Passivation Behavior of Iron-Based Amorphous Coatings in NaCl and H2SO4 Solutions: Postprint

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Abstract

An FeCrMoMnWBCSi amorphous alloy coating was prepared by high-velocity oxygen fuel (HVOF) spraying. The microstructure of the amorphous coating, the composition of the passive film, and the passivation behavior of the coating in NaCl and H2SO4 media of various concentrations were investigated and analyzed, and compared with 304 stainless steel and ND steel. The results indicate that the amorphous coating exhibits a wide passivation range and strong resistance to passive film breakdown due to the high content of Cr, Mo, and W oxides in the passive film; however, the presence of pores reduces its uniform corrosion resistance. The passive film breakdown potential of 304 stainless steel is relatively low and closely correlated with the NaCl solution concentration. Both 304 stainless steel and ND steel only display relatively stable passivation characteristics in concentrated H2SO4 solution; the amorphous structure facilitates the formation of a more stable passive film on the coating in dilute H2SO4 solution. Thinner coatings (200 m) possess higher amorphous phase content, form thicker passive films, and exhibit superior corrosion resistance.

Full Text

Preamble

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Passivation Behavior of Fe-Based Amorphous Metallic Coating in NaCl and H2SO4 Solutions

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Abstract

Amorphous alloy is a new type of material that exhibits exceptional properties or combinations of properties that are often not achievable in conventional crystalline materials. Fe-based amorphous alloys have attracted significant attention over the last few decades because of their low cost and enhanced mechanical performance. However, they are more suitable for industrial application as coatings due to their fatal disadvantage of poor toughness. High velocity oxygen-fuel (HVOF) spraying is an effective method for preparing amorphous metallic coatings (AMCs), as individual droplets are cooled at rates around 10^7 K/s—much higher than the critical cooling rate required for amorphous alloy formation during thermal spraying. Fe-based AMCs obtained by HVOF spraying are important industrial materials due to their high glass-forming ability and exceptional performance, including excellent corrosion resistance, high hardness, and superior wear resistance.

In this work, FeCrMoMnWBCSi AMCs were prepared by HVOF thermal spray. The microstructure and amorphous characteristics of the coatings were characterized by SEM and XRD. The electrochemical corrosion behavior of AMCs was investigated in various concentrations of NaCl and H2SO4 solutions and compared with that of 304 stainless steel and ND steel. The surface films formed on the materials after immersion in the two solutions were analyzed by XPS. The results indicated that HVOF-sprayed Fe-based AMCs exhibited a dense layered structure, high amorphous phase content, and low porosity. The composite structure of AMCs consisted of some nanocrystallite phases embedded in an amorphous matrix. AMCs demonstrated better resistance to pitting corrosion but relatively lower uniform corrosion resistance due to porosity, while the pitting potential of 304 stainless steel was sensitive to NaCl concentration. XPS results revealed that the presence of Cr, Mo, and W oxides in the passive film of AMCs contributed to better corrosion resistance. The enrichment of Mo^{4+} oxides on the surface favored the formation of a more stable and protective layer, which could be assumed responsible for the observed high stability of the passive film. Diminishing or avoiding pores may be beneficial for further improving the pitting corrosion resistance of AMCs in NaCl solution. In all cases, AMCs showed better resistance to H2SO4 solution corrosion due to the high stability of their passive films. 304 stainless steel and ND steel presented stable passivation behavior only in high-concentration H2SO4 solution. In lower-concentration H2SO4 solutions, the amorphous structure of thinner coatings could facilitate the formation of thicker passivation films and lead to higher corrosion resistance. The corrosion resistance of AMCs in H2SO4 solution could be enhanced significantly by forming a high amorphous phase content.

