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Oxidation resistance of iron-based coatings by supersonic arc spraying at high temperature

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ABSTRACT

The high-temperature oxidation behavior of three kinds of iron-based coatings prepared by supersonic arc spraying (HVAS) was investigated in this paper. The characterization of the microstructures, surface morphologies and chemical compositions for the coatings before and after high temperature oxidation at 800 °C and 900 °C were analyzed by optical microscopy (OM), scanning electron microscopy (SEM), energy-dispersive spectroscope (EDS) and X-ray diffraction (XRD). It was illustrated that the FeCrAlTiCRE coating had the best high temperature oxidation resistance among the three coatings. After high-temperature oxidation, a dense and compact oxide layer was formed on the surface of FeCrAlTiCRE coating, which was composed of Cr_2O_3 and Al_2O_3. The oxide film of FeCrAlTiCRE coating was mainly composed of Fe_2O_3 after 100 h oxidation at 800 °C, while it was of Fe_3O_4, Cr_2O_3 and Al_2O_3 after exposure at 900 °C for 100 h. The oxide film formed on the surface of FeCr(C, RE) coating was mainly composed of Cr_2O_3 and spinel crystal $FeCr_2O_4$ which also showed protective effect for the coating at high temperature. The oxide layer on the Fe(Cr_3C_2, RE) coating was mainly composed of loose and porous Fe_3O_4 and a small amount of Cr_2O_3 because there were little Cr and Al. The oxidation mechanism, thermodynamic and kinetic analysis during the failure process was discussed.

1. Introduction

Arc spraying technology, one of the most important technologies in the field of surface engineering, plays an important role in the protection and remanufacturing of mechanical parts. Hot corrosion and wear are main reasons of numerous failures of boilers, steel mills, tubes of thermal power plants, etc. One of the effective methods to protect them against hot-gas corrosion and wear is the deposition of thermally sprayed coatings [1]. Iron-based coatings have been more widely used and developed, although thermally sprayed Ti-based coatings or Ni-based coatings are known to obtain excellent wear and corrosion resistance, however, the price fluctuation of strategic metals such as Ni and Co and the inhalation toxicity problems related to Ni and Co has forced the experts to explore alternative solutions [2,3]. In this scenario, thermally sprayed iron-based coatings are being widely used in order to enhance the properties and make them a future alternative. In addition, it also possesses excellent performances such as high hardness and toughness, low cost and easy processing. The principle of arc spraying technology determines that it can only be used to spray the conductive wire materials. Materials without strong toughness and ductility because of low machinability, are difficult to invest in practical application, which limited the range of arc spraying materials and hindered the development and application of arc spraying technology. The application of cored wires has broadened the application, promoted the further research and application of arc spraying technology in the field of corrosion resistance [4]. Cored wire, which is made of metal skin and various metal or ceramic powders, has the advantages of solid wire and metal/ceramic powder and thus can improve the coating performance by changing the powder composition.

The traditional high-temperature oxidation resistance coating is mainly based on NiCr alloy coating. 45CT solid wire (55 wt%Ni, 43 wt%Cr, 2 wt%Ti), manufactured by the TAFA company of the United States, can be used to prepare a high-temperature oxidation resistance coating which has a service life about 7 years in a hot-gas corrosion and wear environment [5]. The Ni50Cr50 (in mass fraction, the same below) coating developed by British company has excellent resistance to high temperature and corrosion. To explore a coating material with higher cost performance, researchers pay more attention to FeCrAl alloy coating. FeCr26Al6 alloy wire and Fe/Cr core wire, developed by D. Y. He from Beijing University of Technology, has been confirmed to

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Table 1
The main chemical composition of the coatings.

Sample	Elements	C	O	Cr	Fe	Al	Ti
C1	wt%	10.26	12.66	21.50	55.58	–	–
	at.%	28.04	25.85	13.58	32.54	–	–
C2	wt%	9.64	9.39	20.84	51.77	8.29	0.07
	at.%	26.51	19.40	13.25	30.63	10.17	0.06
C3	wt%	8.95	10.45	1.62	78.97	–	–
	at.%	26.17	23.01	1.10	49.73	–	–

have excellent protective performance [6]. The FeCrAl coating generates a protective oxide film composed of Cr_2O_3 and Al_2O_3 which endows the coating an outstanding thermal corrosion and high temperature oxidation resistance. Similarly, because of the generation of continuous and stable Cr_2O_3 oxide film, FeCr alloy coating prepared by Fe/Cr cored wire exhibits good anti-oxidation performance. And with the increase of Cr content in the cored wire, the high temperature oxidation resistance and corrosion resistance significantly improved.

