Titanium and Titanium Alloy Coatings for Corrosion Protection

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Nowadays, long service life is often required because the environmental regulation and labor costs on repairing are expected to become increasingly severe and high. A promising approach to optimize both mechanical properties and corrosion resistance is the use of coating technologies. Titanium and titanium alloys are widely used for corrosion protection because they offer a high chemical resistance against various corrosive media due to a dense self-sealing oxide layer. This paper gives a general review on various surface modification technologies pertaining to titanium and titanium alloys including physical vapor deposition, magnetron sputtering, cold spraying, thermal spraying, and shrouded plasma spraying from the perspective of coating technology. Recent research work has shown that it is a more effective method by the protective titanium or titanium alloys coatings to provide improved corrosion resistance. The proper surface treatment expands the use of titanium and titanium alloys in the aggressive corrosion atmospheres. The recent applications with a gas shroud to deposit titanium and titanium alloy coatings are also discussed in this paper.

Keywords: *Titanium coatings, corrosion resistance, thermal spray, shroud plasma spray*

1. Introduction

Nowadays, long service life is often required because the environmental regulation and labor costs on repairing are expected to become increasingly severe and high. Sometimes the dilemma of materials used in a corrosion environment is characterized by the necessity for improved corrosion resistance, the requirements for mechanical properties and the cost. Measures to improve one property sometimes lead to degradation of the other. Since corrosion attack is mainly limited to the outer region of a component, and very often only localized areas may need protection, a promising approach to optimize both mechanical properties and corrosion resistance is the use of surface modification technologies, particularly coating technologies.

As light metals, titanium and titanium alloys provide high specific strength, exceptional biocompatibility, and excellent corrosion resistance[1-3]. At present, titanium and titanium alloys have been used more and more for corrosion protection because they offer a high chemical resistance against various corrosive media (especially to Chloride-containing) due to a dense self-sealing oxide layer formed immediately when exposed to an oxygen containing atmosphere[4-5]. On the other hand, production steps for titanium and its alloys have to be carried out carefully in inert atmosphere conditions for their affinity of oxygen and other gases. The difficulty in processing makes titanium expensive which hinders a broad use of this metal. So, protective coatings of titanium combined with cheap bulk materials offering the strength and ductility are expect to provide sufficient protection and lower the cost. Research work in the past decades showed that it was a more effective method by the protective titanium or its alloy coatings to provide improved corrosion resistance.

2. Physical Vapor Deposition (PVD)

Physical vapor deposition is processed in vacuum. The target materials are evaporated or sputtered to form atoms, molecules or ions that are subsequently transported to the substrate surface, on which condensation and sometimes some reactions with the materials surface take place leading to film growth. PVD coatings have been paid increasing attention in recent years due to their excellent properties, such as dense structure, good interface bonding and innocuity to environment[6-10]. Unfortunately, pinholes and cracks are often created in PVD coating, and local corrosion occurs in such through thickness defects of these coatings when the corrosive solution attacks the coated sample[10]. Yilbas et al[9] examined the corrosion resistance of plasma nitrided and TiN coated Ti6A14V samples. Ti6Al4V samples were coated by using a PVD technique to obtain uniform TiN coat with 4-6μm thickness, while nitriding was carried out by using a plasma nitriding unit. The potentiodynamic polarization technique was used to measure the corrosion rate and corrosion resistance of the substrates. It was found that TiN coating improves the corrosion properties, but nitriding worsens the corrosion resistance of the substrate. Wu et al[10] deposited a titanium coating on AZ31 magnesium alloy substrate by using PVD. Nitrogen ions were implanted into magnesium alloy prior to titanium coating deposition. The ion implantation induced densification of the original oxide film on the alloy surface with the formation of aluminium nitride and magnesium nitride, as well as an improvement in the adhesion between the coating and the substrate. Therefore, the corrosion resistance of the Ti-coated AZ31 alloy with the above pre-treatment was significantly improved in 3. 5 wt. % NaCl aqueous solution.

3. Magnetron Sputtering

Sputtering is a common method to deposit thin films and its popularity stems from the simplicity of the physical processes involved, versatility, and flexibility. A simple DC glow discharge can be used to sputter conductive targets but radio frequency sputtering is preferred for insulating targets. Magnetron sputtering is one of important sputtering methods. Its sources can be classified as diode devices in which the magnetic fields are used in concert with the cathode surface to form electron traps. The charged particles are confined by a closed magnetic field and high-density plasma is produced in the vicinity of the cathode. This results in a drastic increase in the deposition rate. This sputtering system can deliver large ion currents to the substrates and can be operated under a wide range of pressures. The coatings can be produced on large substrates, even for complex shapes[11,12].

