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Effect of the long-term heat treatment on the cyclic oxidation behavior of Fe-based amorphous/nanocrystalline coatings prepared by high-velocity arc spray process

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ABSTRACT

In this study, Fe-based nanocrystalline coatings were obtained by crystallization of amorphous coatings through heat treatment with different annealing time of 0.5 h, 5 h, 10 h and 100 h, respectively. Cyclic oxidation behaviours of the Fe-based amorphous coating as well as these annealed ones at 750 °C in still air were investigated and compared. The results showed that the grain size of the annealed Fe-based coatings was significantly increased as the pre-annealing time prolonged. However, the cyclic oxidation kinetic curves indicated that the cyclic oxidation resistance of the annealed Fe-based coatings was unexpectedly improved as the increase in grain size. The coating, which was annealed at 700 °C for 100 h, exhibited the lowest accumulated weight gain of 2.8 mg/cm^2 and parabolic rate constant k_p values of 1.7×10^{-11} g^2 cm^{-4} s^{-1}, indicating the highest oxidation resistance. The enhanced oxidation resistance of the annealed coatings was mainly attributed to the elimination of cracks, pores and splat boundaries caused by the intersplat sintering during heat treatment. Cracks and splat boundaries were the primary diffusion paths for the oxygen, resulted in the different diffusion models of oxygen or metal atoms in Fe-based nanocrystalline coatings.

1. Introduction

Refinement of an alloy's grain structure has long been recognized as an attractive approach to improve its high temperature oxidation resistance, which was mainly attributed to the promoted rapid diffusion of Al and/or Cr through the grain boundaries, and thereby reduced the critical Al or Cr concentration required for external alumina/chromia scale formation [1–3]. Thermally grown oxides (TGOs) formed on the nanocrystalline materials was known to possess a combination of merits of a higher compactness and thermodynamic stability, lower growth rate, and superior resistance to cracking and spallation than that formed on the conventional counterparts [4–7]. In the recent decades, significant efforts have been directed at developing high performance nanocrystalline coatings, such as M-Cr-Al-RE (M = Fe [8], Ni [9,10], Co [11]), Cr_3C_2-25(Ni20Cr) [12], WC-CoCr [13], NiCrC [14], etc., which exhibits enhanced mechanical, elevated temperature corrosion and excellent wear resistant properties.

However, it is well-known that the application of nanocrystalline materials is strongly limited by the excessive grain growth, especially at elevated temperatures. Although the oxidation resistance properties of these nanocrystalline coatings were approved to be significantly enhanced, effects of the grain coarsening of nanocrystallines on their oxidation-resistant properties were always ignored. In fact, the improvement of the high temperature oxidation resistance of the nanocrystalline materials was not always in accordance with decreasing alloy grain size. Goedjen [15] reported that the long-term oxidation behavior of plasma sprayed NiAlY coatings was found to be independent of the grain size. The grain size of the nanocrystalline coatings had a significant influence just only on transient oxidation stage [15]. As the oxide scale thickened, the effect of the underlying substrate grain size became less important and eventually negligible [7]. Similar research results also reported by Huang, et al. [4]. Therefore, these research results seem to be contrary to the general considerations caused by grain refinement as discussed above.

With a combination of high mechanical properties, superior corrosion and wear resistance, thermal sprayed Fe-based amorphous coatings have attracted much attention in the recent decades to meet the ever-growing requirements of the industry [16]. Up to now, less works have been reported on the temperature- and time-dependent grain coarsening of thermal sprayed Fe-based amorphous/nancrystalline coatings [5,17], let alone its relative influence on the oxidation behavior. In this study, the effect on the oxidation resistance of the grain growth caused by heat-treatment of arc-sprayed Fe-based amorphous coatings was discussed. Self-designed Fe-based nanocrystalline coatings were prepared by a traditional solid

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Table 1
The nominal composition of the F30 coating (at. %) [18].

Cr	B	C	Si	Nb	Mo	Ni	Fe
<18.8	<25.5	<2.5	<2.0	<2.5	<1.0	<5.0	Bal.

transformation approach [18], i.e., crystallization of thermal sprayed amorphous coatings. After annealing the as-sprayed amorphous coatings for different periods, Fe-based nanocrystalline composite coatings with different grain size could be obtained for this investigation. The related high temperature oxidation mechanism of these nanocrystalline coatings was also discussed.

2. Experimental procedures

Details of the coating preparation process were reported in elsewhere [18]. In this study, an arc-sprayed Fe-based amorphous coating, namely F30 (The onset crystallization temperature: 642.4 °C), was selected for the oxidation trials. The nominal composition of the coating was shown in Table 1 [18]. Prior to the high temperature oxidation tests, the F30 coating was heat treated at 700 °C in a vacuum furnace ($<4\times10^{-3}$ Pa) for different periods (0.5 h, 5 h, 10 h, and 100 h) to obtain full devitrification phase constituents and structural features. The microstructures of the as-sprayed and annealed coatings were characterized by a Philips XL30 scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). Phases were identified by the X-ray diffraction (XRD) that was carried out in a D8 Advance diffractometer (Bruker AXS, Germany) with a Cu Kα target and operated at 40 kV and 40 mA. Scans were run with a step size of 0.01° from 20° to 90° (2θ).

