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Corrosion Protection of Magnesium Alloys by Cold Spray

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1. Introduction

Magnesium is the lightest of all structural metals, being 35% lighter than aluminum and 78% lighter than steel. As a constituent of many minerals, it represents about 2% of mineral deposits and 0.13% of seawater. The lightweight characteristics, high strength-to-weight ratio and wide availability make magnesium alloys ideal for production of weight-sensitive components such as those in aircraft, cars, light trucks, and other transportation modes.
Ever since the extraction of magnesium from its ores was made possible in commercial quantities by 1920, magnesium alloys have been employed to manufacture components in racing cars. In the 1930's the popular Volkswagen Beetle started using magnesium castings. Later in the 60's, there was a surge in the use of magnesium castings in military aircraft [1], particularly rotorcraft in order to further reduce weight while improving performance. By 1971, over 18 kilograms of the metal had been installed in the Beetle's powertrain.

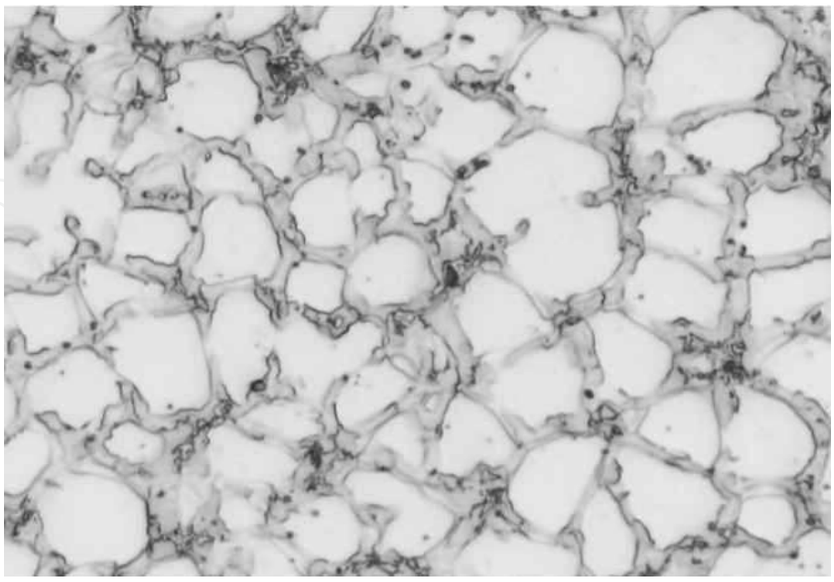


Fig. 1. Corrosion damage in magnesium AM60 alloys showing the preferential attack on the primary (alpha) phase leaving a network of Al-rich beta-phase on the corroded surface.

However, when all vehicles are considered, the percentage of magnesium alloys used in mass-produced vehicles is relatively low, with an average of less than 5 Kg in a typical vehicle. The main reasons for the reluctance to use magnesium in mass-produced vehicles are related to its limitations in corrosion resistance and high temperature (creep) performance. Pure magnesium readily reacts in the presence of oxygen and water producing magnesium hydroxide. Unlike other similar metals, such as aluminum, the passivation film on magnesium could become very unstable in many environments, including neutral or acid ranges of pH. Additionally, magnesium is anodic to most engineering metals, making it very prone to severe galvanic corrosion when coupled with dissimilar metals, such as steel.

Over the years, there have been significant advances in alloy development and as a result, new improved magnesium alloys have become commercially available. This has been possible due to additions of aluminum, zinc, manganese, for better corrosion resistance as well as additions of zirconium, rare earths, thorium, and silver for better elevated temperature mechanical properties all, in combination with the reduction of harmful impurities such as iron, nickel, copper during the alloy making process.

In recent years, the demand for lighter, more fuel-efficient vehicles, has spurred increased interest by automakers to consider the use of magnesium in more critical components such as engine blocks, engine cradles and transmission housings (See Figure 2). This has led to the formation of special interests industrial consortiums to develop solutions to the technical and economical challenges facing wide applications of magnesium and its alloys [2,3]. It has also been reported [4] that costly magnesium components in aircraft often experience significant corrosion issues which often require premature removal from service affecting the readiness, safety and cost of maintenance of aircraft (see Figure 3).