Radjabov et al[13] deposited titanium coatings on steel by magnetron sputtering prior to painting in order to improve the protective ability. The Ti coating was characterized by Rutherford backscattering spectrometry and had a thickness of 3000 A. The corrosion test consisted of immersing the painted samples in a 3% NaCl solution with a pH of 4.5 and an addition of H_2O_2. Their results showed that, in accelerated corrosion tests, paint coatings on surfaces prepared in this way withstood corrosion for periods which were more than an order of magnitude longer than those without surface modification. These coatings also withstood corrosion for significant longer times than paint coatings on phosphatized steel. The advantage of titanium magnetron sputter deposition had been shown for cold-rolled low carbon steels with a real surface micro-profile (unpolished) as an environmentally clean technology for surface treatment of metals prior to painting.

4. Cold Spray

Coating processes using the high-velocity impact of solid particles have been attracting considerable industrial interest in recent years because they can effectively eliminate thermal degradation of the raw materials during processing. The most well-known processes among them are cold spraying, in which metallic powder is accelerated to high velocity by using a supersonic gas nozzle and projected onto a substrate, and rapidly build up as a layer of surface coating, as shown in Figure 1. Upon impact with the target surface, the solid particles undergo plastic deformation and bond to the substrate and each other allowing coatings to be built up rapidly. No melting of the powder occurs and therefore the original powder chemistry can be preserved during spraying[14-16].

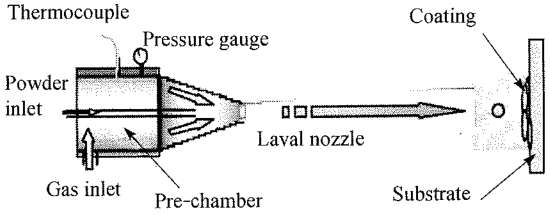

Figure 1. Schematic diagram of cold spray

The main parameter that controls the cold spray process is the critical particle velocity, above which the particles are able to adhere and form the coating. Since particle impacting is very fast, intensive shear plastic deformation takes place at the interface of a powder particle and the substrate. If the impact condition meets a certain criterion such as the particle velocity exceeding a critical value, local heating and softening of the material in this heavily deformed region causes a so-called shear instability, which means local domination of thermal softening over work hardening associated with a discontinuous jump in strain, temperature, and an immediate breakdown of stress[14,15]. Moreover, in this instability region, the viscous flow of softened material generates an out-flowing material jet. All these phenomena can modify the microstructure of the materials and thus influence the bond strength of coatings.

Cold spray of titanium powder has been reported to produce porous but essentially oxygen-free coatings and its density could be improved by post-processing such as machining. Cinca et al[16] studied Ti deposition by using cold gas spraying. The influence of propellant gas temperature, gas pressure, and powder feeding rate had been investigated on cold gas sprayed pure titanium coating onto aluminum substrates. The results showed that cold gas spray is an easy technology to rapidly obtain dense pure titanium coatings. The optimized parameters have been obtained for good porosity and adherence of the deposits. It has been also studied as an alternative to other deposition techniques such as electro-deposition, chemical vapor deposition and vacuum plasma spray, which are more expensive.

Changjiu Li et al[17] also deposited Titanium coating by cold spraying process using nitrogen and helium gases under different temperatures and pressures. The deposition characteristics of the particle in cold spray were studied by the examination of the microstructure evolution of the deposited spot and coating. The effects of the gas type and temperature on the deposition behavior were examined. It was found that the pattern of a sprayed spot in cold spray presented a conical shape. The deposition efficiency of spray particles increases with the increase in gas temperature. Two distinguishable top and inner regions exist in the spot deposit and coating, which are characterized by the porous and dense microstructures. The dense microstructure results from the accumulative effect of tamping on the top porous region by the successive impact of following particles. The tamping effect has great influence on the microstructure of the coating in cold spray.

