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Microstructure and high-temperature oxidation behavior of wire-arc sprayed Fe-based coatings

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ABSTRACT

A series of Fe–*x*Cr cored wires ($x = 15, 20, 25, 30, 35$ and 40% in weight) were used to produce protective coatings for components used in high-temperature environments by wire-arc spraying. The microstructure, morphology and high-temperature oxidation behavior of the Fe–*x*Cr coatings were investigated. The Fe–*x*Cr coatings presented a homogeneous structure with thin oxide inclusions and low porosity. Thermogravimetric analysis was used to evaluate the high-temperature oxidation behavior of the coatings at a temperature of 650 °C under cyclic oxidation conditions. The results showed that all the Fe–*x*Cr coatings exhibited significantly lower weight gain than the uncoated substrate. As Cr content of the coatings increased, the thickness of oxide scales decreased and oxidation resistance improved.

1. Introduction

Increasing efficiencies of thermal power plants is one of major challenges in reducing carbon dioxide emissions, particularly for coal-fired boilers [1]. Therefore a higher operating temperature of these boilers is required. However this leads to more severe high-temperature oxidation and corrosion on the components like the many different kinds of steel tubes used in boilers [2]. As a result of oxidation and corrosion, the tubes become thinner and the structural integrity of the tubes can be impacted. One of the effective approaches to protect high-temperature components in boilers against oxidation and corrosion is depositing protective coatings on the surfaces of the steel tubes with thermal spraying processes. A number of thermal sprayed coatings have been studied in the past decades (e.g. nickel-based and iron-based coatings). Ni–Cr, Ni–Cr–Ti, Ni–Cr–Mo, Ni–Cr–Al–Y, Ni–Cr–B–Si, and Cr_3C_2/Ni–Cr coatings have been deposited by high velocity oxy-fuel (HVOF) spraying [3,4], plasma (APS) spraying [5–7], detonation gun (D-gun) spraying [8,9], or wire-arc spaying [10]. Among these thermal spraying processes, wire-arc spraying has attracted increasing interest because of the following advantages: low cost, high spraying rate, high deposit efficiency, simplicity and flexibility. Most of the above Ni-based coatings can provide good protection and increase the lifetime of high-temperature components and so have been applied in many boilers. Nevertheless the Ni-based coatings are not considered an ideal solution due to at least two reasons. Ni-based alloys are very costly and some of the oxidation and corrosion products of Ni-based alloys like NiO, $NiSO_4$ and $NiCl_2$ are toxic to human health [11,12].

Some iron-based coatings [13–15] have also been designed and deposited by HVOF, APS, and wire-arc spraying processes in order to gain high-temperature oxidation, erosion and wear resistant coatings. Compared to Ni-based alloys, Fe-based alloys have significantly lower costs, and thus are very attractive for high-temperature applications. To improve oxidation resistance, elements such as chromium, silicon or aluminum are used because they form protective oxide scales of Cr_2O_3, SiO_2 or Al_2O_3 at increased temperatures [16,17]. Because chromium influences the least the mechanical properties of alloys [17], a large quantity of research on the oxidation and corrosion behavior of Fe–Cr bulk alloys has been conducted [18–21]. It is found that the Fe–Cr alloys with high Cr content (Cr: 30–40 wt.%) present good high-temperature oxidation and corrosion resistance [22–24]. However, these alloys are difficult to manufacture into solid wires for wire-arc spraying, due to their high hardening tendency during the drawing process. Therefore they are commonly produced by casting and forging. This limitation caused by the hardening tendency can be avoided using a cored wire concept. Fe–Cr alloys with high Cr content can be made using iron and chromium powder as filling material and well-drawable steels as wire cover.

In the present study, Fe–Cr alloy cored wires with different Cr content, including those with high Cr content, were manufactured and deposited into Fe–Cr coatings by wire-arc spraying. The influence of Cr content on the high-temperature oxidation behavior of the Fe–Cr coatings was investigated. For comparison the high-temperature oxidation behavior of a Ni–Cr–Ti coating produced by wire-arc spraying a commercial Ni–Cr–Ti solid wire was studied simultaneously in the same

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experimental condition in order to explore the feasibility of Fe-based oxidation resistant coatings as alternatives to the Ni-based coatings.

2. Experimental procedure

2.1. Materials

A series of Fe–*x*Cr alloy cored wires (x = 15, 20, 25, 30, 35 and 40 wt.%) with a diameter of 2.0 mm were produced. The filling coefficient of the cored wires was 32%. The 0.3 mm thick wire cover was made from stainless steel (Cr: 17 wt.% and Fe: 83 wt.%) tape. The filling material was mixed Fe and Cr powder. The SA213-T2 steel (with dimensions of 20 × 15 × 5 mm^3) was selected as a substrate material in the present study because it is one of the typical materials used for boiler tubes. The wire-arc spraying was performed by TLAS-400C equipment (Xi'an Tongli Mechanical and Electrical Equipment Co., Ltd, China) mounted on a robot. The coatings were sprayed under the following parameters: arc voltage of 30–32 V, current of 180–190 A, a pressure of 0.6 MPa, and a spraying distance of 200 mm. A commercially available Ni–Cr–Ti solid wire (Ni: 55 wt.%, Cr: 44 wt.% and Ti: 1 wt.%) with a diameter of 1.6 mm was applied in order to deposit a coating under the same condition for the high-temperature oxidation test. Before spraying the substrates were degreased by acetone, dried, and then grit-blasted. The average roughness of the blasted surface was about 4.5–5.0 μm. Two kinds of specimens were produced for different experiments: (1) The coatings were deposited on the top surface (with dimensions of 20 × 15 mm^2) of the substrates for 600–700 μm. These specimens were used to study the microstructure of the as-deposited coatings. (2) The coatings were deposited on the top surface of the substrates then the coatings were separated from the substrates. These coatings (without substrates) were used in high-temperature oxidation test.