General corrosion rates of modern high-grade magnesium alloys, especially when adequately coated, are acceptable in most applications. Galvanic corrosion, however, remains a challenge in many situations. Therefore, design considerations need to be made in order to avoid galvanic contact with other dissimilar metals. This is particularly important

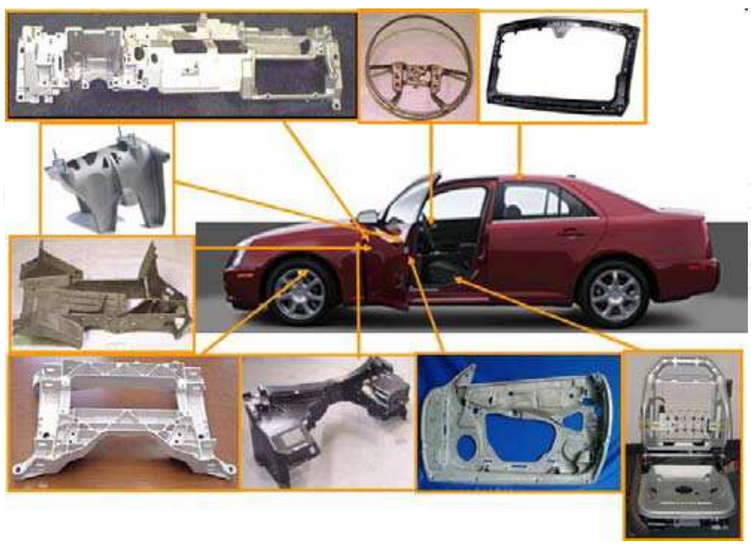


Fig. 2. Automotive applications for Magnesium alloys (Picture courtesy of Dr. Alan A. Luo, General Motors, "Magnesium Front End Development - USAMP Activities", paper presented at the SAE World Congress, Detroit, MI, April 18, 2007).

in components exposed to exterior environments such as road salts and slurries which can easily damage conventional organic coatings, creating sites for rapid electrochemical dissolution of magnesium. This is the case of many dissimilar joints, where salts and debris accumulate around bolts and crevices causing localized galvanic corrosion (See Figure 4).



Fig. 3. Corrosion damage in magnesium alloy castings used in rotorcraft.



Fig. 4. Magnesium alloy casting fastened to a steel bracket using a coated steel bolt. The interface between the steel bracket and the magnesium casting surface is prone to galvanic corrosion.

2. Current methods pf protection for galvanic and general corrosion

Besides the development of more corrosion resistant magnesium alloys, current methods for general corrosion protection of magnesium include conversion and organic coatings. By conversion coatings, the surface of a magnesium component is forced to chemically react in a special chemical bath to produce a uniform and continuous film that protects the material underneath from further corroding. Conversion coatings can be achieved by electrochemical reactions, chemical immersion, or by heat treatments. One of these methods is anodizing, where the formation of complex magnesium oxide films is induced under controlled high-voltage anodic polarization conditions. There are a number of proprietary commercial anodizing techniques including Tagnite, Keronite, Magoxide, and Anomag.

Chromate coatings are excellent for general corrosion protection, however, with the recent restrictions on the use of hexavalent chromium during processing, most of these solutions have been banned, and alternative chromate-free chemistries have evolved [5]. Other low-cost conversion coatings include Alodine and Magpass, which produce a type of protective

chemistries on the magnesium surface in a way very similar to phosphates and chromates; these are done by immersion in specially formulated chemical solutions. Any of these techniques can also be combined with a finishing sealer and then a polymeric coat. For less demanding service, organic coatings are often preferred including epoxy, poly-amide, poly-ester, acrylic, Latex, poly-urethane, and paraffin based products, which can be applied as powders or as water-based paintable solutions.

Both conversion and organic coatings often require stringent surface preparations (water rinsing, alkaline treatment, acid pickling), and post-treatments (neutralization, water rinsing, drying); in most cases, these treatments carry environmental and health risks [6]. Organic coatings are also prone to localized failure due to poor workmanship or chipping damage, which may result in localized, severe corrosion.

