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Effect of rare earth on oxidation resistance of iron base fluxing alloy spray-welding coating

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Abstract

Recently, the studies on application of rare earth (RE) in spray-welding materials has attracted more and more attention. Iron base fluxing alloy powder has been widely used as spray-welding materials due to some of its advantages, such as lower price and good wear resistance. However, its oxidation resistance at high temperature is poor, therefore, RE has been used to improve its properties in the present study. The iron base fluxing alloy powder containing mixed RE alloy were prepared by using the smelting–atomizing process, the coating samples were prepared by using the oxide-acetylene flame spraying process. And the effect of RE on oxidation resistance of iron base fluxing alloy spray-welding coating has been studied. Moreover, the oxide layer of the coating samples was analyzed by using scanning electron microscope (SEM) and the X-ray of electron dispersion analysis (EDAX). It has been shown that the addition amount of mixed RE alloy of 0.2 wt% is suitable. Based on the experimental results the mechanism of RE function has been discussed.

Keywords: Rare earth; Iron base fluxing alloy; Oxidation resistance

1. Introduction

Nowadays, the applications of RE in the field of surface engineering are principally focused in surface chemical heat treating and electroplating. Since 1990, the studies on applications of RE in spray-welding materials have been paid attention. So far, there are only a few studies on effects of RE on the microstructure and wear resistance of the spray-welding alloy coating in literature. Effects of RE on some other properties of the coating alloy, such as oxidation resistance and corrosion resistance, etc. have not been reported yet. The study on effect of RE on oxidation resistance of iron base fluxing alloy spray-welding coating has been carried out in the present paper.

2. Experiment

2.1. Preparation of coating samples

The iron base fluxing alloy powders containing 0, 0.1, 0.2, 0.3, 0.4 and 0.5 wt% mixed RE alloy respectively were prepared by using the smelting–atomizing process, and the coating samples were prepared by using the oxide-acetylene flame spraying process. The composition of iron base fluxing alloy is C 0.7–0.9, B 2.6–3.0, Si 3.0–4.0, Cr 12–14, Ni 12–14 wt%, the rest is Fe. The composition of RE alloy used in the process is Ce 47, La 26, Nd 18 and Pr 5 wt%.

2.2. Oxidation experiment at high temperature

The oxidation experiments were carried out according to the national standard GB/13303 of the People's Republic of China, ''the measurement method of oxidation resistance of steel'' [1]. The dimension of the coating samples was $20\times10\times3$ mm^3, its surface was polished before the experiment. The experiment was carried out as follows:

1. The coating samples containing different amount of mixed RE alloy have been treated to measure the oxidation rate at 1173 K and 1273 K respectively for 12 h in air.
2. The coating samples containing RE and without RE have been treated at 1173 K in air, and they were weighed respectively after being treated for 0, 0.5, 1, 2, 4, 6, 9, 11 and 12 h.

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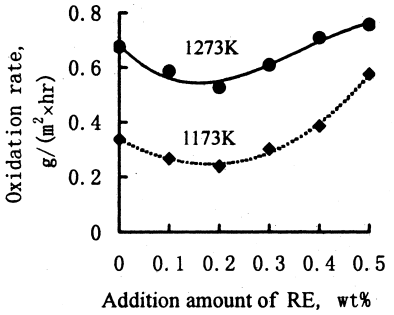

Fig. 1. Relationship between oxidation rate of coating and addition amount of RE.

3. Results and discussion

3.1. Oxidation resistance tests

The relationship between the oxidation rate of coating samples and the addition amount of RE at two different temperatures 1173 K and 1273 K is shown in Fig. 1.

Fig. 1 shows that the oxidation rates of the coating samples gradually decrease with the increase in the addition amount of RE at both 1173 K and 1273 K up to 0.2 wt% mixed RE alloy, then the oxidation rates increase with increasing RE amount.

3.2. Relationship between weight increase of oxidation samples and treated time

The relationship between the weight increase of the coating samples containing 0.0, 0.2 and 0.4 wt% mixed RE alloy respectively and the treating time at 1273 K is shown in Fig. 2.

Fig. 2 shows that the oxidation weight increase in the coating samples without RE almost stops after being treated for an hour, however, when it is treated for 11 h or more, the oxidation weight increase rises suddenly. On the contrary, the oxidation of the coating samples containing RE (0.2 wt%) is more stable after being treated for longer time (11 h) without a sudden increase in the weight

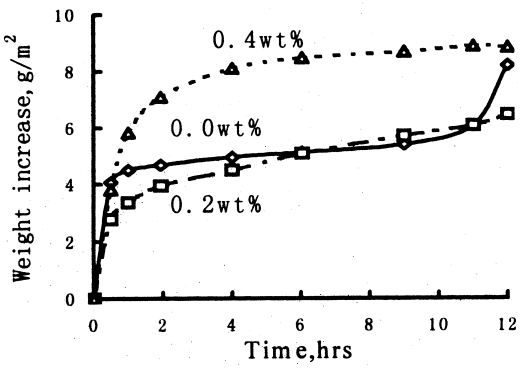

Fig. 2. Relationship between weight increase of coatings containing different RE amount and treating time.

increase of coating samples. But the oxidation weight increase of the coating samples containing 0.4 wt% RE increases with the increase in time, and its weight increase is obviously higher than that of the coating samples containing 0.2 wt%RE. It has been shown that an appropriate addition amount of RE is useful for the increase in oxidation resistance of the coating samples.

