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Corrosion Resistance of Laser Clad Coatings with CeO₂

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Abstract

The effects of rare-earth oxide CeO₂ on the microstructure and corrosion resistance of laser clad Fe-based alloy coatings were investigated. The Fe-based alloy powders with different content of CeO₂ were laser clad on to a steel substrate. The clad coatings were examined and tested for microstructural features. Corrosion tests were performed in two ways: anodic polarization and weight loss. By means of a potentiostat, the anodic polarization curves of laser clad coating specimens were obtained in different corrosive solutions. By means of weight loss, both the corrosion rate and the corrosion dynamics of clad coatings in different solutions were measured. The corrosion morphology of clad coatings was observed using scanning electron microscope (SEM). The results of corrosion test were compared with that for coating without CeO₂. The comparison indicated that addition of CeO₂ can modify the microstructure and corrosion performance of laser clad coatings. The microstructure gets refined. The secondary dendrite spacing and the inclusion percentage of the coatings are reduced. The addition of CeO₂ modifies the electrochemical corrosion behavior. The corrosion resistance of the coatings with CeO₂ is enhanced significantly. The corrosion rate of the coatings is decreased by the addition of CeO₂. The mechanism of these effects is also discussed in this paper.

Keywords: Laser Clad Coating; Rare-earth CeO₂; Microstructure; Corrosion Resistance

1. Introduction

The laser has been recognized as a viable energy source for cladding wear- and corrosion-resistant materials on metal surfaces for decades. The principal advantages of the technique include reduced effect of heat on the underlying substrate, especially reduced grain growth and reduced distortion. Another asset is the minimized dilution of the clad material from the base metal, resulting in unprecedented overlay properties (e.g. maximum hardness and optimum corrosion resistance) [1]. Finally, laser cladding can offer good fusion bonding and fine microstructure of the surface coatings. It can also reduce the degree porosity in the coating [2,3].

Cerium, as a rare earth element, has been successfully applied in steels and for their chemical heat treatments[4]. Efforts have also been made to make use of cerium in many fields of surface engineering, such as flame spraying [5], diffusion heat treatment [6], electroplating [7] and so on. However, there is still very little published information on the application of rare earth elements in laser surface modification technologies [8,9]. In this paper, the microstructure and corrosion resistance of laser-clad Fe-based alloy coatings with and without CeO₂ are studied. The purpose of the study is to enlarge the fields of application of rare earth elements.

2. Experimental procedure

The substrate material used was commercial low alloy steel (AISI 1115), which was cut into specimens measuring 120mm × 120mm × 6mm. Ferrite–base self–fluxing alloy powder, having a grit size of –150+320 mesh, was chosen as laser clad material. Table 1 shows the chemical composition of the powder. CeO₂, having a purity of over 99%, was added to the ferrite-based alloy powder at different ratios ranging from 0wt% to 4.0wt%.

Table 1. Composition of the ferrite-based alloy powder

Element	Ni	Cr	B	Si	C	Fe
Composition (wt%)	12.95	20.7	1.38	2.6	0.074	rest

Firstly the specimens were cleaned in acetone solution. Then laser cladding was achieved by a continuous wave CO₂ laser with a powder feed system. The laser was operated at 3.0 kW and the width of linear beam was 10mm. The laser traverse speed was 2.5 mm s⁻¹. Argon gas was used to minimize oxidation. Finally the coatings with a thickness of 0.7–0.8 mm were obtained.

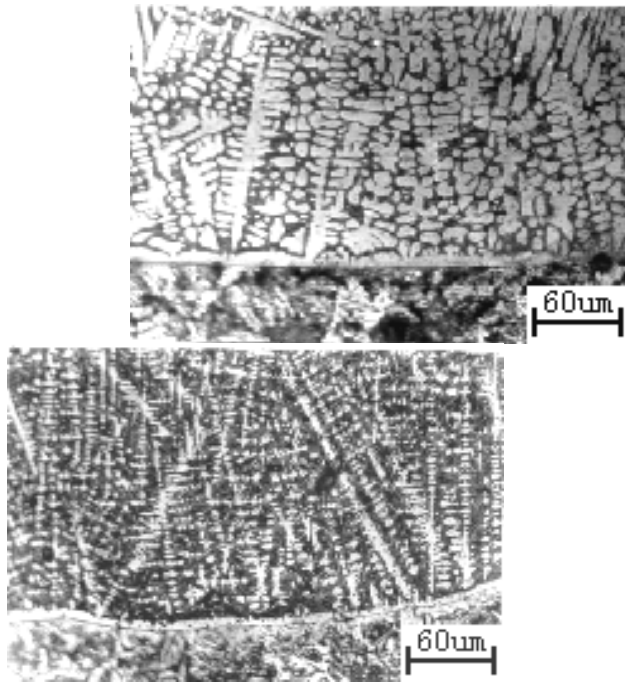
An optical microscope and JSM-6301F scanning electron microscopy (SEM) were used to observe the microstructure of the clad coatings. An image analysis system was used to quantify the percentage of inclusion in the coatings. The effect of CeO₂ on the corrosion resistance of the clad coatings was investigated by measuring anodic polarization curves and weight loss. A JH2C constant potential instrument was used to obtain the anodic polarization curves of various clad coatings with or without CeO₂. The electrochemical experiments were conducted in 1N H₂SO₄, 1N HNO₃, 5%HCl and 5%NaCl solutions, respectively. The corrosion rate of the clad coatings was also measured in 1N H₂SO₄ solution by means of the weight loss method.

