy*, *35*(1), 67–73. doi:10.1179/pom.1992.35.1.67

Fernandes, K. S., Alvarenga, E. D. A., Brandão, P. R. G., & Lins, V. D. F. C. (2011). Infrared-spectroscopy analysis of zinc phosphate and nickel and manganese modified zinc phosphate coatings on electrogalvanized steel. *REM. Revista Escola de Minas*, *64*(1), 45–49. doi:10.1590/S0370-44672011000100005

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Ganesan, S., Padmanabhan, S., Hemanandh, J., & Venkatesan, S. P. (2019). Influence of substrate temperature on coated engine piston head using multi-response optimisation techniques. *International Journal of Ambient Energy*, 1-8.

Gill, A. S., & Kumar, S. (2019). Surface characteristics investigation of tool steel machined by powder metallurgy tool in EDA. *Materials Research Express, 6*(12), 1265b1.

Goff, A. H., Joiret, S., & Abourazzouk, D. (1998). Raman investigation of crevice corrosion in nickel-chromium dental alloys containing beryllium. *Electrochimica Acta*, *43*(1-2), 53–62. doi:10.1016/S0013-4686(97)00234-X

Goldschmidt, A., & Streitberger, H. J. (2003). *BASF handbook on basics of coating technology*. Primedia.

Grimanelis, D., & Eyre, T. S. (2007). Wear characteristics of a diffusion bonded sintered steel with short term surface treatments. *Wear*, *262*(1-2), 93–103. doi:10.1016/j.wear.2006.04.006

Hashemi, A., Krasheninnikov, A. V., Puska, M., & Komsa, H. P. (2019). Efficient method for calculating Raman spectra of solids with impurities and alloys and its application to two-dimensional transition metal dichalcogenides. *Physical Review Materials*, *3*(2), 023806. doi:10.1103/PhysRevMaterials.3.023806

Hayez, V., Guillaume, J., Hubin, A., & Terryn, H. (2004). Micro-Raman spectroscopy for the study of corrosion products on copper alloys: Setting up of a reference database and studying works of art. *Journal of Raman Spectroscopy: JRS*, *35*(8-9), 732–738. doi:10.1002/jrs.1194

Honda, K., Atake, T., & Saito, Y. (1992). Infrared spectra of oxide films on SUS430 stainless steel formed at temperatures between 473 and 1073 K. *Journal of Materials Research*, *7*(1), 80–84. doi:10.1557/JMR.1992.0080

Hu, B., & Tian, G. (2012). Morphological instability of γ'phase in nickel-based powder metallurgy superalloys. *Chin Shu Hsueh Pao*, *48*(3), 257–263. doi:10.3724/SP.J.1037.2011.00731

Islam, M. R., Yamada, M., Abrosimov, N. V., Kiyama, M., & Tatsumi, M. (2004). Raman scattering characterization of residual strain and alloy composition in bulk Si1-xGex crystal. *The European Physical Journal Applied Physics*, *27*(1-3), 325–328. doi:10.1051/epjap:2004124

Jacob, L. J., & Deigner, H. P. (2018). Nanoparticles and Nanosized Structures in Diagnostics and Therapy. In Precision Medicine (pp. 229-252). Academic Press. doi:10.1016/B978-0-12-805364-5.00010-X

James, W. B., & West, G. T. (2002). *Ferrous powder metallurgy materials. In powder technologies and applications* (Vol. 7). ASM International.

Jasinski, R., & Iob, A. (1988). FTIR measurements of iron oxides on low alloy steel. *Journal of the Electrochemical Society*, *135*(3), 551–556. doi:10.1149/1.2095656

Kahraman, N., & Gulenc, B. (2002). Abrasive wear behaviour of powder flame sprayed coatings on steel substrates. *Materials & Design*, *23*(8), 721–725. doi:10.1016/S0261-3069(02)00075-4

Kim, B., Kim, S., & Kim, H. (2018). Effects of Alloying Elements (Cr, Mn) on Corrosion Properties of the High-Strength Steel in 3.5% NaCl Solution. *Advances in Materials Science and Engineering*, *2018*, 1–13. doi:10.1155/2018/7638274

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Klar, E., & Samal, P. K. (2007). *Powder metallurgy stainless steels: processing, microstructures, and properties*. ASM international.

