# INVESTIGATE THE CORROSION PROPERTIES OF STELLITE COATED ON AZ91D ALLOY BY PLASMA SPRAY TECHNIQUE

### by

# Mathivanan KANNAN<sup>a\*</sup>, Thirumalaikumarasamy DURAISAMY<sup>a</sup>, Thirumal PATTABI<sup>a</sup>, and Ashokkumar MOHANKUMAR<sup>b</sup>

<sup>a</sup>Department of Mechanical Engineering, Government College of Engineering, Bargur, Krishnagiri, Tamil Nadu, India

<sup>b</sup>Department of Manufacturing Engineering, Annamalai University, Chidambaram, India

Original scientific paper https://doi.org/10.2298/TSCI200722209K

Stellite alloys are primarily preferred in various component manufacturing industries due to its magnificent mechanical and electrochemical properties. The stellite powder is deposited over the materials by various thermal spray methods in industries. This research proposed investigating the micro-structure and corrosion properties of stellite powder that is deposited on an AZ91D magnesium alloy substrate by atmospheric plasma spraying process. The SEM, optical microscopy, and atomic force microscopy are typical of the coatings. Immersion experiments in sodium chloride conditions are conducted at varying pH levels, chloride ion concentration, and exposure time. In addition, XRD examined the phase change properties of the powder and sprayed condition of coatings along with corrosion testing. The corrosion experiments were conducted to establish several regression models based on the central composite design and the response surface process. The accuracy of the regression models was sufficient to allow correlations between input parameters and responses through variance analysis. It was found that the pH value significantly influences the corrosion behaviour of stellite coatings followed by other parameters such as chloride ion concentration and exposure time, even in corrosion tests, plasma-sprayed coatings performed better.

Key words: corrosion properties, plasma spray, stellite coating, AZ19D alloy

#### Introduction

Generally, Mg alloys are preferred in aerospace manufacturing industries for its greater strength and good shock resistance. Various surface treatments can improve material properties through various deposition methods, oxidation processes, and spraying techniques.

Distinctive alloys are often used to enhance the life expectancy of the coating machine elements in service. Stellite is a Co-Cr-WC alloy with outstanding corrosion and wear resistance over a wide temperature range [1]. Chromium coating can increase me-

<sup>\*</sup>Corresponding author, e-mail: mathikan25@gmail.com

chanical strength and also increase corrosion protection. Tungsten coating increases the Mg alloy strength, which was in vanes and blades of turbines [2-4]. Stellite material is the combination of cobalt and chromium elements, which is mostly preferred for the coating over the application materials by plasma spray coating technique and various vapour deposition methods [5, 6]. The AISI309L is used to manufacturing the turbine plates, which have good corrosion resistance by stellite coating [4]. The AISI1015 steel is one type of low carbon steel, which is used to prepare high precision mechanical components. The Co-Cr alloy-based coating deposited over AISI1015 steel using micro laser welding [6-8]. In high temperature applications, stellite is the most suitable material, Especially in various manufacturing industries. The CO<sub>2</sub> laser continuously works at 2.5 kW over the stellite 6 and AISI304 SS. The specimen were investigated by thermal cycle test and crack analysis [9-11]. Based on the literature work, most of the research proves the stellite materials used to improve the corrosion resistance and thermal properties. This paper discussed the AZ91D selected as the base material and deposited the stellite coating over the AZ91D alloy under the immersion environment. Ion concentration and microstructural analysis were carried out the prepared specimen.

# **Experimental procedures**

The AZ91D Mg alloy contains with Al-Zn-Mn composition. The AZ91D Mg alloy sheet was selected as the workpiece, which was prepared in the required specific shape (16 mm  $\times$  15 mm  $\times$  4 mm) shown in fig. 1. Before the coating process, the AZ91D alloy was cleaned by ultrasonic bath hand-dried operations. The cleaning operations were carried out at 40 bar and 300 °C. The stellite-21 powder is selected for coating over the Mg alloy for improving the thermal characteristics and good corrosion resistance. The grain size of the stellite-21 powder is 20 mm shown in fig. 2. The micro-structure of the coating specimen captured by optical microscopy is shown in fig. 3.