These factors drive the continuous evolution of new corrosion protection strategies [5]. Although any of these techniques can be acceptable to prevent general corrosion of magnesium, they lack the ability to locally protect magnesium in the area of galvanic attack [2]. Galvanic corrosion typically occurs within 5 mm of fasteners or dissimilar interfaces. Therefore, one of the methods to combat galvanic attack is to use isolation materials to prevent direct electrical contact between bare magnesium and the dissimilar metal, increasing the electrolytic resistance of the corrosion cell. Where a high torque load is required, such isolation materials must be made of special metals or inorganic substances that take the loading without failure. In fact, the use of aluminum washers in dissimilar joints, despite the associated costs, has been a standard practice with automakers in an attempt to stop galvanic corrosion of magnesium. The effectiveness of such method depends on the chemical composition of the washer (See Figure 5).

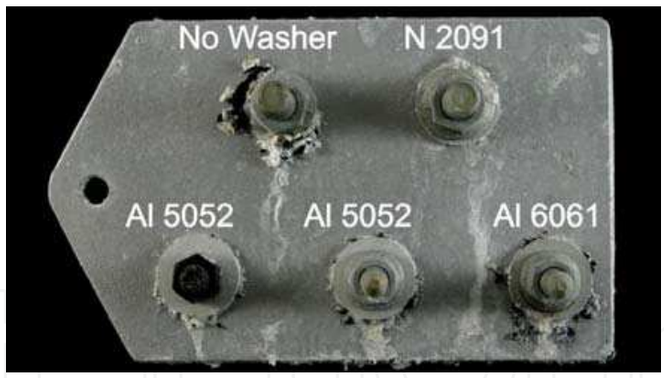


Fig. 5. Conversion-treated and powder-coated magnesium AM60 alloy plate after 40 days testing following the GM9540P standard. This sample shows different levels of corrosion when utilizing aluminum washers of various compositions coupled with different nuts. Note that, even in powder-coated magnesium, severe galvanic corrosion may still occur if no aluminum washer is utilized [7].

3. Cold spray technology

In conventional thermal spray processes the elevated process temperatures expose both the coating and substrate materials to rapid oxidation, metallurgical transformations and adverse residual stresses. Unlike thermal spray, cold spray is capable of producing dense and thick coatings exhibiting extremely low porosity (< 0.5%), while avoiding oxidation,

phase transformations and adverse residual stresses for a wide selection of metals, cermets, and other material mixtures.

Cold spray is a solid-state spraying process in which the coating materials are not melted in the spray gun (such as in conventional thermal spray); instead, the kinetic energy of fast-travelling solid particles is converted into interfacial deformation and localized heat upon impact with the substrate [8], producing a combination of mechanical interlock and metallurgical bonding. The bonding mechanisms for cold spray can be quite complex. It is generally accepted that spray-able materials require a critical amount of energy (related to the velocity of the particles and impact temperature) for effective bonding to occur [9]. Around the particle-substrate collision interface, high strain rate deformation occurs producing microscopic protrusion of material and localized heating which may lead to metallurgical bonding [8].

The original concept for cold spray was published early in the 1900's [10]. However, it was not until the 80's that a new generation of researchers at the Institute of Theoretical and Applied Mechanics in Novosibirsk, Russia, rediscover the "cold spray" phenomenon and designed a device for accelerating powder particles to produce thick dense coatings [11,12,13]. Later on, early in the 90's, researchers at the Obninsk Center for Powder Spraying (OCPS), Obninsk, Russia, introduced new developments [14], which enabled the fabrication of low-cost portable cold spray equipment suitable for a wide number of repair and restoration applications. The latter was the foundation of one of the lead manufacturers of cold spray equipment in Russia. Widespread commercial development of the cold spray technology outside Russia started only in the early 2000s. Ever since, there has been increased interest in the cold spray technology as demonstrated by the exponential growth of publications and patent applications [10]. Today, all of the cold spray methods may be categorized within three main families of processes, namely high pressure cold spray, low pressure cold spray, and shockwave-induced spraying.