KEY WORDS amorphous metallic coating (AMC), high-velocity oxygen-fuel (HVOF), passivation, electrochemical corrosion

Introduction

Amorphous alloys are rigid solid materials far from equilibrium with disordered structures that exhibit many unique physical and chemical properties. Due to the absence of defects such as grain boundaries and segregation found in crystalline materials, they demonstrate superior performance unattainable in conventional alloys, including near-theoretical high strength, hardness, elastic limit, excellent magnetic isotropy, and outstanding corrosion resistance. Since the 1980s, amorphous alloys have been a key research focus in materials science and condensed matter physics worldwide, hailed as the third revolution in materials following steel and plastics [1]. Since the development of the first bulk Fe-based amorphous alloy $Fe_{73}Al_5Ga_2P_{11}C_5B_4$ in 1995, Fe-based amorphous alloys have remained a hot research topic [2]. Their high strength, corrosion resistance, high glass-forming ability, low cost, and simple preparation process make them promising candidates for novel engineering materials.

Like all amorphous alloys, high brittleness and low plasticity limit the application of Fe-based amorphous alloys as structural materials. However, preparing them as coating materials could broaden their application scope [3–6]. High velocity oxygen-fuel (HVOF) spraying technology enables the preparation of amorphous metallic coatings (AMCs) and has gradually become a research focus. HVOF, developed in the 1980s, is a thermal spray technology that increases droplet jet velocity while reducing particle overheating, producing coatings with low porosity that are widely used for corrosion-resistant alloy coatings [3]. While typical amorphous formation requires critical cooling rates above 10^6 K/s, HVOF thermal spraying can achieve cooling rates around 10^7 K/s, allowing most alloy compositions to be sprayed above the critical rate to form amorphous structures. Additionally, crystallization and oxidation during thermal spraying are difficult to avoid; however, crystalline phases increase coating hardness, which benefits wear resistance, making AMCs particularly suitable for harsh environments involving corrosive wear [7–10]. Preparing highly corrosion- and wear-resistant Fe-based amorphous coatings using HVOF technology has become a breakthrough for the industrial application of amorphous alloys, promising to become a highly valuable industrial material that could bring enormous benefits [11].

As engineering applications of amorphous materials advance, attention to their corrosion issues becomes particularly important. The single-phase homogeneous structural characteristics and flexible compositional design of amorphous alloys provide a new perspective for in-depth corrosion research. The corrosion resistance of amorphous alloys depends primarily on their chemical homogeneity and passivation capability. Fe-based amorphous alloys exhibit excellent passivation characteristics in corrosive media such as NaOH [12], NaCl [8,13–14], HCl [15], and H2SO4 [13,16], showing wide passivation regions in polarization curves without pitting even when anodically polarized to 1 V (vs. Ag/AgCl). Although amorphous coatings have the same composition as bulk amorphous alloys, their different microstructural features result in distinct passivation behaviors that have not yet been systematically evaluated. Since the formation and dissolution processes of passive films are directly related to the nature of the test solution, studying the stability of passive films in different corrosive solutions is crucial for understanding the passivation mechanism of amorphous coatings.

This work prepared Fe-based amorphous coatings using HVOF, analyzed their microstructure and organization, investigated the passivation performance of amorphous coatings in NaCl and H2SO4 solutions using electrochemical workstations, and analyzed the structure and composition of passive films on the coating surfaces to determine the passivation stability mechanism of amorphous coatings in these two corrosive media.

1. Experimental Methods

A master alloy with composition $Fe_{54\cdot2}Cr_{18\cdot3}Mo_{13\cdot7}Mn_{2\cdot0}W_{6\cdot0}B_{3\cdot3}C_{1\cdot1}Si_{1\cdot4}$ (mass fraction) was prepared by electromagnetic induction melting. Amorphous powders were then produced by gas atomization, with particle sizes less than 45 m.

HVOF spraying was performed using a DJ2700 system with 304 stainless steel (06Cr19Ni10) as the substrate. The spray distance was 250 mm, powder feed rate was 20 g/min, and oxygen/fuel ratio was 4.6:1. Coating thicknesses of 200 m and 400 m were prepared, designated as AMCs1 and AMCs2, respectively. Additionally, amorphous ribbons with the same composition were prepared by melt spinning, with widths of 2–3 mm and thicknesses of about 50 m.