Cyclic oxidation trials in still air were carried out in a box furnace for 20 cycles at 750 °C. Each cycle consisted of 5 h heating and followed by 20 min cooling to room temperature. Each specimen was kept in a crucible to make sure that the spalled scale was also included during the weight change measurements. Total weight change measurements were taken at the end of each cycle using an electronic balance machine (FA2004N) with a sensitivity of 0.1 mg. After oxidation, the phase composition and morphology of the oxide scales formed on the corroded coatings were examined by XRD, SEM, and EDS analysis.

3. Results

3.1. XRD analysis of the as-sprayed and annealed coatings

Fig. 1 illustrates the XRD patterns of the F30 coating before and after annealed at 700 °C for 0.5 h, 5 h, 10 h, and 100 h, respectively. It is clear from the presence of the diffraction halo around $2\theta\approx45°$ that the as-sprayed F30 coating was mainly composed of an amorphous structure. No peaks of crystalline phases were identified in the XRD patterns of

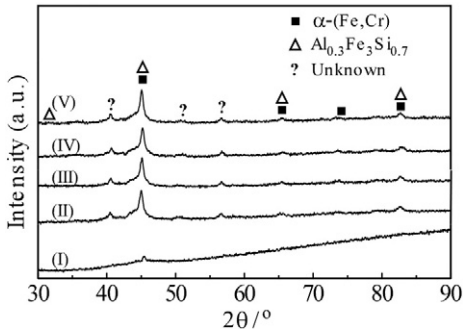


Fig. 1. XRD patterns of the as-sprayed and annealed Fe-based coatings. (I) as-sprayed, (II) annealed at 700 °C for 0.5 h, (III) annealed at 700 °C for 5 h, (IV) annealed at 700 °C for 10 h, (IV) annealed at 700 °C for 100 h.

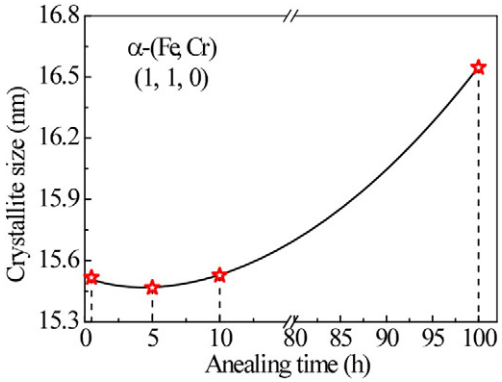
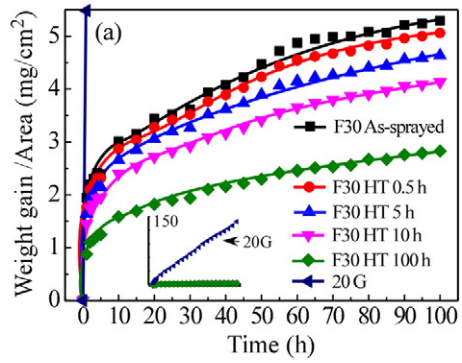


Fig. 2. Crystallite size of the Fe-based coatings before and after annealing at 700 oC for 0.5, 5, 10, 100 h.

the as-sprayed coating. After annealed the as-sprayed coating at 700 °C for 0.5 h, the broad halo nearly disappeared and the peaks became remarkably shaper, indicating that all the annealed coating was devitrified completely. α-(Fe,Cr) (JCPDS 41-1466) was identified as the main phase of these annealed coatings with small amount of $Al_{0.3}Fe_3Si_{0.7}$ (JCPDS 45-1206). As the annealing time prolonged, the main crystallization peak around $2\theta\approx45°$ slightly shifted towards higher diffraction angles, indicating that solute atoms precipitated out from the supersaturated α-(Fe,Cr) solid solution, which was formed at the initial stage of the crystallization process. An average crystallite size (D) of the α-(Fe,Cr) calculated from most intense Bragg's reflection (1,1,0) using Debye-Scherer's formula [19] was shown in Fig. 2.

$$D = k\lambda/(\beta\cos\theta) \quad (1)$$

where $k=0.89$ is the Scherrer constant, $\lambda=0.15405$nm is the X-ray wavelength, β is the peak width of half maximum (FWHM) and θ is the Bragg's diffraction angle. It is reasonable that grain size in the



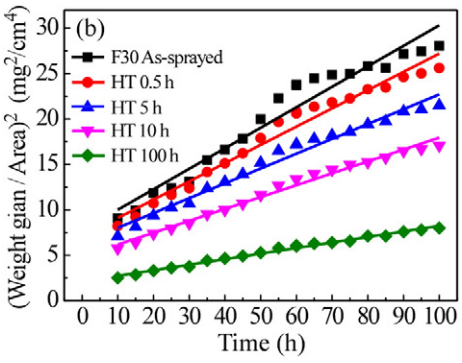


Fig. 3. Weight gain vs. corrosion time (a) and square weight gain vs. corrosion time (b) plots for the as-sprayed and annealed F30 coatings subjected to cyclic oxidation in air at 750 °C for 100 h.