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Electrochemical corrosion behaviour of HVOF sprayed iron-based amorphous metallic coatings on AISI 316 stainless steel in an NaCl solution

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Abstract:

New thermally sprayed amorphous metallic coatings have been developed recently that may provide a viable coating option for fluid handling equipment such as propellers, impellers and pumps. They possess the inherent risk of flow-dependent erosion-corrosion problems. In this investigation, iron based (Fe) amorphous coatings were deposited on AISI 316 stainless steel substrate by the high velocity oxy-fuel (HVOF) spraying process, and the coating microstructure was characterised using an optical microscope and scanning electron microscopy. The Fe-based amorphous coating consisted of an amorphous phase, an absence of dislocations, a nanocrystalline phase, less porosity and high hardness. The corrosion behaviour of the substrate and Fe-based amorphous coatings were evaluated by means of electrochemical tests in 3.5 wt.% NaCl solution. Three kinds of electrochemical tests were employed to identify the corrosion resistance of the coating and substrate. The results showed that the Fe₃₀Cr₂₅Mn₅Mo₂₀W₁₀B₅C₃Si₂ amorphous metallic coating had a superior corrosion resistance than 316 stainless steel. It was attributed to the amorphous structure and the presence of the corrosion resistant element chromium (Cr).

Keywords: corrosion resistance, high velocity oxy fuel spraying, iron-based amorphous metallic coating

DOI: 10.1515/jmbm-2018-0015

1 Introduction

Corrosion costs India's Department of Defence billions of dollars every year, with an immense quantity of material in various structures undergoing corrosion. For example, in addition to fluid and seawater piping, ballast tanks and propulsions systems, approximately 345 million square feet (105 million square metre) of structures aboard naval ships and crafts require costly corrosion control measures. The use of advanced corrosion-resistant materials to prevent the continuous degradation of this massive surface area would be extremely beneficial. The iron (Fe)-based corrosion-resistant, amorphous-metal coatings under development may prove of importance for applications on ships [1].

The possible advantages of amorphous metals have been recognised for some time. Such materials could also be used to coat the entire outer surface of containers for the transportation and long-term storage of spent nuclear fuel, or to protect welds and heat affected zones, thereby preventing exposure to environments that might cause stress corrosion cracking [2]. In the future, it may be possible to substitute such high-performance Fe-based materials for more expensive alloys, thereby enabling cost savings in a wide variety of industrial applications. It should be noted that thermal spray ceramic coatings have also been investigated for such applications.

Fe-based amorphous materials are good candidates for use in various industrial sectors, due to their low cost with high hardness, high corrosion and wear resistance [3]. Several thermal spraying techniques such as plasma spraying, twin wires arc spraying, cold gas dynamic spraying and high velocity oxygen fuel spraying have been used to deposit Fe-based amorphous metallic coatings in recent investigations. Among the thermal spraying techniques, high velocity oxygen fuel spraying has played a significant role in coating preparation because of its high velocity of operation and ability to produce coatings with low porosity and high hardness.

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Bobzin et al. studied the wire arc sprayed Fe-based coatings and the results of their investigation showed that the adding further elements like Cr, carbon (C), silicon (Si), aluminium (Al) and magnesium (Mg) should enhance the forming of the amorphous phase [4]. The appropriate anneal treatment could minimise the porosity and maximise the hardness of the arc-sprayed Fe-based amorphous coating significantly, which showed a superior abrasive wear resistance than arc-sprayed coating [5]. Fe-based coating consisted of an amorphous structure with fine nanocrystals and had a good erosion resistance under high temperature environments [6]. Similarly, Shan-Lin Wang et al. reported that Fe-based amorphous metallic coating was deposited with the powder mixtures of Fe-based metallic glass of $\text{Fe}_{80.6} \text{C}_{1.8} \text{Si}_{2.0} \text{B}_{1.3} \text{P}_{5.7} \text{Cr}_{2.5} \text{Mo}_{5.1} \text{Al}_{1.2}$ (wt.%) synthesised with industrial raw materials, nickel chromium (NiCr) alloy and the tungsten carbide (WC) particle by high velocity oxygen fuel (HVOF) spraying and its corrosion resistance was evaluated, compared with 304L stainless steel, in a real-time application as an anti-corrosive and anti-wear material in various corrosive environments [7]. However, the investigations on the corrosion behaviour of HVOF sprayed Fe-based amorphous coatings are scant. In this study $\text{Fe}_{30} \text{Cr}_{25} \text{Mn}_5 \text{Mo}_{20} \text{W}_{10} \text{B}_5 \text{C}_3 \text{Si}_2$ amorphous metallic coating was deposited on AISI 316 stainless steel by an HVOF spraying process. The microstructures, mechanical properties and corrosion resistance of the coatings and uncoated 316 stainless steel were also characterised.