3. Results

3.1. Microstructure observation

The microstructure of the clad coatings at the transition zone between coating and substrate and at the surface of the coating was observed by SEM, the results being presented in Fig.1 and Fig.2 separately. It can be seen that the microstructure of the coatings mainly consists of dendrite grains and eutectic. The microstructure of the coatings containing CeO₂ is finer than that without RE. The morphology and distribution of dendrite become modified with the addition of CeO₂. The refined dendrite boundaries form a more compact network structure. CeO₂ also effects a reduction in the secondary dendrite spacing, as shown in Fig. 3.

However, it should also be pointed out that when the CeO₂ concentrate is too high, for example, greater than 2.0 wt.%, the grain size of the clad coating becomes larger, rare earth may accumulate to form inclusion, and the secondary dendrite spacing becomes greater (shown in Fig.3 and Fig.4)

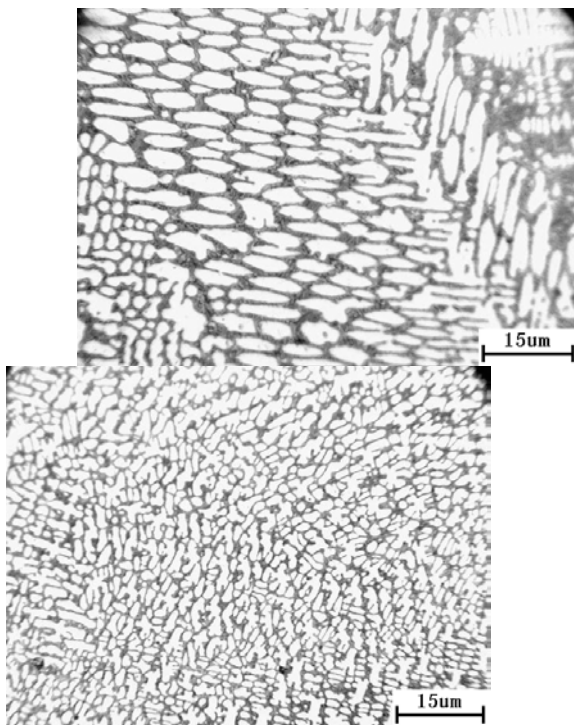


(a)

(b)

Fig.1 Microstructure revealed by SEM of the clad coatings at the transition zone between coating and substrate:

(a) without CeO_2 ; (b) with 1.2% CeO_2



(a)

(b)

Fig.2 Microstructure revealed by SEM at the surface of the coating:

(a) without CeO_2 ; (b) with 1.2% CeO_2

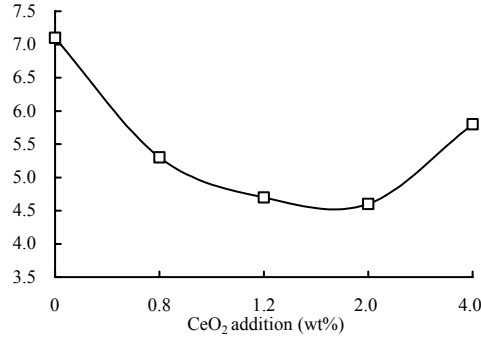


Fig.3 Secondary dendrite spacing of the clad coatings.

3.2. Inclusion percentage in the coatings

Fig. 4 illustrates the relationship between CeO₂ addition and inclusion percentage in the coatings. With the addition of CeO₂ the amount of inclusions dropped significantly.