Kolawole, M. Y., Aweda, J. O., Iqbal, F., Ali, A., & Abdulkareem, S. (2019). Mechanical Properties of Powder Metallurgy Processed Biodegradable Zn-Based Alloy for Biomedical Application. *International Journal of Materials and Metallurgical Engineering*, *13*(12), 558–563.

Konnov, A. Y., Demchenko, M. V., Sisanbaev, A. V., Nafikov, M. Z., & Farkhshatov, M. N. (2019). Estimation of the Corrosion Resistance of the Metal Coatings Formed by Powder Metallurgy. *Russian Metallurgy (Metally)*, *2019*(12), 1285–1288. doi:10.1134/S0036029519120097

Krishna, M. E., & Patowari, P. K. (2013). Parametric optimisation of electric discharge coating process with powder metallurgy tools using Taguchi analysis. *Surface Engineering*, *29*(9), 703–711. doi:10.1179/1743294413Y.0000000207

Lara, J. P. H., Labra, M. P., Hernández, F. R. B., Serrano, J. A. R., Dávila, E. O. A., Thangarasu, P., & Ramirez, A. H. (2017). Structural Evolution and Electrical Properties of $BaTiO_3$ Doped with Gd^{3+}. *Materials Research*, *20*(2), 538–542. doi:10.1590/1980-5373-mr-2016-0606

Lawley, A., & Murphy, T. F. (2003). Metallography of powder metallurgy materials. *Materials Characterization*, *51*(5), 315–327. doi:10.1016/j.matchar.2004.01.006

Lee, P. W., Trudel, Y., German, R. M., Ferguson, B. L., Eisen, W. B., Mover, K., . . . Davidson, G. M. (1998). ASM handbook. Powder Metal Technologies and Applications, 7, 1146.

Link, R. (1998). Modern Pre-alloyed PM Steels and Advanced Process Technology. *PM World Congress Microstructure*, 596-606.

Liu, Y. B., Lim, S. C., Lu, L., & Lai, M. O. (1994). Recent development in the fabrication of metal matrix-particulate composites using powder metallurgy techniques. *Journal of Materials Science*, *29*(8), 1999–2007. doi:10.1007/BF01154673

Mahade, S., Narayan, K., Govindarajan, S., Björklund, S., Curry, N., & Joshi, S. (2019). Exploiting suspension plasma spraying to deposit wear-resistant carbide coatings. *Materials (Basel)*, *12*(15), 2344. doi:10.3390/ma12152344 PMID:31344804

Makino, Y., Mizuuchi, K., Agari, Y., & Ito, M. (2016). Characterization of Interfaces in Diamond/Metal Composites by Raman Scattering Spectroscopy. *Journal of the Japan Society of Powder and Powder Metallurgy*, *63*(7), 479–483. doi:10.2497/jjspm.63.479

Mirzaali, M. J., Bobbert, F. S. L., Li, Y., & Zadpoor, A. A. (2019). Additive Manufacturing of Metals Using Powder Bed-Based Technologies. In *Additive Manufacturing* (pp. 94–127). CRC Press. doi:10.1201/9780429466236-4

Mitchell, R. J., Rae, C. M. F., & Tin, S. (2005). Grain boundary transformations during isothermal exposure of powder metallurgy nickel base superalloys for turbine disc applications. *Materials Science and Technology*, *21*(1), 125–132. doi:10.1179/174328405X16261

Miyajima, M., Kitamura, K., & Matsumoto, K. (2017). Characterization of Tribochemical Reactions on Steel Surfaces. *Nippon Steel Sumitomo Met Tech Rep*, *114*, 101–107.

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Mocarski, S., Hall, D. W., Chernenkoff, R. A., Yeager, D. A., & McHugh, C. O. (1996). Master alloys to obtain premixed hardenable powder metallurgy steels. *Powder Metallurgy*, *39*(2), 130–137. doi:10.1179/pom.1996.39.2.130

Narasimhan, K. S. (1996). Recent advances in ferrous powder metallurgy. *Advanced Performance Materials*, *3*(1), 7–27. doi:10.1007/BF00136857

Narasimhan, K. S. (2001). Sintering of powder mixtures and the growth of ferrous powder metallurgy. *Materials Chemistry and Physics*, *67*(1-3), 56–65. doi:10.1016/S0254-0584(00)00420-X

Nouicer, E., Benlahreche, F., & Nouicer, A. (2017). Spectroscopic Characterization of Titanium Alloy Surface in a Biological Medium. *Acta Physica Polonica A*, *131*(1), 28–31. doi:10.12693/APhysPolA.131.28

