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Environmentally assisted fracture behavior of Fe-based amorphous coatings in chloride-containing solutions

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ABSTRACT

Environmentally assisted fracture behavior of Fe-based amorphous metallic coating (AMC) sprayed on 316L stainless steel was investigated in chloride-containing solutions using a slow strain rate test method in situ electrochemical measurements and subsequent fractography analysis. A systematic detrimental effect of applied loading and aggressive ions on passive current density and localized corrosion was found. The high applied loading deteriorated the stability of passivation of AMC, which increased the passivation density and the pitting tendency. The fracture surface of AMC exhibited brittle fracture morphology with no significant crack branching. A mechanism was proposed in which the localized corrosion taking place preferentially at coating defects, and for producing the necessary crack-tip geometry. The tensile stresses accelerated the localized corrosion susceptibility near the defects by forming microcracks and promoting fast diffusion path for chloride ions. The poor environmental cracking resistance of AMC was attributed to the low protective effect of the passive film for the stress assisted localized corrosion at the crack tip and to the metastable nature of the amorphous structure.

1. Introduction

Fe-based amorphous metallic coatings (AMC) are promising materials with enhanced hardness, excellent corrosion resistance, high hardness, strong glass forming ability and relatively simple preparation processes, which can to be used in harsh abrasive and/or corrosive environments [1–4]. Thermal spraying is the most commonly used method to prepare the AMC, such as the plasma spraying, explosion spraying, high-velocity oxygen fuel (HVOF) and high-velocity air fuel (HVAF). These techniques are based on heating a powder close or beyond the melting temperature to obtain molten or semi molten state particles that are sprayed at high speed to the workpiece surface. Upon the rapid cooling rate of the particles on the substrate, the amorphous structure are formed. Most recently, an activated combustion HVAF (here referred to as AC-HVAF) technique has been developed to deliver higher spraying rate and deposition efficiency, compared to conventional hypersonic flame spraying technology, which results in high-impact coatings with extremely low porosity and high bonding strength [5,6]. However, to date, only very limited studies have been conducted to evaluate the properties of AMC prepared by AC-HVAF method.

Whilst it is known that the environmental interaction on stressed materials are the most important factors that lead to the failure and fracture, there is still a lack of systematic study on the behavior of AMC under the synergistic effect of stress and corrosion which can lead to stress corrosion cracking (SCC) [7]. Ultimately, the austenitic stainless steels are highly susceptible to chloride SCC despite their excellent general corrosion resistance. The effects of applied stress, sensitizing temperature, sensitizing time, applied potential and environmental factors (pH, anion concentration, anion species, inhibitor and test temperature) on the SCC behavior of stainless steels have been widely investigated using a slow strain rate and constant applied stress technique [8–13]. Many are the proposed theories to explain the SCC of austenitic stainless steels, and these include dissolution-based theory (film-rupture/anodic-dissolution mechanism) [14], film-induced cleavage [15], adsorption-based theory [16], hydrogen-based theory [17], and corrosion-enhanced localized-plasticity theory [18].

Amorphous alloys are kinds of high strength metastable materials and often referred to as bulk metallic glasses (BMGs). These

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materials can be used in the process of tensile loading to fracture, however the fracture criterion of the traditional crystal material does not completely agree with the fracture behavior of amorphous material [19]. At present, few studies have been carried out to the tensile fracture behavior of BMGs, for the low glass-forming abilities and small critical diameters of samples to be prepared [19,20]. The BMGs have diverse fracture modes ranging from purely brittle to compressive plasticity, and display multifarious fracture features such as various fracture modes, fracture paths, obvious deviation from the maximum shear stress plane, which are completely different from traditional crystalline alloys. The fracture behavior of BMGs is very sensitive to intrinsic and extrinsic factors such as composition, strain rate, fracture mode, the crack propagation speed, and measuring environments. Although the mechanical performance of BMGs has been well documented, and it is known that BMGs show satisfactory fracture toughness and fatigue resistance, its corresponding properties in the presence of a corrosive environment have been far less impressive [21]. In fact, it is difficult to test the tensile behavior of BMGs for SCC tests. Recently, Zr-based BMGs can be casted into glassy cylindrical rod with diameter up to 18 mm and exhibit high tensile strength in conjunction with high corrosion resistance [22–26]. Zr-based BMGs have been shown to be highly susceptible to SCC in the presence of aqueous NaCl solution, and crack propagation is assumed to proceed by an anodic dissolution assisted mechanism [12]. The environmentally influenced cracking behavior of Zr-based BMGs shows that the crack growth in aqueous solution is driven by a stress-assisted anodic reaction at the crack tip [24]. Zr–Cu–Al BMGs are highly susceptible to SCC in 0.5 M NaCl solution, and this is attributed to crack initiation at pits and presumed hydrogen-induced subcritical crack growth [25]. The SCC behavior of the Zr-based BMGs in 0.01 M Na_2SO_4+0.01 M NaCl electrolyte shows that pitting takes place preferentially at edges of flat rectangular samples and those pits can act as precursors to cracking [26]. In summary, those first reported studies clearly reveal a high sensitivity of Zr-based BMGs to SCC in chloride-containing aqueous environments. However, so far few selected Fe-based BMGs compositions are studied for SCC or environmentally assisted fracture. Limited research has showed that Fe–Co–B–Si BMGs with good resistance to pitting corrosion in the absence of load are found to exhibit SCC in acidic chloride-containing environments [27]. However, to the best of the knowledge of the current authors, all other SCC behavior of Fe-based BMGs receive comparatively less attention and little is known about crack initiation and propagation mechanisms. Moreover, from the perspective of structure, Fe-based AMC are different from those of the counterpart of BMGs. There are no defects existing in the structure of BMGs, and BMGs always show more compact and uniform microstructure than that of AMC. But correspondingly, the Fe-based AMC prepared by thermal sprayed methods exhibit typical layered structure, and there exist few defects of pores or oxides/carbide inclusions in the coatings compared to the counterpart of BMGs [5,6]. Further, the development of the AMC makes it possible for the application of amorphous materials. However, the complexity structure of AMC makes the failure behavior of them more unstable than that of BMGs when serviced in the corrosive medium and tensile loading environments. In our earlier study, the residual stress is shown to affect the uniform corrosion and pitting corrosion of AC-HVAF AMC [6], the defective structure of the AMC plays a very important role during the process of uniform corrosion, however, more systematic and detailed studies of the effects of applied stresses on the microstructure and localized corrosion performance of AC-HVAF AMC are needed. Furthermore, a comprehensive mechanistic investigation of environmentally assisted fracture on AMC in chloride-containing solutions should be conducted.