Kim et al[18] used titanium powder particles to deposit coatings at high velocity on a steel substrate. Titanium particles impacted on the steel substrate in solid state and were not melted during the plastic deformation, subsequent heating, and cooling. Extremely fine grains, several tens of nanometers in size, were observed along the interfacial boundary of the deposited particles known as splats and the substrate, where the most severe deformation had taken place. Therefore, the extremely fine grains observed were formed not from quenching from a melt but from the dynamic recrystallization induced by adiabatic shear instability which played the major role.

5. Thermal Spraying

Thermal spraying is a generic coating technique whereby heat sources like electric arc discharge, combustion, and plasma are used to melt the powder feedstock or wire consumable, enabling any material that melts or partially melts without decomposition, and then projected at speed onto a substrate to build up a coating[19,20], as presented in Figure 2.

Thermal spraying can be divided into following main categories,

- High velocity oxy-fuel (HVOF) spraying
- Plasma spraying
- Arc spraying
- Flame spraying
- Detonation spraying
- Warm spraying

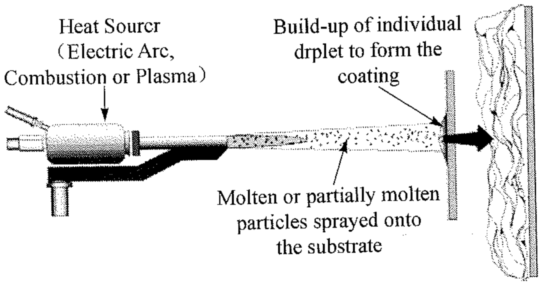

Figure 2. Schematic diagram of coating formation process during thermal spray

Thermal sprayed coatings are formed by successive impingements and inter-bonding materials among the splats, solidified individual molten particles. Thermal spraying can provide thick coatings (approx. thickness range is 20 micrometers to several mm, depending on the process and feedstock), over a large area at high deposition rate as compared to other coating processes such as electroplating, physical and chemical vapor deposition. The density of the coating is dependent on the material, the state of the particle on impact and the particle velocity. Adhesion of the coating to the substrate depends on all of these factors plus the condition of the substrate surface, which must be clean and roughened by grit blasting or machining prior to spraying. The bond between a sprayed coating and the substrate is primarily mechanical, and not metallurgical or fused. Usually coating quality is assessed by measuring its porosity, oxide content, macro and micro-hardness, bond strength and surface roughness.

Jin Kawakita et al[21] developed a modified high velocity oxy-fuel (HVOF) spray process to deposit very dense Ti coatings with high corrosion resistance by introducing a mixing chamber between the combustion chamber and the powder feed port. Nitrogen gas was fed into the mixing chamber to control the temperature of the combustion gas generated in the combustion chamber. By controlling the flow rate of nitrogen, various Ti coatings with different degrees of oxidation and porosities could be fabricated. The densest coating produced by this process with surface polishing treatment maintained excellent corrosion protection over a steel substrate in artificial seawater in a laboratory test over 1 month.

Attempts to improve the sensitivity of crevice corrosion of Ni-base alloys by spraying titanium had been reported[22,23]. McCaw et al[22] fabricated titanium coatings by using high velocity oxy-fuel (HVOF) spraying onto the mating faces of flanges where an o-ring was inserted as a seal. The assembled component was tested for one year by flowing seawater and little corrosion attack was observed in spite of the fact that the coating contained several percent of oxides and porosity. Corrosion resistance of flame sprayed titanium coatings was reported to be satisfactory when proper sealing is applied despite of the significant oxidation within the coatings[23]. This was attributed to the material's low sensitivity to corrosion at the crevice-like features such as oxide-metal and metal-sealant boundaries.

Moreover, production of rough and porous titanium coatings for surgical implants has been another active field of research. Such coatings are expected to act as an interlayer between the bone and the structural implants made of alloys such as Ti6Al4V or stainless steels. Chuan-xian Ding et al[24-26] investigated titanium coatings by using vacuum plasma spraying. The fabricated silver-containing titanium coatings experienced a chemical treatment of silver-containing calcification solution, by which it could be an effective way to introduce antibacterial silver into titanium coating meanwhile maintaining bioactivity for the coating. Results showed that all of the three kinds of coatings exhibited more than 90% antibacterial ratio.