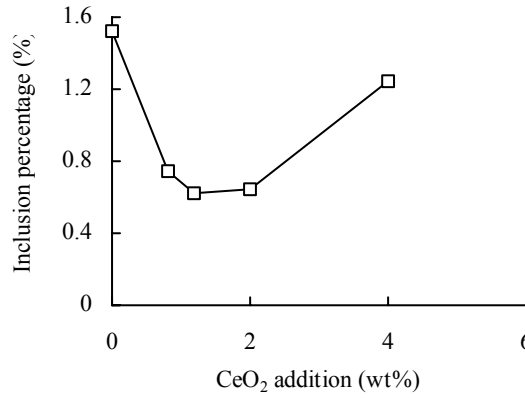


Fig.4 Inclusion percentage in the clad coatings.

3.3. Corrosion tests

Anodic polarization curves of various clad coatings in 1N H₂SO₄, 1N HNO₃, 5% HCl and 5% NaCl solutions were recorded, as presented in Fig. 5. Fig.5(a) and (b) shows that the values of i_p (the peak current corresponding to the active-to-passive transition) and $i'_{p'}$ (the current corresponding to passivation) of the specimens with RE are lower than those of the specimens without RE. The coatings with RE have a clear passive zone. This reveals an increasing tendency of being passive and an excellent corrosion resistance of clad coatings with RE. It is clear that the addition of CeO₂ reduces the passive current and the critical current; this reveals an increasing tendency of being passive and an excellent corrosion resistance of the clad coatings with RE in H₂SO₄ and HNO₃ solutions.

In HCl and NaCl solutions (Fig.5(c) and (d)), it is difficult to form passive film on the coatings. The passive effect of the coatings is weak and there exists no clear passive zone. However, the addition of RE results in the reduction of corrosion current density, and this indicates a lower corrosion rate and therefore an improvement in corrosion resistance.

From the above, it is seen that the addition of RE can modify the electrochemical corrosion behaviour of the coatings in different solutions.

By means of weight loss method, the corrosion rate of the clad coatings in 1N H₂SO₄ solution was also measured. The results are presented in Table 2. It can be seen that the corrosion rate of the coatings with RE was reduced.

The corrosive dynamics curve of the coatings 1N H₂SO₄ solution are shown in Fig.6. It can be found that the addition of CeO₂ offers a lower corrosion weight loss, which shows an increase in the corrosion resistance of the coatings.