X-ray diffraction (XRD) analysis of the amorphous ribbons and coatings was conducted using a Rigaku D/max2400 diffractometer. The microstructure of the amorphous coatings was observed using a Quanta600 scanning electron microscope (SEM). Glass transition and crystallization behavior were examined using a Netzsch-404C high-temperature differential scanning calorimeter (DSC) at heating and cooling rates of 20 K/min.

Passivation performance tests were conducted on an EG&G PAR 2273 electrochemical workstation using a three-electrode system, with a Pt electrode as the auxiliary electrode, the sample as the working electrode, and a saturated calomel electrode (SCE) as the reference electrode. The corrosive media were NaCl and H2SO4 solutions. Comparative materials included 304 stainless steel (06Cr19Ni10) and ND steel (09CrCuSb) for sulfuric acid resistance. During electrochemical testing, potentiodynamic polarization curves were measured at a scan rate of 0.1667 mV/s after the open-circuit potential stabilized. Electrochemical impedance spectroscopy (EIS) was performed using a 10 mV perturbation potential over a frequency range of 10^4 to 10^{-2} Hz. The pitting potential of stainless steel was determined according to GB/T17899-1999 standard, while the passive film breakdown potential of coatings was defined as the potential at which current density increased sharply on the polarization curve.

X-ray photoelectron spectroscopy (XPS) surface analysis was performed on an ESCALAB 250 surface analyzer using an Al target as the X-ray source. XPS testing was conducted on amorphous coatings, 304 stainless steel, and ND steel after immersion corrosion in NaCl and H2SO4 solutions for 10 h.

2.1 Microstructure and Structural Characteristics of Amorphous Coatings

[Figure 1: see original paper] shows the DSC curves of the amorphous ribbon and coatings. Both the ribbon and coatings exhibit distinct glass transition points, supercooled liquid regions, and crystallization exothermic peaks, indicating they underwent glass transition and crystallization processes. The amorphous phase content varied with coating thickness: AMCs1 (200 m) contained 74.9% amorphous phase, while AMCs2 (400 m) contained 70.1%, showing a decreasing trend with increasing thickness due to localized heating of deposited coatings by accumulated heat during spraying [4,17].

The XRD spectra in [Figure 2: see original paper] reveal that the amorphous ribbon shows diffuse diffraction peaks in the 40°–50° range, indicating a fully amorphous structure. In contrast, the coating spectra exhibit some sharp crystalline peaks, which are more pronounced in the thicker coating. The crystalline phases consist primarily of carbides, borides, and minimal oxides.

The surface and cross-sectional microstructural characteristics of the amorphous coatings are shown in [Figure 3: see original paper]. The as-sprayed surfaces are generally uniformly melted, with a few locally unmelted or semi-melted particles that tend to create pores near and between these particles (Figs. 3a and d). Polished surfaces contain numerous pores (Figs. 3b and e). The cross-sections exhibit typical layered features from HVOF processing (Figs. 3c and f), with large-scale pores between layers and some gray oxide regions. Comparing the two coatings, the number of unmelted particles, porosity, and oxidation degree increase with thickness. The amorphous coatings show good, dense bonding with the substrate without obvious interfacial defects.

2.2 Passivation Behavior of Amorphous Coatings in NaCl Solution

[Figure 4: see original paper] presents the potentiodynamic polarization curves and EIS spectra of the amorphous ribbon, coatings, and 304 stainless steel in 1% and 3% NaCl solutions (mass fraction). Both the amorphous ribbon and coatings show distinct passivation characteristics, with similar passive film breakdown potentials around 1.1 V, reflecting comparable resistance to localized corrosion. In contrast, 304 stainless steel exhibits lower pitting potentials that decrease with increasing NaCl concentration, from 0.4 V in 1% NaCl to 0.1 V in 3% NaCl, indicating reduced resistance to localized corrosion. The amorphous coatings demonstrate significantly higher resistance to localized corrosion than 304 stainless steel in NaCl solutions.