3.3. Microstructure of oxidic layer of coating samples

The SEM morphology of the oxidic layers of coating samples treated at 1173 K for 12 h is shown in Fig. 3.

Fig. 3a shows that there is apparent break in the oxidic layer of coating sample without RE. Fig. 3b shows that there is no apparent break in the oxidic layer of the coating sample containing 0.2 wt%RE alloy. Fig. 3c shows that the morphology of oxidic layer of coating sample containing 0.4 wt%RE looks very loose. Based on above experiments, it can be thought that an appropriate addition amount of RE (such as 0.2 wt%) will increase the adhesion of oxidic layer to matrix resulting in improving the interfacial structure. But, if the addition amount of RE is too much (such as 0.4 wt%), it will lead to loosening the oxidic layer structure of coating.

The data of EDAX analysis for points A, B, C on Fig. 3a and b are listed in Table 1.

Table 1 shows that the Cr contents in both coating samples without RE and containing 0.2 wt% RE decrease from outer to inner layer. The Si content on the interface between the oxidic layer and the matrix of the coating samples containing RE is higher than that of the coating samples without RE.

Fig. 4a is SEM image of the oxidic layer of coating samples containing 0.2 wt% RE treated for 12 h at 1173 K in air. Analysis results of point D on Fig. 4a with EDAX is shown in Fig. 4b.

Fig. 4b shows that there are five kinds of elements, Si, O, Cr, Ce and Fe in point D, RE also concentrates in the oxide phase of Si, Cr and Fe($(Si, Cr, Fe)_xO_y$), and Si content is high, it agrees with the data in Table 1.

As stated above, it can be thought that the increase in oxidation resistance of coating samples at high temperature results from the following reasons:

1. When an appropriate amount of RE is added, the oxidation resistance of the coating samples can be increased resulting from improving the adhesion of the oxidic layer to the matrix: (1) The oxidation resistance of the coating is improved resulting from the silicon element enriched on the interface between the oxidic layer and the matrix of the coating. It is shown that an appropriate addition amount of RE can promote silicon oxidation in the inner layer resulting in changing the composition, increasing the adhesion of oxidic layer, and increasing the oxidation resistance of the coating alloy, it agrees with literature [2] in which the study on