Ordonez, A. A., & Prieto, M. (2012). Technical and methodological aspects of fourier transform infrared spectroscopy in food microbiology research. In *Fourier Transform Infrared Spectroscopy in Food Microbiology* (pp. 1–18). Springer. doi:10.1007/978-1-4614-3813-7_1

Park, J., Lee, S., Kang, S., Jeon, J., Lee, S. H., Kim, H. K., & Choi, H. (2015). Complex effects of alloy composition and porosity on the phase transformations and mechanical properties of powder metallurgy steels. *Powder Technology*, *284*, 459–466. doi:10.1016/j.powtec.2015.07.029

Prince, R. M. R., Selvakumar, N., Arulkirubakaran, D., Sreedharan, C. E. S., Thulasiram, R., & Kumar, R. M. (2020). Surface structural features and wear analysis of a multilayer Ti6Al4V-B_4C thin film coated AISI 1040 steel. *Materials Research Express*, *7*, 1–17.

Rana, A., Singh, B., & Sharma, R. (2018). Raman Study of Ga Doped Ge-S Glassy Alloy. *International Journal of Chemical and Physical Sciences*, *7*, 638–641.

Rath, S., Hsieh, M. L., Etchegoin, P., & Stradling, R. A. (2003). Alloy effects on the Raman spectra of $Si_{1-x}Ge_x$ and calibration protocols for alloy compositions based on polarization measurements. *Semiconductor Science and Technology*, *18*(6), 566–575. doi:10.1088/0268-1242/18/6/330

Reinshagen, J. H., & Witsberger, J. C. (1991). Processing and properties of 400 series PM stainless steels. *Metal Powder Report*, *46*(5), 38–44. doi:10.1016/0026-0657(91)91757-W

Reis, M. A. L. D., Neto, N. M. B., Sousa, M. E. S. D., Araujo, P. T., Simões, S., Vieira, M. F., ... Assuncao, P. D. (2018). Raman spectroscopy fingerprint of stainless steel-MWCNTs nanocomposite processed by ball-milling. *AIP Advances*, *8*(1), 015323. doi:10.1063/1.5018745

Šalak, A., & Selecká, M. (2012). *Manganese in powder metallurgy steels*. Springer Science & Business Media. doi:10.1007/978-1-907343-75-9

Šalak, A., Selecká, M., & Danninger, H. (2005). *Machinability of powder metallurgy steels*. Cambridge International Science Publishing.

Salgado, L., Filho, F. A., Neto, R. L., Rossi, J. L., Colosio, M. A., & Filho, C. H. (2001). P/M high-speed steels for valve seat insert application. *SAE Transactions*, 261–264. doi:10.4271/2001-01-0395

Samal, P., & Newkirk, J. (2015). ASM handbook: Vol. 7. *Powder metallurgy*. ASM International. doi:10.31399/asm.hb.v07.9781627081757

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Schade, C. T., Schaberl, J. W., & Lawley, A. (2008). Stainless Steel AISI Grades for PM Applications. *International Journal of Powder Metallurgy*, *44*(3), 57–67.

Shanmugasundaram, D., & Chandramouli, R. (2009). Tensile and impact behaviour of sinter-forged Cr, Ni and Mo alloyed powder metallurgy steels. *Materials & Design*, *30*(9), 3444–3449. doi:10.1016/j.matdes.2009.03.020

Sheban, M., Abu-Dalo, M., Ababneh, A., & Andreescu, S. (2007). Effect of benzotriazole derivatives on the corrosion of steel in simulated concrete pore solutions. *Anti-Corrosion Methods and Materials*, *54*(3), 135–147. doi:10.1108/00035590710748605

Sierra, M. T. H., Sánchez, M. G. B., Báez, J. E., Camacho, L. D. A., Miranda, J. S. G., & Moreno, K. J. (2019). Improvement Effect of Green Lubricants on the Tribological and Mechanical Performance of 4140 Steel. *Applied Sciences (Basel, Switzerland)*, *9*(22), 4896. doi:10.3390/app9224896

Skoglund, P., Litstrom, O., & Flodin, A. (2013). Improvement of Powder Metallurgy Gears for Engines and Transmissions. *SAE International*, *26*, 1–8. doi:10.4271/2013-32-9102

Smith, B. C. (2011). *Fundamentals of Fourier transform infrared spectroscopy*. CRC Press., doi:10.1201/b10777

Šolic, S., Schauperl, Z., & Tropša, V. (2019). Wear behaviour of TiAlN PVD coating on deep cryogenically treated HSS substrate. *Kovove Mater*, *57*, 429–434.