2 Experimental procedure

2.1 Materials and coating procedure

The coating material used in this investigation was a commercially available atomised Fe-based amorphous powder (Figure 1) with particle size ranging between -53 and $+15 \mu\text{m}$ (SHS 7574). Due to the spherical shape of the particle there is a good flowability during spraying. The Fe-based amorphous powder was directly sprayed on to the grit-blasted substrate with a surface roughness R_a ($5 \mu\text{m}$). AISI 316 stainless steel, widely used in many marine components, was used as the substrate material and the optical micrograph of the substrate is shown in Figure 2. The chemical composition of the substrate material and coating material was found by the optical emission spectroscopy method and is presented in Table 1. An HVOF (HIPOJET-2700, Metallizing Equipment Co., Jodhpur, India) spraying system was used to deposit Fe-based amorphous coatings with a thickness of $300\text{--}350 \mu\text{m}$. The thickness of the coatings was measured using a digital micrometer (with an accuracy of 0.001 mm) for each and every run conditions. The optimised HVOF process parameters to attain the coating with optimal porosity and maximum hardness as shown in Table 2 [8].

Figure 1: SEM of an Fe-based amorphous metallic powder.

Figure 2: Light optical micrograph of the substrate material.

Table 1: Chemical composition (wt.%) of substrate and coating material.

Elements	C	Si	Cr	Ni	Mn	P	Mo	S	W	Fe	B
Substrate material	0.08	1	18	14	2	0.045	3	0.03	–	Bal	–
Coating material	3	2	25	–	5	–	20	–	10	Bal	5

Table 2: Optimised process parameters of HVOF spraying.

Factor	Notation	Unit	Levels
Oxygen flow rate	O	lpm	252
LPG flow rate	L	lpm	64
Powder feed rate	F	gpm	32
Spray distance	S	mm	230
Carrier gas flow rate	C	lpm	13

2.2 Porosity analysis

As per the procedure laid out in ASTM B 276 standard [9], the porosity measurement was carried out on the well-polished cross-sectional area of the coating, using an optical microscope (MIL-7100; Meiji Techno Co., Ltd, Chikumazawa, Japan) equipped with image analysing software (Metal Vision Version 6). In this study, the images captured under 1000× magnification by optical microscopy were chosen for porosity analysis as desired features like open pores and network of cracks were properly revealed. Initially, a $400 \times 400 \mu\text{m}^2$ area was selected on the polished cross-section of the coating and the image was analysed. The same procedure was repeated at five random locations to find the average percentage volume of porosity (explained in Figure 3).

Figure 3: Measure the porosity level using computer image analysing software.

2.2 Coating characterisation

The phase composition of the coatings was determined by X-ray diffraction (XRD) with Cu K α radiation. The microhardness of Fe-based amorphous coatings was recorded using a Vickers micro-hardness tester (HMV-2T; Shimadzu, Japan). A dwell time of 15 s and a load of 300 g were used to measure the hardness. Hardness was measured on the mid thickness of the coating at 15 different locations and the average value was used for further analysis.

2.3 Corrosion test

The corrosion resistance of the coatings was evaluated using the electrochemical test with the help of the GAMRY 600 electrochemical system. Before the test, the coatings were degreased in an ultrasonic bath and dried in air, following the guidelines of the standard ASTM G1-03 [10]. The test was conducted in 3.5 wt.% sodium chloride (NaCl) solution with a specimen electrode as a working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a platinum wire as a counter electrode. To ensure the accuracy of the measurement, the remaining surface was covered with epoxy resin, leaving an area of about 1 cm² of the coating exposed to the 3.5 wt.% NaCl aqueous solution. Three kinds of electrochemical tests, namely the open circuit potential (OCP) test, the potentiodynamic polarisation test and the electrochemical impedance spectroscopy (EIS) test, were carried out according to ASTM G3-89 standard [11]. The immersion time of the OCP tests was 1 h. As the OCP became steady, potentiodynamic polarisation curves were recorded at a sweep rate of 0.5 mV/s. Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were evaluated at the intersection point of linear fits to the anodic and cathodic polarisation curves, according to the Tafel extrapolation technique. Electrochemical impedance studies were done by applying a sinusoidal potential excitation amplitude of 10 mV at the OCP over frequencies ranging from 100 kHz to 10 MHz. All measurements were repeated at least 3 times to ensure the accuracy of the result.