2.2. Microstructure characterization

The as-deposited coatings were polished for the phase composition analysis using X-ray diffraction (XRD) with Cu Kα radiation. The surface morphology and cross-sectional microstructure of the coatings were characterized by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), with an electron beam energy of 20.0 keV. Fifteen cross-sectional micrographs of each coating were taken by an optical microscope to evaluate their average porosity. The porosity was measured by image analysis using an Image Pro Plus system.

2.3. High-temperature oxidation test

The high-temperature oxidation behavior of the Fe–*x*Cr and Ni–Cr–Ti coatings was investigated by thermogravimetric analysis under cyclic oxidation conditions. The oxidation test was carried out at 650 °C in a box muffle furnace for 22 cycles. The first three cycles lasted 1 h, 4 h and 5 h respectively while the subsequent nineteen cycles had duration of 10 h each. Hence the total time for oxidation test was 200 h. Before the oxidation test, each as-deposited specimen was washed by acetone and dried. Subsequently each specimen was kept in a crucible and the total weight of each specimen with the crucible was determined as the baseline weight. After being weighed, the specimens were introduced into the muffle furnace to be subjected to high-temperature oxidation at 650 °C. The total weight of specimens with the crucible was measured at the end of each cycle by an electronic balance with a sensitivity of 0.1 mg. The kinetics curves of oxidation were plotted according to the increase of the relative mass of the specimens per unit area across time. XRD and SEM/EDX techniques were used to analyze the oxidation products on the coatings.

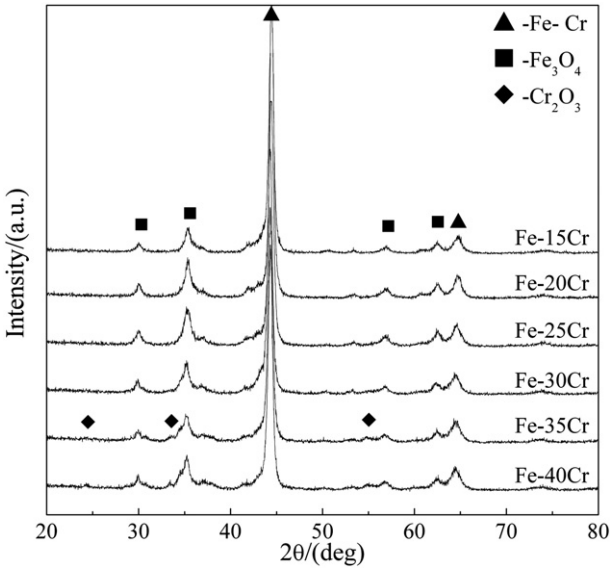

Fig. 1. XRD patterns of the as-deposited Fe–Cr coatings.

3. Results and discussion

3.1. Coating microstructure and morphology

The X-ray diffraction patterns of the as-deposited Fe–*x*Cr coatings are shown in Fig. 1. It is evident that the principal phase of all the coatings is Fe–Cr solid solutions. The secondary peaks pertaining to Fe_3O_4 are also visible in all coatings. In contrast to Fe–15Cr, Fe–20Cr, Fe–25Cr and Fe–30Cr, the Cr_2O_3 peaks are recognizable in the diffraction patterns of Fe–35Cr and Fe–40Cr coatings. It indicates that during spraying of Fe–(15, 20, 25, 30)Cr cored wires, the oxide Fe_3O_4 was formed mainly. With the increase of Cr to 35 and 40 wt.%, Cr_2O_3 oxide was additionally formed during spraying.

The microstructures of the as-deposited Fe–15Cr, Fe–25Cr and Fe–35Cr coatings are for example shown in Fig. 2. It is recognizable that the Fe–*x*Cr coatings presented homogeneous microstructures. All the coatings are composed of well-flattened particles with porosities around 5%. The coatings have relatively low porosities for the wire-arc spraying process. No evident cracks are observed in the coatings. A huge amount of dark-contrast thin oxide inclusions are visible between the light-contrast particles, indicating that the molten particles were severely oxidized during spraying. According to the EDS and XRD analysis results, the light-contrast particles in Fig. 2 are Fe–Cr solid solutions. The oxide inclusions in Fig. 2(a) and (b) are mainly Fe_3O_4, and the oxide inclusions in Fig. 2(c) are Fe_3O_4 and Cr_2O_3.

3.2. High-temperature oxidation test

Fig. 3 shows the oxidation kinetics curves of the Fe–*x*Cr coatings and the commercial Ni–Cr–Ti coating subjected to cyclic oxidation tests in comparison to the uncoated substrate at 650 °C. The uncoated substrate exhibits the highest weight gain among all the specimens. During the oxidation test the surface of the uncoated substrate suffered the most severe oxidation because the oxide scale that formed on it was non-protective. With the increase of oxidation time, the oxide scale cracked and spalled from the substrate leading to the fresh metal's exposure to the atmosphere again. This is attributed to the serious stresses that develop as a result of the presence of iron oxide [4]. Therefore the uncoated substrate exhibits an extremely high weight gain with a nearly linear rate law.

It can also be seen from Fig. 3 that all the coatings exhibit better high-temperature oxidation resistance than the uncoated substrate. The commercial Ni–Cr–Ti coating demonstrates the lowest weight