Figure 1. The AZ91D sheet



Figure 2. Stellite-21 powder



Figure 3. Optical micrograph of coating

For all deposits, the coating thickness was maintained at  $200 \pm 15$  mm. This was done by the following procedure. The feedstock's chemical composition was 28 Cr, 5.5 Mo, 2.5 Ni, 0.3 C, 1 Si, Festell 2, W 0.5, and Cobalt balance. The AZ91D substratum plate of a Mg alloy of 20504 mm<sup>3</sup> was used as a substratum. Alumina was sandblasted on the substratum. The samples were cut as-sprayed and placed in the resin. In accordance with the ASTM E3-95, the installed samples were prepared polished by 6 µm and 1 µm monocrystalline diamond suspensions. Optical and SEM examined the polished crosssections to determine the impact of the spraying process on the micro-structure of coatings, the percentage of porosity, and the consistency of the coating. The coating thickness was calculated using captured image analysis software on 200 ranges of magnified OM

912

micrographs. The picture was taken at the cross-section of the coating and recorded an average of five measurements.

Measurement of the Vickers microhardness profile on the cross-section of the coating was performed. This calculation has been replicated in three lines, and their mean value is recorded. The gap of 100  $\mu$ m between the indentations was chosen to prevent a reciprocal effect of indented points against the findings. For 15 seconds, the load of 100 grf has been applied.

Immersion corrosion testing was conducted according to ASTM standard G31-72 to determine the corrosion properties of stellite-21 coated AZ91D alloys. The corrosion resistance ability of the stellite-coated samples were examined at various chloride ion concentrations process, pH weight methods, and exposure time using an immersion test in NaCl solution. Two coated specimens were prepared and tested for each experimental case.

#### **Results and discussion**

#### Micro-structure

Figure 4 illustrates the SEM image of the pre-alloyed Stellite 6 superalloy powder used in the experiments. It was seen in the SEM images that Stellite 6 powders had a spherical form. The results of EDAX is shown in fig. 5, Ni has the maximum contribution at the range of 20 wt.%, fig. 5.



Figure 4. The SEM images of stellite powder



Figure 5. The EDAX analysis of stellite

Figure 6 demonstrates the micro-structure of the as-sprayed coating. The coating is made of single splats. During the grit blasting process, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles were periodically detected at the boundary between the coating and the substratum embedded in the substrate material.

Analysis of micro-structure and energy-dispersive X-ray spectroscopy patterns revealed that the stellite coating formed had a lamellar structure consisting of phases  $\alpha$ -Co and  $\ddot{y}$ -Co and carbides rich in chromium, fig. 7. The existence of two allotropic modifications of pure Co and its alloys (high temperature fcc phase and low temperature hcp phase) is described in the literature.



Figure 6. Micro-structure of the as-sprayed coatin



2 4 6 8 10 12 14 16 18 20 Figure 7. The EDS analysis of coating

### Immersion corrosion test

# Effect of pH value on the corrosion rate of immersion corrosion

This study investigates the impact of pH level, chloride ion concentration, and the constant exposure time at 0.6 M, 120 hours, while the pH level was changed from 3-11. Figure 8 represented compare the impact of pH value on the corrosion rate.



Figure 9 displays the SEM photos of the Mg alloy corroded uncoated and coated AZ91D immersed in NaCl solution. A brown Tarnish colour on the surface of the uncoated magnesium alloy AZ91D at a low pH value. This change in colour because of the advancement of the uniform dezincification and the sharp separation line between the dark side of the materials. In the presence of MgCl2 in the solution, the dezincification was happened, which could be proof of the conversion or dissolution of Mg+ into the electrolyte. These chloride layers are reason for destroying the Mg film, fig. 9(a), particu-

larly in acidic solutions, which lead to higher corrosion rates. Corrosion in stellite coatings occurs mainly by dissolving the Cr process and removing W particles in the matrix. Deletion of W particles in the matrix of the Fe-Cr

914

Kannan, M., et al.: Investigate the Corrosion Properties of Stellite
THERMAL SCIENCE: Year 2022, Vol. 26, No. 2A, pp. 911-920

binder is shown in fig. 9(b). The presence of oxidizers at lower pH values increases the oxidation reactions in acidic solutions, resulting in a maximum corrosion rate. At the neutral pH level, the coating does not show true passivity, meaning in an entire matrix, corrosion film is not formed continuously. The Cr was eliminated from the Fe-Cr matrix, while chloride was exposed and form the  $Cr_2O_3$ . At a higher pH level, the proof of corrosion product formation is a high-density gold coloured layer formed over the surface of coated and uncoated and coated material surface, as shown in fig. 9(c). Iron and chromium appear to form the chloride layers while exposed to chloride ion conditions. Oxides of chromium and iron were gradually lost, and corrosion was observed.