3 Results and discussion

3.1 Microstructure and mechanical property

The Fe-based amorphous powder and the as-sprayed coatings were examined by XRD and are presented in Figure 4. XRD patterns show a broad diffraction hump at $2\theta = 40\text{--}50^\circ$ without any Bragg peaks. From the figure, the broad diffraction hump can be seen without any refraction from crystal phases indicating the coating is mostly amorphous [12], [13], [14]. HVOF coatings have a superior surface finish compared to other thermal spray processes and the microstructure reveals the plastic deformation of the unmelted particles result in rapid

solidification of droplets upon substrate impingement. The optimised process parameter and appropriate particle size of powder leads to proper melting of in-flight particles to achieve efficient surface splat formation of the coating on the 316 stainless steel substrate. As the Fe-based amorphous coating was deposited at an optimised process condition, it exhibited less porosity and high hardness as shown in Figure 5 and Figure 6.

Figure 4: XRD pattern analysis of (A) powder and (B) coating.

Figure 5: SEM micrograph of the coating deposited using optimised HVOF spray conditions.

Figure 6: Indentation images of coatings produced (C) under optimum conditions with other conditions (A, B).

3.2 Electrochemical corrosion behaviour

Figure 7 shows the OCP curves for the stainless steel and Fe-based amorphous coatings obtained in 3.5 wt.% NaCl solution. The OCP stabilised after a duration of 1 h. After 1 h, the OCP values of stainless steel are -184 mV vs. SCE while Fe-based amorphous coating had an OCP value of 85 mV vs. SCE.

Figure 7: OCP curves for an Fe-based amorphous coating.

A higher OCP value of the coating indicated a superior corrosion resistance of the coating than that of the 316 SS substrate. The higher the amorphous phase fraction of the coating, the higher was the OCP value. The increase of the amorphous phase fraction limits the galvanic effect possibility between the two phases which inevitably led to a low alloying content phase corrosion [15], [16], [17]. It can be found that an Fe-based amorphous coating could provide the best protection to the substrate from corrosion as it had most compact and amorphous structure with desirable alloying elements such as molybdenum (Mo) and Si for better passivity as compared to that of 316 stainless steel [18], [19], [20], [21]. The potentiodynamic polarisation curves of 316SS and HVOF sprayed Fe-based amorphous coatings are shown in Figure 8. The electrochemical parameters are calculated and listed in Table 3. The pitting potential potentials (E_{pit}) of 316 stainless steel were about -157 mV vs. SCE. The Fe-based amorphous coating exhibited a pitting potential of 1012 mV vs. SCE, due to its desirable passivating alloying elements such as Cr, Mo and Si being uniformly distributed in the coating [22], [23], [24]. The oxides could hinder the formation of a dense passive film and even became the diffusion channels for electrolytes to cause inner corrosion [25]. The corrosion current densities (I_{corr}) of 316 stainless steel and the Fe-based amorphous coating were almost of same value viz., 1.12 and $1.33 \mu\text{A}/\text{cm}^2$. However, the pitting potential of Fe-based amorphous coating exhibited a much higher value than that of 316 stainless steel. First, it was attributed to the homogeneous structure of the amorphous and low porosity. Second, the element Cr was employed to protect the coating from dissolution by forming a Cr-rich passive film. The stability of the Cr-rich passive film was further enhanced by the presence of Mo [26]. The amorphous structure of the coating contributed to the high corrosion resistance because of the absence of surface heterogeneities such as segregation, dislocations and grain boundaries. The excellent corrosion resistance of the HVOF sprayed Fe-based amorphous metallic coating was further verified by the EIS results. Figure 9 shows the EIS results of HVOF sprayed Fe-based amorphous coatings and 316 stainless steel, with the help of the Nyquist plot. It was apparent from figure that all impedance spectra was revealed as a capacitive semicircle at the whole frequency, but the diameters of the capacitive semicircles were different. It indicated that the corrosion rate was different for the coated and uncoated specimens. In general, the diameter of the capacitive semicircle is associated with the charge transfer resistance, i.e. the corrosion resistance in the corrosion process [27]. It was seen that 316 stainless

steel had a small semicircle, and HVOF sprayed Fe-based amorphous coatings had the largest semicircles. The HVOF sprayed Fe-based amorphous coatings had the slowest corrosion rate and the best corrosion resistance. An equivalent circuit presented in Figure 9 could be used to fit the experimental Nyquist plot of the coating and stainless steel materials. It proved further that HVOF sprayed Fe-based amorphous coatings had better corrosion resistance than 316 stainless steel.