In low pressure cold spray (CGSP-L), pressurized air, nitrogen, or helium (5 - 17 bar) is heated (up to 550^{o}C) and forced through a converging-diverging nozzle (*DeLaval* nozzle) where the gas accelerates to about 600 m/s . The feedstock is introduced downstream into

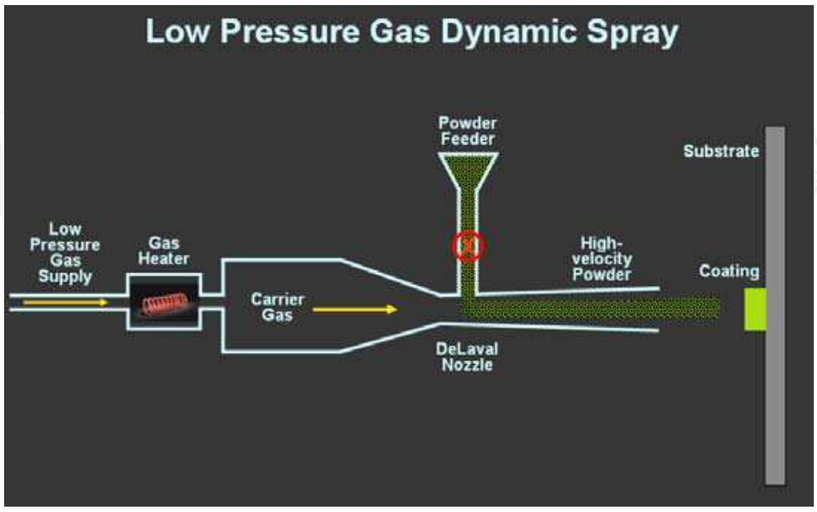


Fig. 6. Principles of low-pressure cold spray



Fig. 7. Commercial low-pressure cold spray equipment (Picture courtesy of OCPS, Obninsk, Russia).



Fig. 8. Commercial low-pressure cold spray equipment (Picture courtesy of SST, a Division of CenterLine (Windsor) Ltd.).

the divergent section of the nozzle at low pressures [5,8] (see Figure 6). Subsequently, CGSP-L systems can be simple, portable, and relatively inexpensive to operate. Low pressure systems are best suited for spraying ductile metals such as aluminum, copper, zinc, tin, nickel, or even titanium onto a variety of metallic and ceramic substrates, including magnesium. Pure metals can be mixed with aluminum oxide or other ceramic constituents to further enhance spray-ability, producing a coating of high density and bond strength. Today, there are a number of commercially available low pressure cold spray systems in the market (See figures 7 and 8).

High pressure cold spray (CGSP-H) can use helium or nitrogen as carrier gases at higher pressures (up to 55 bar). The gases can be accelerated to supersonic speeds (up to 1200 m/s) by heating them up to 1000ºC and forcing them through a *DeLaval* nozzle. In this case, the

feedstock powder is introduced in the high pressure side of, prior to the nozzle throat [11,12] (See Figure 9). The levels of energy that can be attained are sufficient to spray higher temperature less ductile materials including 316L s steels, Nickel alloys, Tantalum, Titanium, and Molybdenum. However, these high energy levels can only be achieved at the expense of more equipment complexity, higher operational costs, and lower portability.

In shockwave Induced Spraying [1,9,15] (SISP), fast opening/closing of a control valve downstream of a high pressure gas source generates trains of shockwaves that compress the gas in front of them as they travel through a straight nozzle. This creates pulses (10-30Hz) of heated supersonic wave fronts, where each front can be matched with a determined amount of powder in the nozzle. As the gas pulse passes through the powder dispensing zone, the powder is picked up, heated (below its melting point) and accelerated down the nozzle (See Figures 10 and 11). In contrast to traditional cold spray, a converging-diverging *DeLaval* nozzle is not required and therefore, materials can be accelerated and heated at the same time. This allows the effective deposition of other materials such as stainless steels (300 and 400 series), aluminum alloys, nickel alloys, titanium, WC-Co / WC-Cr, copper alloys, and brazing alloys.

