



# Pitting mechanism in a stainless steel-reinforced Fe-based amorphous coating



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## ABSTRACT

There is keen interest in developing Fe-based amorphous composite coatings with superior bonding strength and mechanical properties for load-bearing applications. However, the interfaces between the added second phase and the amorphous matrix always suffer from pitting corrosion in harsh  $\text{Cl}^-$  solutions, leading to the degradation of performance of these composite coatings. The underlying pitting mechanism has remained elusive. In this study, the pits initiation behaviour of a Fe-based amorphous coating reinforced with stainless steel powders is systematically investigated in a 3.5% NaCl solution through polarization, electrochemical noise, scanning Kelvin probe and ‘*in-situ*’ observation’ measurements, as well as high-resolution transmission electron microscopy. The pitting resistance was found to be deteriorated obviously when stainless steel phase was added to the amorphous coating. The results indicated that pitting at the interfaces was not caused, as generally believed, by microgalvanic corrosion between the stainless steel phase and the amorphous matrix, but caused by the formation of  $\text{Fe}_3\text{O}_4$  oxide at the interfaces due to the strong tendency towards oxidation of stainless steel particles in thermal spraying processes. This oxide is unstable in a  $\text{Cl}^-$ -containing environment and acts as reactive sites for pits initiation. The present work emphasizes the effect of oxidation of the reinforcement on the pitting resistance of amorphous coatings and provides an alternative recommendation to the design of amorphous composite coatings for corrosion and load-bearing applications.

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## 1. Introduction

Fe-based amorphous coatings are new surface engineering materials with an extraordinary combination of properties, such as high hardness, outstanding corrosion and wear resistance, as well as high neutron absorption ability [1–6]. Possible applications thus include nuclear waste storage, disk cutters for tunnel-boring, infrastructure, petroleum and chemical industries [1]. However, monolithic amorphous coatings exhibit low bonding strength with steel substrates [7,8] and poor damage tolerance upon impact loading [1,9], which has seriously restricted their industrial applications.

These drawbacks, fortunately, could be, to some extents, alleviated by incorporating crystalline dispersions as strengthening phases into the amorphous coatings. Fe-based amorphous composite coatings have sparked increasing interest because of

their superior load-bearing properties than monolithic amorphous coatings. For example, Terajima et al. reported on WC/12Co-reinforced Fe-based amorphous coatings exhibiting enhanced adhesion strength and approximately four times higher friction/wear resistance with respect to the original monolithic amorphous coatings [10]. Similarly, Yoon et al. suggested incorporating a hard  $\text{B}_4\text{C}$  ceramic phase to inhibit the deformation and fracture of amorphous coatings due to sliding wear, thus endowing the composite coatings with superior wear resistance [11]. In our previous works [12], the fracture toughness and impact resistance of amorphous coatings could be remarkably improved by adding  $\text{Al}_2\text{O}_3$  particles owing to the combination effect of mitigation of the stress concentration and crack-tip shielding in the ceramic phase upon loading. In addition to ceramic reinforcement, 316L stainless steel (SS) dispersion could also increase dramatically bonding strength and fracture toughness, compared with monolithic amorphous coatings [13]. However, research efforts, so far, have been devoted mainly to the physical and mechanical properties of the second-phase reinforced amorphous composite coatings, paying little attention to the corrosion mechanism. The recent researches demonstrated that the added second phases produced

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an adverse effect on the corrosion resistance of many Fe-based amorphous coatings [14,15]. For instance, Cui et al. reported that corrosion resistance decreased with increasing  $\text{Al}_2\text{O}_3$ -13% $\text{TiO}_2$  phase, as verified by higher corrosion rate and passive current density in Fe-based amorphous coatings [14]. Wang et al. indicated that WC-reinforced amorphous coating exhibited inferior corrosion resistance in alkaline solutions, because the WC phase generated galvanic corrosion with the parent amorphous matrix [15]. More recently, it was found that  $\text{Fe}_{48}\text{Mo}_{14}\text{Cr}_{15}\text{Y}_2\text{C}_{15}\text{B}_6$  (at. %) amorphous coatings reinforced with 8 vol. % stainless steel powders exhibited a high pitting susceptibility at the reinforcement/matrix interface. However, there is a lack of direct evidence on how the added second crystalline phase affects pitting and passivation behaviour of Fe-based amorphous composite coatings and the nature of the pits initiation at micrometre or nanometre scale is still unclear, delaying the advance of this type of materials.

It is generally suggested that a galvanic corrosion effect between the second phases and the glassy matrix plays a critical role in the corrosion of the amorphous matrix composites [16–18], particularly for metallic reinforcements. However, in this work, our findings provide an alternative insight into the role of oxidation-resistant ability of reinforcements on the corrosion of the composite coatings, which will be very helpful for the design of advanced amorphous coatings. The system studied here is a stainless steel-reinforced Fe-based amorphous coating, in which both the stainless steel and the amorphous phases have a high Cr content and good corrosion resistance. Pitting behaviour of the coatings is systematically investigated through various electrochemical approaches, including polarization, electrochemical noise, scanning Kelvin probe and “*in-situ*” observation tests, as well as high-resolution TEM. The pitting mechanism is discussed in terms of the microstructure of the composite coating.