Figure 9(a). Uncoated AZ91D Mg alloy pH value = 3 Corrosion time = 120 hours Cl - concentration = 0.6 M



Figure 9(b). Coated AZ91D Mg alloy pH value = 3 Corrosion time = 120 hours Cl - concentration = 0.6 M



Figure 9(c). Uncoated AZ91D Mg alloy pH value = 11 Corrosion time = 120 hours Cl – concentration = 0.6 M



Figure 9(d). Coated AZ91D Mg alloy pH value = 11 Corrosion time = 120 hours Cl - concentration = 0.6 M

Stellite-coated AZ91D Mg alloy exposed to environmentally containing chloride, the deposits the chloride layer on the binding metals cannot kill the greater corrosion protection. The corrosion rate in magnesium alloy AZ91D coated thus shows low. In fig. 9(d), but some porosity and pits occurred because of these electrolytes, galvanic coupling between metals and corrosion is reported in the coating and forms. Study of atomic microscopy was performed on the top surface of the corroded specimens to understand the process of material removal from the surface. Figure 9(a) shows the pH-value impact of uncoated AZ91D Mg alloy on corroded surfaces. It is inferred from the picture that the Mg alloy AZ91D experiences higher material removal and can be visualised in the higher Ra shape, while fig. 9(b) the coated AZ91D Mg alloy has a lower surface roughness value relative to the bare substrate and its material loss. Although the depth of the pit is shallow in the coated surface, it also affects the area in the coating that is exposed to corrosion media. Low corrosion rate was observed at higher pH level, but the degree of undulation is minimal, figs. 9(c) and 9(d).

The pH value has an inverse proportional relationship with the corrosion rate from the fundamentals; *i.e.* if the pH value increases, the corrosion rate decreases. The highest corrosion rate was observed at pH 3 and at neutral pH, the corrosion rate remained approximately constant and the alkaline solution showed a comparatively low corrosion rate. It is proposed that when compared with low concentration in neutral and alkaline solutions the pH effect in corrosion rate is high at higher concentration. Accordingly, corrosion domains of selective chromium leaching and dissolution of both iron and chromium can be found in the AZ91D magnesium alloy.

# Impact of chloride ion concentration on the corrosion rate of immersion corrosion

The influence of chloride ion concentration on the corrosion rate of uncoated and coated AZ91D Mg alloy in fig. 10. In the experimental process, the pH value was 7 Hr, and the exposure time is 120 hours, But the chloride ion was at a different level (0.2 to 1 M).

Figures 11(a)-11(d) represent the chloride iron concentration in various concentration levels like 0.2 and 1. The minimum amount of macropores be seen in fig. 11(a). The chloride ion-containing level is very high to the uncoated AZ91D, and small chloride ions are the reason for less effect over the region. Light brown color indicates the matrix corrosion shown in fig. 11(b). It seems obvious that the corrosion may occur in the thick hard phase matrix around the splat boundary, which is the reason for a macro trap. The pit appeared to by lower concentration of chloride ions. But the pit narrowed and became

deeper in higher concentration. Even the depth of the pit increases as the solution concentration increases, as displayed in fig. 11(c). Figure 11(d) represents that micro galvanic attack leads the microscale level pits over the coating surface.



Figure 10. Impact of chloride ion concentration on corrosion rate



Figure 11(a). Uncoated AZ91D Mg alloy pH value = 7 Corrosion time = 48 hours Cl - concentration = 0.2 M



Figure 11(b). Coated AZ91D Mg alloy pH value = 7 Corrosion time= 48 hours Cl - concentration = 0.2 M

#### Impact of exposure time on the corrosion rate

The impact of different exposure times on corrosion rate is denoted in fig. 12. The result was observed the material loss is directly proportional to the exposure time maximum materials loss occurred by high exposure time. The average materials surface



Figure 11(c). Coated AZ91D Mg alloy pH value = 7 Corrosion time= 48 hours Cl - concentration = 0.2 M



Figure 11(d). Coated AZ91D Mg alloy pH value = 7 Corrosion time = 48 hours Cl - concentration = 1 M





area of the pit is larger, which means that there are few exceptionally large pits in the corroded zone in fig. 13(a) because of extreme localized deep-corrosion attack, carbide phase loss was observed at lower exposure time. Figure 13(b), many cracks occurred on the film surface. A small number of corrosion pits were found on the surface of Mg alloy AZ91D after 168 hours of immersion. In the NaCl solution, the corrosion layer on the surface of the specimen is considerably compacted, thereby effectively preventing further reaction. Consequently, the film's growth rate remains sluggish and creates shallower dimples of corrosion, fig. 13(c). Figure 13(d) represents the coated Mg alloy corroded uniformly due to eliminating the carbide phase from the matrix.