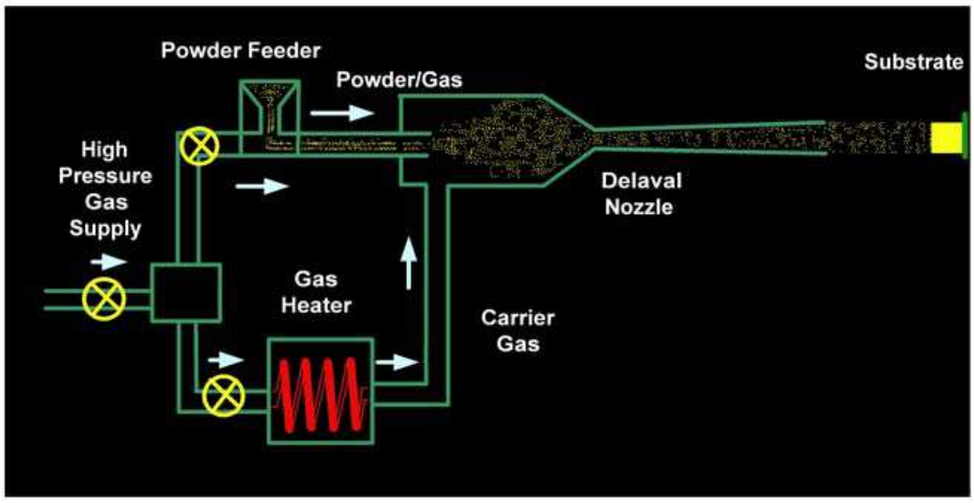


Fig. 9. Principles of high-pressure cold spray

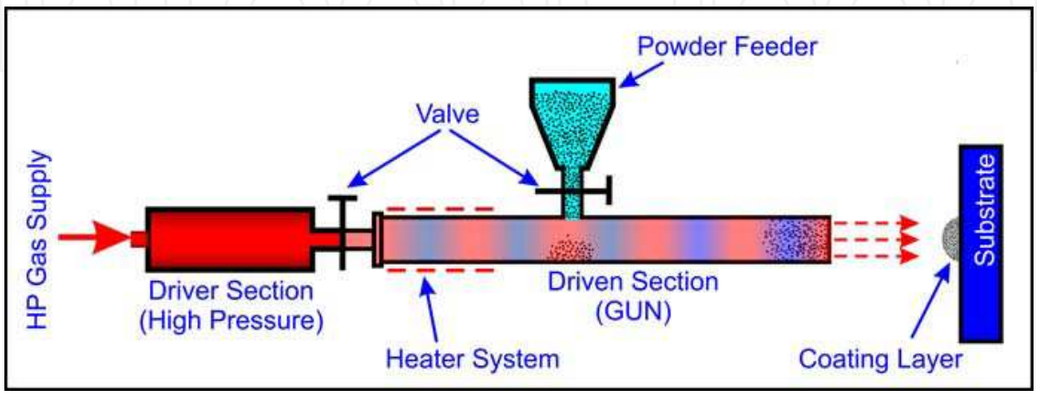


Fig. 10. Working principle for shockwave induced spraying



Fig. 11. Shockwave Induced Spraying (SISP) equipment or "Waverider". (Picture courtesy of CenterLine (Windsor) Ltd.).

4. Corrosion protection by cold spray

While there are numerous applications for cold spray [15], metallic coatings for localized corrosion protection come up as the most attractive application for this technology, given the economical, technical and environmental challenges posed by traditional coating methods. Because of its passivation behavior, Aluminum has superior general corrosion resistance compared to other metals. Cold spray represents a cost- effective technique to deposit thick metallic aluminum coatings on magnesium alloy surfaces with minimum surface preparation and without mechanically or thermally compromising the substrate properties (see Figure 12). The presence of aluminum on the surface of magnesium has been shown to reduce the general and galvanic corrosion tendency of magnesium components (see Figure 13a). In galvanic corrosion, only small areas surrounding the dissimilar interface require protection, for which cold spray represents an innovative alternative to the use of washers and insulating bushings (see Figure 13b).