## 2. Experimental procedure

### 2.1. Materials and microstructure

Amorphous powders with a normal composition of  $\text{Fe}_{48}\text{Mo}_{14}\text{Cr}_{15}\text{Y}_2\text{C}_{15}\text{B}_6$  (at. %) were prepared through gas atomization by high-pressure argon. Commercially available 316L stainless steel (SUS 316L) powders (the compositions are 17.96 at. % Cr, 11.96 at. % Ni, 1.3 at. % Mo,  $S \leq 0.03$  wt. %,  $C \leq 0.03$  wt. % and balanced with Fe) were used as reinforcements. The mixing powders with 92 vol. % Fe-based amorphous particles (size: 33–55  $\mu\text{m}$ ) and 8 vol. % 316L stainless steel particles (size: 33–55  $\mu\text{m}$ ) were blended in a low-energy ball mill and used as feedstock powders for the coating preparation; this composition exhibited the optimal mechanical properties for the coatings according to our previous study [13]. The composite coatings were prepared with a high-velocity oxy-fuel thermal spraying system using the same processing parameters as in the previous works [9,13]. AISI 1045 mild steel plates with dimensions of  $100 \times 100 \times 6$  mm<sup>3</sup> were used as the substrate, which were mechanically polished, cleaned by acetone and subsequently grit-blasted prior to thermal spraying. The microstructures of the as-deposited coatings were examined through X-ray diffraction (XRD, X'Pert PRO) using Cu-K $\alpha$  radiation, a scanning electron microscope (SEM, Quanta 200) coupled with an energy-dispersive X-ray system (EDX) and transmission electron microscopy (FE-TEM, Tecnai G2 F30). The overall oxygen content in the coatings was measured using an oxygen determinator (LECO Ro-416DR).

### 2.2. Electrochemical characterizations

Corrosion rate of the freestanding coatings peeled from the substrates was examined by immersion test in a 3.5 wt. % NaCl

solution for 15 days. The corrosion behaviour of the coatings was investigated by various electrochemical tests. Before testing, all the samples were wet ground up to 2000 grid using SiC abrasive papers, then polished to a mirror finish and ultrasonically cleaned in acetone. Electrochemical polarization measurements were performed with a potentiostat (PARSTAT 4000) in a standard three-electrode system with a platinum net as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the coating specimen as the working electrode. The specimens for the corrosion tests were closely sealed with epoxy resin (E-44 type), leaving only an end-surface (surface area:  $10 \times 10$  mm<sup>2</sup>) exposed for testing. A little silica gel was filled in the crevice between sample and epoxy resin to avoid crevice corrosion. The samples were polarized from  $-250$  mV (vs. OCP) to  $1400$  mV (vs. OCP) at a rate of  $0.5$  mV s<sup>-1</sup> in a 3.5 wt. % NaCl solution after the open-circuit potential (OCP) became almost steady. Each test was repeated at least three times. The micrographs of the coatings after polarization tests were further examined by SEM and EDX.

Electrochemical noise (EN) measurements were carried out in 3.5 wt. % NaCl solution using a setup of electrochemical noise mode, wherein two identical samples were used as working electrodes and a saturated calomel electrode (SCE) as reference electrode (RE). The potential and current noise data were continuously recorded for 12 h with a data-sampling interval of 0.25 s. The direct current trend of the noise data was removed using fifth-order polynomial [19]. The reciprocal of noise resistance ( $1/R_n$ ) was defined as the ratio of the standard deviations of the potential and the current noise, which was roughly proportional to the corrosion rate [20–22]. In order to obtain pits initiation information along, the EN data was further analysed based upon the combined stochastic theory and shot-noise theory. It is assumed that shot-noise is generated in the present systems, so the average corrosion current  $j_{\text{corr}}$  can be written as [23,24]:

$$j_{\text{corr}} = qf_n \quad (1)$$

Where  $q$  is the average charge in each pitting event and  $f_n$  is frequency of the events. According to the literatures [22–25],  $f_n$  is given by:

$$f_n = B^2/A\Psi_E \quad (2)$$

where  $B$  is the Stern-Geary constant,  $\Psi_E$  is the low frequency limit (0.01 Hz) of power spectral density (PSD) of the potential and  $A$  is the sample area. From a set of  $f_n$ , the cumulative probability  $F(f_n)$  at each  $f_n$  data can be estimated by using mean rank approximation, wherein all calculated  $f_n$  data are arranged in order from the smallest, then  $F(f_n)$  is calculated as  $M/(N+1)$ , where  $M$  is the rank in the ordered  $f_n$  and  $N$  is the total number of  $f_n$ . To understand the stochastic characteristics of pitting corrosion, the probability of  $f_n$  was analysed using the Weibull distribution function [24–26], as being expressed by:

$$\ln\{\ln[1/(1-F(1/f_n))]\} = m \ln(1/f_n) - \ln n \quad (3)$$

where  $m$  and  $n$  are the shape and scale parameters, respectively, that can be directly obtained from the slope and intercept in the  $\ln\{\ln[1/(1-F(1/f_n))]\} - \ln(1/f_n)$  plots. It had been pointed out that the region with the higher  $1/f_n$  values generally corresponds to dominant pitting corrosion [26,27], thus we only fitted and analysed the regions where pitting corrosion occurred. Using the obtained values of  $m$  and  $n$ , the conditional event generation rate  $r(t)$  of pitting corrosion can be calculated by:

$$r(t) = m/n (t^{m-1}) \quad (4)$$

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