The passive current densities of both the amorphous ribbon and coatings increase with NaCl concentration. The ribbon's passive current density increases from 10^{-6} A/cm^2 to 10^{-5} A/cm^2, while the coatings increase from 10^{-4} A/cm^2 to 10^{-3} A/cm^2. Compared with the ribbon of the same composition, the coatings exhibit higher passive current densities in the same medium, attributed to the effect of coating porosity on uniform corrosion resistance. Reducing porosity is key to improving the uniform corrosion resistance of amorphous coatings [4]. 304 stainless steel shows the lowest passive current density ($<10^{-6}$ A/cm^2) with minimal variation across NaCl concentrations, indicating the highest uniform corrosion resistance in the tested concentration range. In solutions of the same concentration, the thicker coating AMCs2 exhibits lower passive current density than the thinner coating AMCs1, resulting from enhanced diffusion barrier effects against Cl^- penetration in thicker coatings [9,18].

The Nyquist plots in Figs. 4b and d show that all materials exhibit a semicircular capacitive arc characteristic in the high-frequency region, with larger arcs reflecting higher corrosion resistance [19]. In 1% NaCl solution (Fig. 4b), the corrosion resistance ranking is: ribbon > 304 stainless steel > thick coating > thin coating. This order remains unchanged with increasing NaCl concentration, though all impedance values decrease (Fig. 4d), indicating that higher NaCl concentration reduces corrosion resistance, consistent with the polarization curve analysis. Both amorphous coatings and ribbons demonstrate rapid and stable passivation characteristics with wide passivation regions and excellent resistance to passive film breakdown. In contrast, 304 stainless steel shows a narrower passivation region with lower pitting potential and poor resistance to passive film breakdown. These differences are closely related to the distinct amorphous structures and passive film compositions.

2.3 Passivation Behavior of Amorphous Coatings in H2SO4 Solution

[Figure 5: see original paper] shows the potentiodynamic polarization curves and EIS spectra of the amorphous ribbon, coatings, 304 stainless steel, and ND steel in 20% and 50% H2SO4 solutions (mass fraction). At lower H2SO4 concentrations (Fig. 5a), the amorphous coatings exhibit typical passivation characteristics with wide and stable passivation regions, where the thin coating AMCs1 shows lower passive current density than the thick coating AMCs2. The amorphous ribbon has the lowest passive current density. The passive film breakdown potential of 304 stainless steel is similar to that of the amorphous ribbon and coatings (approximately 1.1 V), indicating comparable corrosion resistance in H2SO4 solution. However, 304 stainless steel shows a significantly widened passivation region with active dissolution followed by passivation in the anodic polarization curve, reflecting an extremely unstable passive film. ND steel only forms a passive film at potentials above 0.5 V with small current density, where high potentials favor the formation of more stable passive films on ND steel. Additionally, its higher passive film breakdown potential (1.6 V) indicates superior corrosion resistance compared to the amorphous ribbon, coatings, and 304 stainless steel.

At higher H2SO4 concentrations (Fig. 5c), all materials form relatively stable passivation regions with similar passive film breakdown potentials to those in dilute H2SO4 solution, while passive current densities decrease by the same order of magnitude. Notably, the thin and thick amorphous coatings show opposite corrosion tendencies: AMCs1 exhibits lower passive current density in dilute H2SO4 but higher in concentrated H2SO4. The EIS spectra in Figs. 5b and d are consistent with the polarization results, showing that AMCs1 has higher impedance values in dilute H2SO4 solution (Fig. 5b).