Kannan, M., *et al.*: Investigate the Corrosion Properties of Stellite ... THERMAL SCIENCE: Year 2022, Vol. 26, No. 2A, pp. 911-920



Figure 13(a). Uncoated AZ91D Mg alloy pH value = 7 Corrosion time =36 hours Cl - concentration = 0.6 M



Figure 13(b). Coated AZ91D Mg alloy pH value = 7 Corrosion time = 36 hours Cl - concentration = 0.6 M



Figure 13(c). Uncoated AZ91D Mg alloy pH value = 7 Corrosion time = 168 hours Cl - concentration = 0.6 M



Figure 13(d). Coated AZ91D Mg alloy pH value = 7 Corrosion time = 168 hours Cl - concentration = 0.6 M

#### Conclusion

This report draws the following significant conclusions. The relationship was developed to investigate the corrosion rate of AZ91D Mg alloy plasma-sprayed stellite coatings, integrating chloride ion concentrations, pH value, and immersion times. The defined partnership will effectively predict the 95% confidence level of corrosion of stellite coatings on AZ91D Mg alloy. The stellite coatings do not offer sufficient corrosion protection to Mg alloy substratum in longer exposures in acidic NaCl solution, pH 3. Stellite coatings were found to be highly susceptible to localised degradation, and could not provide adequate corrosion resistance to Mg alloy substrates in solutions containing higher chloride concentrations.

#### References

- Zhang, L., et al., Wear and Corrosion Resistance of Cold Sprayed Cu-Based Composite Coatings on Magnesium Substrate, J. Therm. Spray. Tech., 28 (2019), July, pp. 1212-1224
- [2] Sidhu, T. S., et al., Hot Corrosion Studies of HVOF NiCrBSi and Stellite-6 Coatings on a Ni-Based Superalloy in an Actual Industrial Environment of a Coal Fired Boiler, Surf. Coat.Technol., 201 (2006), 3-4, pp. 1602-1610
- [3] Mirshekari Daee, G. R., et al., Effect of Interlayers on the Microstructure and Wear Resistance of Stellite 6 Coatings Deposited on AISI 420 Stainless Steel by GTAW Technique, Surf. Interface., 9 (2017), Dec., pp. 79-92
- [4] Rajeev, G. P., *et al.*, Hardfacing of AISI H13 Tool Steel with Stellite 21 Alloy Using Cold Metal Transfer Welding Process, *Surf. Coat.Technol.*, 326 (2017), Part A, pp. 63-71
- [5] Apay, S., Gulen, B., Wear Properties of AISI 1015 Steel Coated with Stellite 6 by Microlaser Welding, *Mater. & Des.*, 55 (2014), Mar., pp. 1-8
- [6] Dinesh, S., et al., Modelling and Optimization of Machining Parameters for Turning Automotive Shafts Using RSM and Grey Relational Analysis, Int. J. Vehicle Structures & Systems, 12 (2020), 4, pp. 375-379
- [7] Houdkova, S., et al., Microstructure and Sliding Wear Properties of HVOF Sprayed, Laser Remelted and Laser Clad Stellite 6 Coatings, Surf. Coat. Technol., 318 (2017), Sept., pp. 129-141
- [8] Frenk, A., Kurz, W., Microstructural Effects on the Sliding Wear Resistance of a Cobalt-Based Alloy, Wear, 174 (1994), pp. 81-89
- [9] Luo, F., et al., Characteristics of Stellite 6 Deposited by Supersonic Laser Deposition Under Optimized Parameters, J.Iron& Steel Res.Int., 20 (2013), pp. 52-57.
- [10] Rao, K. P., et al., Friction Surfaced Stellite 6 Coatings, Mater. Charact., 70 (2012), pp. 111-116
- [11] Sakthivel, P., et al., Analysis of Centerless Grinding Process Parameters in Machining SS 316 L Steel for Improved Productivity, in: Advances in Industrial Automation and Smart Manufacturing, Lecture notes in Mechanical Engineering, Springer, Singapore, 2021, pp. 447-453
- [12] Yu, H., et al., A Comparison of the Tribo-Mechanical Properties of a Wear Resistant Cobalt-Based Alloy Produced by Different Manufacturing Processes, J.of. Tribol., 129 (2007), July, pp. 586-594

920