Thermal spraying processes have been widely used for many years throughout all the major engineering industry sectors for component protection and reclamation. Recent equipment and process developments have improved the quality and expanded the potential application range for thermal-sprayed coatings. Titanium and titanium alloys offer a high chemical resistance against various corrosive media. Economical restriction still hinders titanium to be used as construction material outside of special applications in aircraft and medical technology. Generally most applications only deserve a thin protective coating. Consequently, thermal spray processing of titanium is a very challenging topic of research. Thermal spray processes allow combining cheap structural materials with a thin layer of high value material. However, it should be taken into account that titanium is a very reactive metal at high temperatures because of its strong affinity with gases such as oxygen, nitrogen and hydrogen.

6. Shrouded Plasma Spraying

Among all thermal spray technologies plasma spray is considered to be the most flexible coating technique. However, air plasma spraying of corrosion-resistant coatings of titanium is difficult because dense coatings are not produced, and oxidation of these metals increases coating porosity. On the other hand, molecules of nitrogen and oxygen from the air are subjected to thermal dissociation when heated by plasma. This endothermic reaction removes energy from plasma and results in a sharp drop of velocity and temperature. In order to prevent titanium from too much oxidation the spray process has to be carried out in vacuum or inert atmosphere. Within the thermal spray area, low pressure plasma spray (LPPS) or vacuum plasma spray (VPS) has been the promising technique used for titanium deposition because of its inert atmosphere and ability to form dense coatings with low porosity and oxygen content less than 0. 2 mass %[21)]. Corrosion resistance similar to that of bulk Ti has been reported if proper spray parameters including the size of the feedstock powder are optimized[27-29)]. However, this process has limitation of the size of components and is rather expensive.

Shrouded plasma spray can be considered as a useful technology to produce low oxygen containing titanium coatings[21)], as shown in Figure 3. This is to modify plasma spray torches by using a gas-shrouded attachment onto an atmospheric plasma spraying torch[30-37)]. The attachment itself shields the plasma jet as it exits the torch. A gas shroud envelops the plasma jet as it leaves the attachment. The additional shroud gas, usually an inert gas such as argon, is injected around and envelopes the plasma jet, shielding the molten particles from reacting with the surrounding environment, reducing the amount of entrainment of cold and heavy ambient air and delaying the corresponding drop in velocity and temperature, and thus retards particle cooling and reduces oxygen content, oxidation and porosity of the resulting coating. Meanwhile, Gas-shrouded nozzles can extend the hot core of the jet by rearranging the gas flow to increase the dwell time of particles in the plasma. Gas-shrouded attachments for atmospheric plasma spraying were first mentioned in 1978[30)]. Since then, they have been used with some success. The shrouded plasma spraying by using external gas shielding is applicable for large components and when spraying under field conditions.

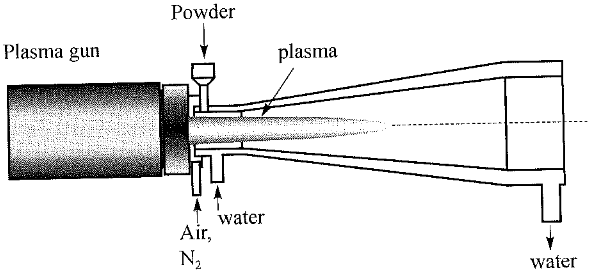

Figure 3. Schematic of a plasma torch equipped with a shroud

Kinos et al[38)] fabricated both titanium and tantalum coatings by Shrouded plasma spraying. In his study, oxidation during plasma spraying was reduced with a shrouding system. Porosity and oxide content also were minimized by optimizing the spraying parameters. However, the coatings still had open porosity and thus were incapable of protecting the substrate material against corrosion in water solutions containing 3% NaCl.

7. Conclusions

As discussed above, we can know that a large variety of different methods have been applied to fabricate titanium and titanium alloy coatings. With regard to practical application, the key issues include adhesion of the coating and long term stability of the coating. Adhesion of coating is a prerequisite for its effectiveness. The deposition process largely determines the adhesion of coatings in the initial stages. 'Hot' processes such as plasma spraying provide coatings with typically good adherence, while coatings produced by 'cold' processes such as sputtering often require post-deposition heat treatment to provide adequate adhesion.

On the other hand, the variety of the deposition techniques used suggested that even contemporary research and development has not yet brought an optimum solution to titanium and titanium coating for corrosion protection. To date, no coating system has been proven usable in long term service. However, coating systems are believed to have a realistic chance for practical application in the near future.

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