Stuart, B. H. (2004). *Infrared spectroscopy: Fundamentals and applications*. John Wiley & Sons., doi:10.1002/0470011149

Sułowski, M., & Matusiewicz, P. (2013). Comparison of mechanical properties of Mn-Cr-Mo steels sintered in different conditions. *Diffusion and Defect Data, Solid State Data. Part B, Solid State Phenomena*, *197*, 33–40. doi:10.4028/www.scientific.net/SSP.197.33

Sundararajan, G., Sen, D., & Sivakumar, G. (2005). The tribological behaviour of detonation sprayed coatings: The importance of coating process parameters. *Wear*, *258*(1-4), 377–391. doi:10.1016/j.wear.2004.03.022

Swięch, D., Paluszkiewicz, C., Piergies, N., Pięta, E., Borkowska, U. L., & Kwiatek, W. (2018). Identification of Corrosion Products on Fe and Cu Metals using Spectroscopic Methods. *Acta Physica Polonica A*, *133*(2), 286–288. doi:10.12693/APhysPolA.133.286

Tengzelius, J., & Grinder, O. (2008). Powder Metallurgy in Denmark, Finland, and Sweden. *International Journal of Powder Metallurgy*, *50*(2), 57–66.

Tian, Y., Zhang, S. T., Ma, J. H., & Xie, J. G. (2006). Development and application of abradable sealing coating. *Nonferrous Metals*, *1*, 96–99.

Upadhyay, R. K., & Kumaraswamidhas, L. A. (2014). Surface modification by multilayered W/W2N coating. *Surface Engineering*, *30*(7), 475–482. doi:10.1179/1743294414Y.0000000260

Vaskova, H. (2011). A powerful tool for material identification: Raman spectroscopy. *Int. J. Math. Model. Methods Appl. Sci.*, *5*, 1205–1212.

SEFA CELIK (scelik@istanbul.edu.tr)
Downloaded: 9/13/2020 6:14:08 PM
IP Address: 178.240.37.134

Wang, M. C. (1994). Properties of high density powder forged iron based alloy. *Powder Metallurgy*, *37*(3), 201–205. doi:10.1179/pom.1994.37.3.201

Wang, W. F. (2005). Effect of alloying elements and processing factors on the microstructure and hardness of sintered and induction-hardened Fe–C–Cu alloys. *Materials Science and Engineering A*, *402*(1-2), 92–97. doi:10.1016/j.msea.2005.04.016

Warke, V. S., Sisson, R. D. Jr, & Makhlouf, M. M. (2009). FEA model for predicting the response of powder metallurgy steel components to heat treatment. *Materials Science and Engineering A*, *518*(1-2), 7–15. doi:10.1016/j.msea.2009.04.003

Wu, C., Niu, M., Bao, S., Sun, Y., & Zhang, X. (2020). Friction and Wear Properties of Ni3Si Alloy with Ti Addition at High Temperatures. *Materials (Basel)*, *13*(4), 982. doi:10.3390/ma13040982 PMID:32098307

Xu, Z., He, Z., Song, Y., Fu, X., Rommel, M., Luo, X., Hartmaier, A., Zhang, J., & Fang, F. (2018). Topic review: Application of Raman spectroscopy characterization in micro/nano-machining. *Micromachines*, *9*(7), 361. doi:10.3390/mi9070361 PMID:30424294

Xu, Z., Hodgson, M. A., & Cao, P. (2015). A comparative study of powder metallurgical (PM) and wrought Fe–Mn–Si alloys. *Materials Science and Engineering A*, *630*, 116–124. doi:10.1016/j.msea.2015.02.021

Yang, L., Newton, J., & Fieselmann, B. (1989). Raman Spectroscopy of a. SiGe: H Alloys. *MRS Online Proceedings Library Archive, 149*.

Yu, C. J., Eifert, H. H., Banhart, J., & Baumeister, J. (1998). Metal foaming by a powder metallurgy method: Production, properties and applications. *Materials Research Innovations*, *2*(3), 181–188. doi:10.1007100190050082

Yu, Y., Lindqvist, B., & Tengzelius, J. (2004). Höganäs Chair–an industry/university cooperation. *Powder Metallurgy*, *47*(4), 304–308. doi:10.1179/pom.2004.47.4.304