The aim of this paper is therefore to characterize the effect of external loading on the electrochemical behavior and environmentally assisted fracture characteristics of Fe-based AMC deposited on 316L Stainless Steel (SS) via AC-HVAF when immersed in chloride-containing solutions. The environmentally assisted fracture behavior for the AMC is investigated in various chloride-containing solutions in aerated solution (open to air) using a Slow Strain Rate Test (SSRT) method combined with *in-situ* electrochemical measurement. The electrochemical behavior is investigated via potentiodynamic polarization, current–time transient (I-t), and electrochemical impedance spectroscopy (EIS) analyses. Scanning electron microscope (SEM) is also used to investigate the nature and characteristics of the fracture. Finally, the environmentally assisted fracture mechanism of AMC is proposed and discussed.

2. Material and methods

2.1. Materials

The $Fe_{54.2}Cr_{18.3}Mo_{13.7}Mn_{2.0}W_{6.0}B_{3.3}C_{1.1}Si_{1.4}$ wt% master alloy was produced by induction-melting of high-purity elemental base constituents Fe: 99.9%, Cr: 99.9%, Mo: 98.5%, Mn: 99.7%, W: 99.9%, FeB:99% (20.06 wt% boron), C: 99.9%, and Si: 99.9% in an arc furnace under an argon atmosphere. Subsequently the powders were prepared by high pressure argon gas atomization using a close-coupled annulus nozzle with a melt delivery inner diameter of 3 mm, at 1600 K and a dynamic pressure of 7 MPa. The atomized powders were then sieved, and only those with a particle size lower than 45 μm were used for spraying onto the 316L SS substrate. Prior to the spraying coating being applied, the surfaces of the substrate were smoothed by a grinding machine, degreased with acetone, cleaned with alcohol, and grit-blasted. An AK-07-03 Gun was employed for AcuKote–HVAF thermal spraying and the AC–HVAF spraying parameters were as follows: spray distance 180 mm, powder feeding rate 3 g min^{-1}, turntable rate r·min^{-1}, reciprocal time 10 cycles, air pressure 82 psi, and fuel pressure 70 psi. The thickness of the AMC was about 150 μm.

2.2. Characterization of the AMC

X–Ray Diffraction (XRD) analyses were carried out on the powder and AMC on a Rigaku D/max 2400 X–ray diffractometer. The microstructural features of the powder and AMC were observed using a JMS–6301 scanning electron microscope (SEM). The micro-hardness was measured on the cross-section of the AMC using a hardness tester (MVK-H3) with indentation load of 100 g for duration of 10 s. During the hardness testing, special attentions were paid to avoid closed porosities and micro-cracks in the coatings and thus to ensure the validity of the hardness values. The hardness values given here were from an average of 10 measurements.

2.3. Environmentally assisted fracture and electrochemical measurements

Tensile specimens with gauge dimensions of 122 ± 0.3 mm in length, 23 ± 0.2 mm in width and 3 mm in thickness were machined from the sheet samples. The size of the tensile specimen was in line with international standard ISO 7539-7. Prior to the tensile tests, the peripheral surface of each specimen was mechanically polished to a mirror finish in order to minimize the data variability in the tests. The tensile specimens were installed in an SSRT machine (Xi'an Lichuang SSRT) which was equipped with a 10 kN load cell and a glass cell. All *in-situ* electrochemical