Figure 8: Potentiostatic polarisation curves in 3.5 wt.% NaCl solutions for 316 stainless steel and an Fe-based amorphous coating.

Table 3: Corrosion current density (I_{corr}) and pitting potentials (E_{pit}) of AMC coatings and 316 stainless steel.

Samples	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{pit} (mV)
316 SS	1.12	157
Coating	1.33	1012

Figure 9: Nyquist diagrams for 316 stainless steel and an Fe-based amorphous coating.

Figure 10 shows the surface morphologies of the uncoated 316 stainless steel and HVOF sprayed Fe-based amorphous coated specimens after potentiodynamic polarisation measurement. As expected the Fe-based amorphous coating does not degrade through pitting and exhibited general corrosion morphology. However, 316 stainless steel exhibited severe pitting corrosion. Figure 10A shows the surface morphology of the 316 stainless steel. Due to lower Mo content and possible grain boundary depletion of Cr due to C content greater than 0.03%, in 316 stainless steel, pits initiate easily and grow rapidly in 3.5 wt.% NaCl with any repassivation possibility [28], [29]. Figure 10B shows the HVOF sprayed Fe-based amorphous metallic coating after potentiodynamic polarisation had a compact and homogeneous structure. Due to the amorphous nature of the coating with some nanocrystalline grains and without any heterogeneity due to crystalline grains and grain boundaries, the coating exhibited good passivity (as explained in the next section) [30], [31], [32].

Figure 10: Surface morphologies after potentiodynamic polarisation in 3.5 (wt.%) NaCl solution (A) uncoated AISI 316 stainless steel specimen (B) HVOF sprayed Fe-based amorphous coated specimen.

Figure 11 shows the substrate and coated samples immersed in 3.5 wt.% NaCl solution for 1 h. In the coating, many oxides form during the spraying deposition, and some limited porosities, microcracks and semi-molten particles are present in the coating. The chemical composition of the coating by energy-dispersive X-ray (EDAX) analysis is B1.68-C 5.58-Si 0.04-Cr 0.14-Mn 0.01-Fe 0.40-Mo 0.09 at.%. When the coatings are immersed in 3.5 wt.% NaCl solution, this oxide dissolution, which creates defects, pores and cracks, facilitates the electrolyte penetration, and the corrosion of substrate is caused by the attack by chloride ions, leading to the formation of a large amount of pitting corrosion products. The corrosion products can block the pores/cracks of the coating. However, for this sample, it seems that oxide dissolution and some active sites were maintained in the regions where the electrolyte was in contact with the substrate. The amorphous coating shows a higher OCP value. It suggests a slow electrolyte penetration through the coating, delaying its contact with the substrate. This can be attributed to a denser and more homogeneous structure formed because of the high compressed air flow used during the thermal spray process, which produces a more compact coating. Therefore, the corrosion resistance of the amorphous coatings in the corrosive environments containing chloride ions to induce pitting, such as NaCl solutions, is again superior to 316L stainless steel materials.

Figure 11: EDAX analysis of substrate and Fe-based amorphous coatings after potentiodynamic polarisation in 3.5 wt.% NaCl solution.

4 Conclusion

- I. The passivation of the coating is wider than the uncoated material during the potentiodynamic polarisation test, which means the corrosion resistance of the coated material possesses high corrosion resistance.
- II. From the Nyquist plot a semi-circular shape was obtained for uncoated and coated samples. A large magnitude of the impedance was observed in the amorphous coated sample and a small magnitude of the impedance was noted on the uncoated sample. Hence, the amorphous coated sample shows an enhanced corrosion resistance.
- III. The Fe-based amorphous coating exhibits superior corrosion resistance than 316 stainless steel due to the stability of the Cr-rich passive film present in the coating which is further enhanced by the presence of Mo. Preparation of coatings with high amorphous fractions and minimum amounts of coating defects and oxides is very important for a highly anti-corrosive coating with applications in a 3.5 wt.% NaCl solution.

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