Evidently, conventional crystalline materials such as 304 stainless steel and ND steel exhibit stable passivation characteristics only in concentrated H2SO4 solution, primarily due to the strong oxidizing nature of H2SO4, which enhances oxidation with increasing concentration [13]. In crystalline materials, defects such as grain boundaries and second phases tend to accumulate more corrosion products, thereby inhibiting further corrosion medium attack [20]. In dilute H2SO4, thin amorphous coatings form more stable passive films, indicating that H2SO4 medium favors improved passivation stability of amorphous coatings. This results from two factors: first, thin amorphous coatings have higher amorphous phase content (approximately 74.9%), which benefits passivation stability; more importantly, it relates to the different passive film structures formed in dilute versus concentrated H2SO4 solutions.

2.4 Analysis of Passive Film on Fe-Based Amorphous Coatings

The corrosion resistance of amorphous alloys is primarily manifested in their outstanding resistance to passive film breakdown and excellent passivation behavior [21]. Amorphous alloys exist as single-phase solid solutions without defects such as grain boundaries, dislocations, and stacking faults, and without compositional segregation or second-phase precipitation. This high degree of structural and compositional homogeneity provides favorable conditions for resisting localized corrosion, enabling rapid formation of uniform, dense, and well-covering passive films on amorphous alloy surfaces. Furthermore, the addition of rare earth and beneficial transition elements that improve glass-forming ability [22,23] also enhances solid solution formation capability, thereby improving localized corrosion resistance and enabling excellent resistance to passive film breakdown. The formation ability and stability of these passive films depend not only on the amorphous structure but also significantly on the types and contents of elements in the passive film.

In NaCl solution, amorphous coatings exhibit lower uniform corrosion resistance but higher passive film breakdown potentials than 304 stainless steel, which is mainly related to the different passive film compositions formed by the two materials. The full XPS spectra of passive films formed on AMCs1 and 304 stainless steel after 10 h immersion in 1% NaCl solution are shown in [Figure 6: see original paper]a. The passive film on the amorphous coating contains characteristic peaks of Fe2p, Cr2p, Mo3d, Mn2p, W4f, Cl2p, O1s, and C1s, consisting mainly of Fe, Cr, Mo, Mn, and W. The passive film on 304 stainless steel shows only distinct peaks of Fe2p, Cr2p, Ni2p, and Mn2p, indicating it consists mainly of Fe, Cr, Ni, and Mn [9].

Comparison of the full spectra in [Figure 6: see original paper]a reveals that the passive film on the amorphous coating contains significantly higher contents of Cr, Mo, and W than 304 stainless steel, particularly the presence of Mo in the coating film. Generally, Cr-rich oxides in passive films can improve the corrosion resistance of amorphous alloys [15]. The formation of Mo-rich oxides in the film typically has dual effects on enhancing passivation capability and localized corrosion resistance: first, Mo^{4+} oxidation products can block corrosion media, reducing film dissolution rate; second, Mo-rich oxides can alter passive film composition, where Mo^{6+} oxides increase film thickness (e.g., MoO_3) and stabilize inner Cr oxides (e.g., Cr_2O_3), inhibiting passive film breakdown and localized corrosion [24].

The high-resolution Mo3d spectrum of the amorphous coating surface after corrosion without sputtering is shown in [Figure 6: see original paper]c. The Mo3d spectrum consists of overlapping $3d_5/_2$ and $3d_3/_2$ peaks, primarily containing metallic Mo^0 and oxidized Mo^{4+} and Mo^{6+} sub-peaks. Based on the area of each sub-peak, the Mo3d spectrum is dominated by oxidized Mo^{4+}. Low-valence Mo^{4+} oxides in the film can greatly enhance passive film stability [6], thereby improving localized corrosion resistance. Thus, the presence of Mo oxides in the passive film of amorphous coatings is the main reason for their improved resistance to passive film breakdown. Additionally, W oxides in the outer layer of the passive film have low dissolution rates [25], which can inhibit further film dissolution and improve passivation capability.