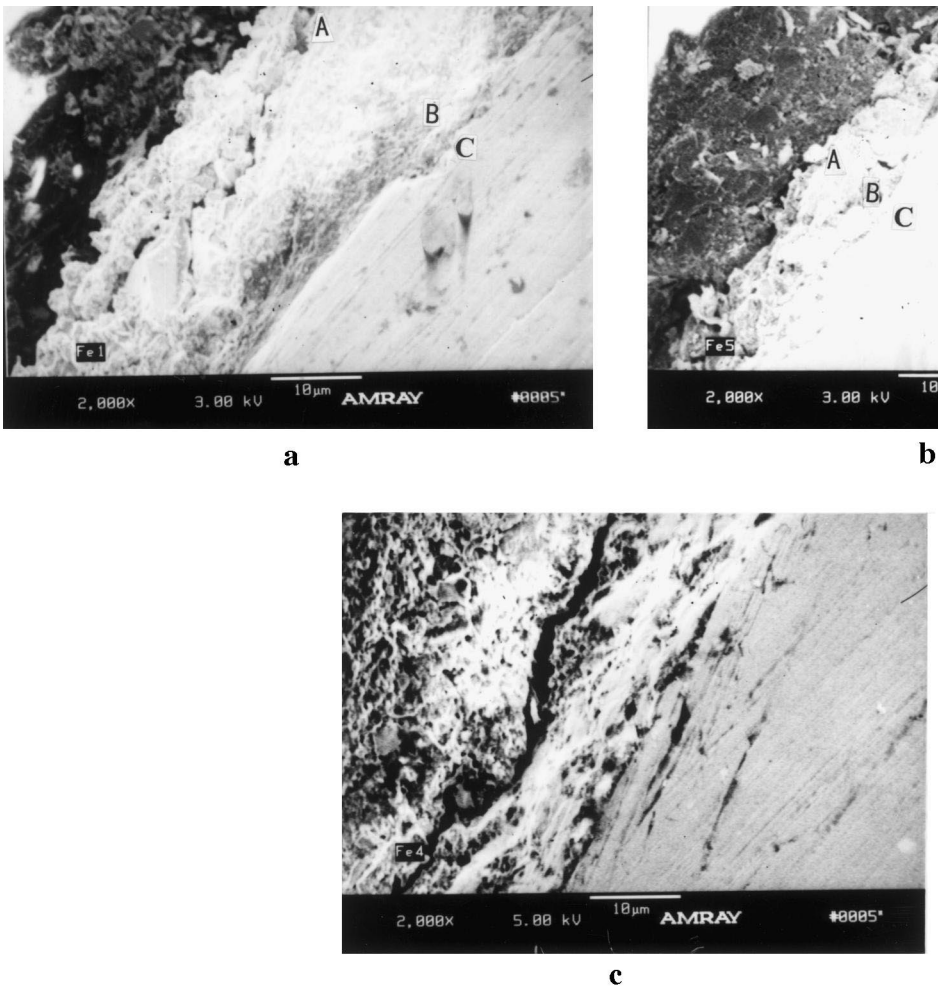

Fig. 3. SEM image of oxidic layer of coating. (a) 0.0 wt%RE; (b) 0.2 wt%RE; (c) 0.4 wt%RE.

oxidation of 20Cr30NiFe alloy at 1273 K in air was reported. (2) In the oxidation process, oxygen ions fastly diffuse along the crystal boundaries into the matrix, and the RE elements enriching on the boundaries are easy to react with oxygen ions to form RE oxides, then, the adhesion of the oxidic layer to the matrix is strengthened because of the binding effect of RE oxides on the surface of the matrix, it is similar with the studies on effects of RE in FeCrAl alloy in literature [3].

2. The oxidation resistance of the coating samples decreases with too much addition amount of RE (such as 0.4 wt% addition amount), this phenomenon appeared in the studies on effect of RE in steel preparation [2], but it did not explain for this. In our view, besides effects of RE on refining the microstructure, RE apparently affect the boundary properties of the materials resulting from the effects of RE on the segregation of harmful impurities (such as sulfides) on the crystal boundaries and the types and condition of the inclusions.The growth process of the oxidic layer is a diffusion process of ions, and it is mostly affected by the boundary properties. Thus, an appropriate addition amount of RE will decrease the enrichment of sulfides,

Table 1
Element distribution of oxidic layer analyzed by EDAX

RE addition amount, wt%	0.0 (Fig. 3a)		0.2 (Fig. 3b)		
Position	Outer (A)	Interface (C)	Outer (A)	Interface (B)	Interface (C)
Elements					
Si	0.80	0.23	0.25	8.51	12.88
Cr	43.84	13.82	40.14	14.43	10.97
Fe	55.36	85.96	59.11	77.05	76.16

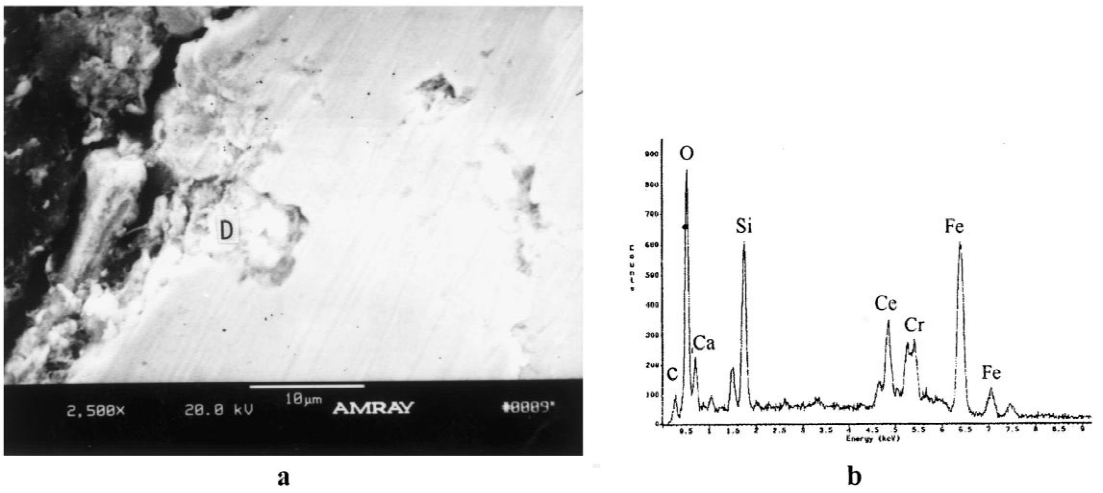

Fig. 4. RE distribution in Fe–Cr oxide phase of oxidic layer of coating sample (a) SEM image of oxidic layer, 0.2 wt%RE; (b) EDAX spectrum of point D in (a).

improve the types and condition of inclusions on the boundaries, it results in strengthening bounderies and improving oxidation resistance. On the contrary, if the amount of RE is added too much, the boundary properties will decrease because of segregation of too much sulfides and RE oxides on the crystal boundaries, it results in the decrease in the oxidation resistance of coating samples.

4. Conclusion

1. The oxidation resistance of iron base fluxing alloy spray-welding coating can be improved resulting from silicon enriching on the interface between the oxidic layer and the matrix, the adhesion of the oxidic layer to the matrix is strengthened.
2. The binding effect of RE oxides on the interface between the oxidic layer and the matrix results in strengthening the adhesion of the oxidic layer to the matrix, therefore, the oxidation resistance for a long time at high temperature is improved apparently.

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