2. Experimental procedures

2.1. Coating preparation

In this paper, three kinds of iron-based coatings were deposited by wires as FeCr(C, RE), FeCrAlTiCRE and Fe(Cr_3C_2, RE), which were marked as C1, C2 and C3 coatings for simplicity. They were deposited by cored wires, except for FeCrAlTiCRE coating. The main chemical compositions of the coatings are presented in Table 1. Due to low RE contents and the burning loss in the spraying and smelting process, Inductive Coupled Plasma Emission Spectrometer (ICP) was used to detect the trace rare earth elements in coatings, the results are shown in Table 2. Therefore the article devotes no research to explain the reason for the oxidation resistance of coatings from the perspective of RE elements. The 45# steels were fabricated into cylindrical samples with dimensions of Ø16mm × 35 mm, then was polished from #200 to # 5000 by silicon carbide abrasive papers. Finally the iron-based coatings were deposited on the cross-section of the cylindrical samples by SX-600 supersonic arc spraying equipment. Because the smooth surface of # 45steel plus the thicker coating (the average thickness was between about 0.5–1.0 mm), there was really a poor bonding strength between coatings and substrates. Immediately after the coating was deposited on the substrate and maintained at a high temperature, it was easily to peel off the coatings from the substrates. To compare the high temperature oxidation resistance of as-deposited coatings and substrates, coatings and substrates were separated for the high temperature oxidation tests. The substrate material such as 12CrMoV steel used for the water wall of the boiler was selected as the reference sample. To obtain coatings with high bonding strength and density, the optimized-parameters of arc spray process were selected by five factors and four levels orthogonal experiments. The influence to iron-based coatings of different parameters at different levels was as follows: Air pressure > Spraying distance > Wire feed rate > Spraying voltage > Spraying current. The optimized parameters of the supersonic arc spraying technique are given in Table 3.

Table 3
Parameters of the supersonic arc spraying technique.

Voltage/V	Current/A	Distance/mm	Air pressure/MPa	Wire feed rate/cm·min^{-1}
30	180	150	1.0	80

2.2. High-temperature oxidation test

The coating samples detached from the 45# steels were wafers with thickness from 0.6 to 0.8 mm and a diameter of 16 mm. 12CrMoV steel used for substrate materials was processed into rectangular blocks with dimension of about 20 × 10 × 5 mm. All the samples were cleaned in acetone for 5 min by ultrasonic wave equipment, and then were dried. Experiments selected five parallel specimens for each samples to improve the accuracy. High temperature oxidation tests were carried out at 800 °C and 900 °C in SX2-10-13 electric furnace for 13 cycles. The first 4 cycles lasted 1 h, 2 h, 2 h, and 5 h respectively while the subsequent 9 cycles had continued of 10 h each, hence the total time of oxidation test was 100 h. Each interval was cooled in air for 1 h, and after cooling to room temperature the weight of the samples was conducted. The samples were weighed by Tg328 Photoelectric Analytical Balance with an accuracy of 0.01 mg after every cycle oxidation.

2.3. Characterization

The surface morphologies and energy spectrum analysis were taken by Hitachi SU8220 field emission scanning electron microscope (FESEM). Phase analysis was characterized by X-ray diffractometer (XRD) and the specific conditions are Cu Kα radiation, wavelength λ = 0.15418 nm, a scanning range of 20–90°, a scanning speed of 6°/min, a tube voltage of 40 kV, a tube current of 40 mA. The cross-sectional morphology was observed by AXIO IMAGER A2M ZEISS metallurgical microscope.

3. Result and discussion

3.1. High-temperature oxidation behavior

Fig. 1(a) shows the cumulative mass gains of the samples and illustrates the oxidation kinetics curves follow the power function law. Obviously, the mass gain of the substrate materials is much higher than those of the coatings. In the three kinds of coatings, C3 has the maximum mass gain and C2 the minimum. The mass gain of C2 is 4.5% of C3, 6.9% of C1, and 2.2% of 12CrMoV steel. Fig. 1(b) shows the mass gain of the samples increased with the increase of oxidation temperature. The oxidation kinetics curves of each sample (except C3) are still in accordance with the power function law. Sequence of mass gains for three coatings was C3 > C1 > C2. Mass gain of C2 was about 2.50 mg/cm^2 and 4.23 mg/cm^2 at 800 °C and 900 °C respectively. For the C1 and C3 coating, it was more than 36.17 mg/cm^2 and 43.62 mg/cm^2 at 800 °C, while it was 43.62 mg/cm^2 and 130.52 mg/cm^2 at 900 °C, respectively. Mass gain curve of C3 was conform to linear law (after 30 h) and decreased slightly after 50 h. It demonstrates that the oxide layer on the surface of coatings are oxidized and flaking off. However, the high temperature oxidation resistance of C2 is still the best of these three coatings. Compared with all samples, the mass gain

Table 2
The contents of rare earth elements in three iron-based coatings.

Sample	Elements	Dy	Tb	Ho	Sm	Gd	Eu	Lu
C1	wt%	–	–	–	–	0.0053	0.0005	0.0021
C2	wt%	–	0.0014	–	0.0001	0.0008	0.0002	–
C3	wt%	0.0001	0.0013	0.0001	–	–	–	–