In H2SO4 solution, amorphous coatings, 304 stainless steel, and ND steel all exhibit obvious passivation behavior. The polarization curves in Figs. 5a and c show that ND steel has significantly stronger resistance to passive film breakdown than amorphous coatings and 304 stainless steel, which is determined by differences in passive film composition. The full XPS spectra in [Figure 6: see original paper]b show that the main elemental peaks in passive films on amorphous coatings and 304 stainless steel are at the same positions as in [Figure 6: see original paper]a, with only slight differences in peak intensity, indicating that the passive film compositions in H2SO4 solution are basically consistent with those in NaCl solution. The different peak intensities reflect slight variations in element content. In addition to Fe2p, Cr2p, Mn2p, Ni2p, O1s, and C1s characteristic peaks, the XPS full spectrum of ND steel's passive film also contains Cu2p and Sb4d peaks not present in the other materials, with Cu2p being dominant. Cu-rich oxides in the passive film are key factors for improving material passivation stability [26]. The high-resolution spectrum after peak fitting for Cu2p is shown in [Figure 6: see original paper]d. The Cu2p spectrum consists of two sets of separated $2p_3/_2$ and $2p_1/_2$ peaks, each containing metallic and oxidized sub-peaks (mainly Cu^{2+} and Cu^{4+}). The high passive film breakdown potential of ND steel in H2SO4 solution is closely related to the formation of Cu^{2+} and Cu^{4+} oxides in the film. The enrichment of Cu^{2+} and Cu^{4+} oxides in the passive film enhances the passive film breakdown potential and improves passivation stability of ND steel in H2SO4 solution.

Additionally, H2SO4 solution concentration directly affects the passivation stability of amorphous coatings, with thin coating AMCs1 showing better corrosion resistance in dilute H2SO4. XPS depth analysis can provide not only surface composition information but also three-dimensional information along the depth direction perpendicular to the surface. The depth profiles of alloying element contents in the surface layer of passive films formed on amorphous coatings in the two H2SO4 solutions are shown in [Figure 7: see original paper]. The content of each element was calculated based on its peak area. Differences in passive film thickness can be simply quantified by oxygen element distribution, with film thickness typically defined as the depth where oxygen content drops to half of that in the outermost layer [6,23,27]. Using this method, both amorphous coatings formed passive films approximately 4 nm thick in concentrated H2SO4 solution (Figs. 7c and d). In dilute H2SO4 solution, the two coatings showed opposite trends: the thin coating AMCs1 formed a thicker passive film (approximately 4 nm) compared to the thick coating AMCs2 (approximately 2 nm) (Figs. 7a and 7b). Thus, the excellent corrosion resistance of AMCs1 in dilute H2SO4 solution is related to the formation of a thicker passive film on its surface.

It can be concluded that the presence of an amorphous structure benefits passivation stability improvement of coatings in dilute H2SO4 media, and preparing coatings with high amorphous content is key to achieving stable application in H2SO4 environments.

Conclusions

1. High-velocity oxygen-fuel spraying technology can produce FeCrMoMnWBCSi amorphous alloy coatings with high amorphous content, uniform structure, good bonding with the substrate, and low porosity.
2. In NaCl solution, Fe-based amorphous coatings exhibit excellent resistance to passive film breakdown but relatively low uniform corrosion resistance. The high contents of Cr, Mo, and W in the passive film enhance passivation stability, while the presence of Mo^{4+} oxides increases resistance to passive film breakdown. Pore formation in coatings reduces uniform corrosion resistance, and reducing porosity is key to improving passivation stability of amorphous coatings in chloride-containing media.
3. In H2SO4 solution, Fe-based amorphous coatings demonstrate stable passivation characteristics, with the amorphous structure facilitating passivation in dilute H2SO4. Higher amorphous content leads to thicker passive film formation and improved passivation stability. Preparing coatings with high amorphous content is a prerequisite for enhancing passivation stability in H2SO4 environments.

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Note: Figure translations are in progress. See original paper for figures.