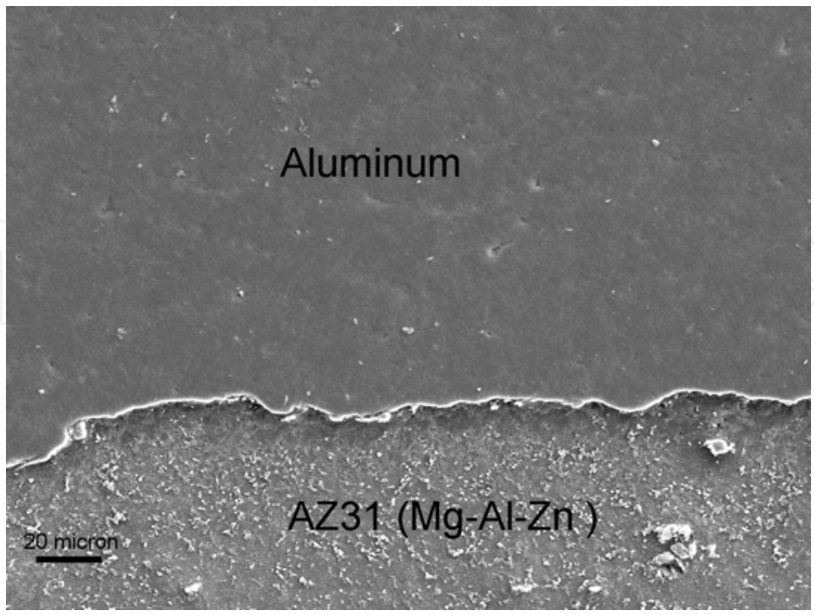


Fig. 12. Scanning electron micrograph illustrating a high-density aluminum cold spray deposit on magnesium alloy AZ31.



(a) (b)

Fig. 13. (a) Magnesium casting alloy AE44 plate on which the central area was selectively cold sprayed with aluminum, after 100 hours of salt-spray exposure, as per ASTM B117. Note that the cold-sprayed area (between the three washers) is free of corrosion attack. (Courtesy of CANMET-MTL, Natural Resources Canada) (b) Magnesium alloy AM60 plate, where the area surrounding the fastener hole was selectively cold sprayed with aluminum, after 1000 hours corrosion test, as per ASTM B117. (Courtesy of *NRC Integrated Manufacturing Technologies Institute*, London, Ontario, Canada)

5. Conclusion

Corrosion protection by cold spray is a revolutionary method whereby protective metals can be directly and locally applied to magnesium alloys to reduce or eliminate general or galvanic corrosion in specific areas. Cold spray represents a viable alternative to traditional methods for localized galvanic corrosion protection of magnesium and its alloys. The use of Al alloy powder as the coating materials means a good galvanic compatibility between the coating and the underlying substrate. The relatively soft nature of Al powder also leads to high-degree of deformation in the powder particle during the deposition process producing a dense coating layer with low permeabilityto corrosion agents such as salts.

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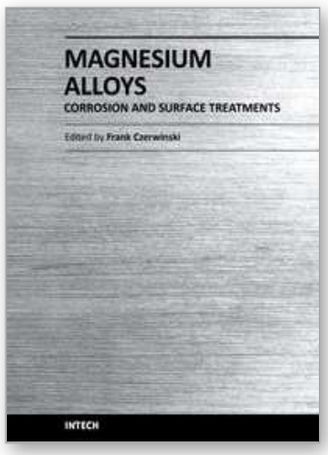
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Magnesium Alloys - Corrosion and Surface Treatments

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A resistance of magnesium alloys to surface degradation is paramount for their applications in automotive, aerospace, consumer electronics and general-purpose markets. An emphasis of this book is on oxidation, corrosion and surface modifications, designed to enhance the alloy surface stability. It covers a nature of oxides grown at elevated temperatures and oxidation characteristics of selected alloys along with elements of general and electrochemical corrosion. Medical applications are considered that explore bio-compatibility of magnesium alloys. Also techniques of surface modifications, designed to improve not only corrosion resistance but also corrosion fatigue, wear and other behaviors, are described. The book represents a valuable resource for scientists and engineers from academia and industry.

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