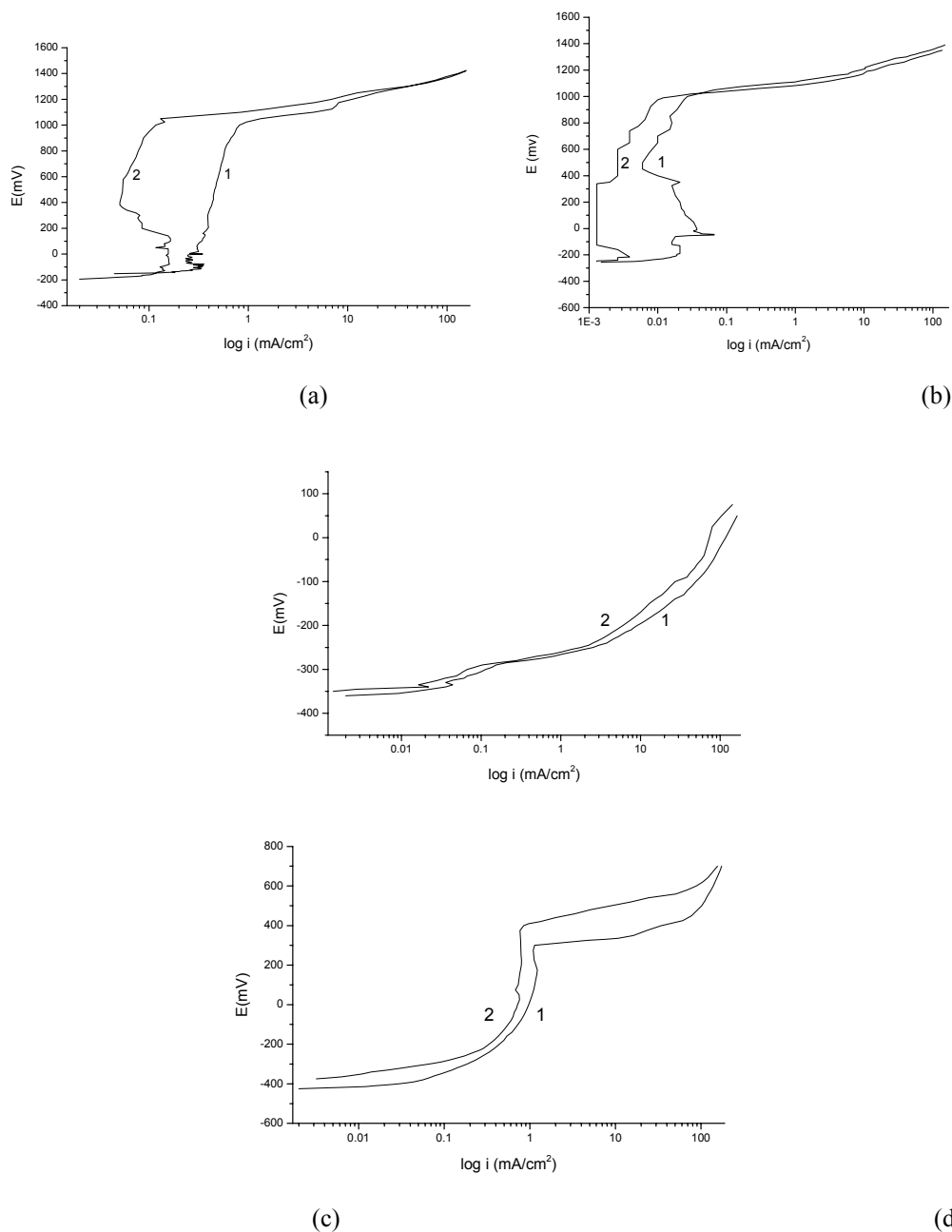


Fig.5 Anodic polarization curves of the clad coatings.(1–without CeO_2 ; 2–with 1.2% CeO_2).
(a) 1N HNO_3 ; (b) 1N H_2SO_4 ; (c) 5% HCl and (d) 5% NaCl

Table 2 Corrosion rate of clad coatings with different content of CeO_2 in 1mol/L H_2SO_4 ($\text{g}/\text{m}^2 \text{ h}$)

Corrosion time /h	Content of CeO_2 / wt. %				
	0	0.8	1.2	2.0	4.0
10	2.28	2.16	1.90	2.16	2.17
20	1.76	1.57	1.28	1.70	1.72

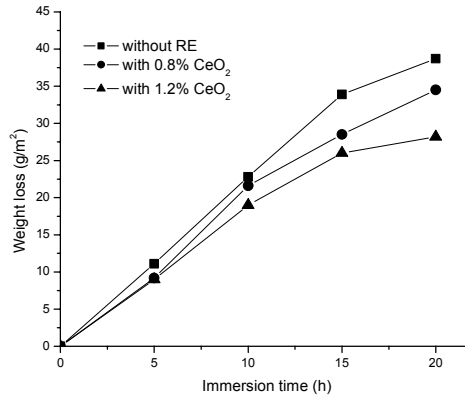
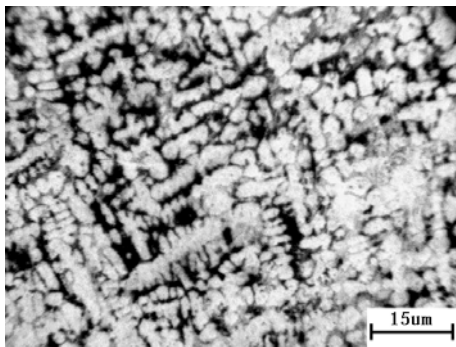
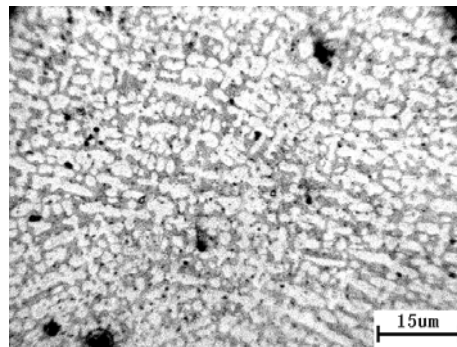


Fig. 6 . Weight loss vs. time of laser clad coatings in 1 mol/L H₂SO₄ solution

The corrosion morphology of the coatings 1N H₂SO₄ solution is presented in Fig. 7. After the specimens had been placed in H₂SO₄ for 20 days, the surface of the specimen without RE was attacked: the morphology was changed completely, and the attack was not uniform. In contrast, the surface with RE was the same as before testing, thus having the character of the rapid melt-solidification morphology produced by laser remelting. The surface was rather uniform and smooth, and evidence for attack was hardly found. The morphology analysis illustrates that RE could offer a lower corrosion rate and better corrosion properties for laser clad coatings.



(a) without RE



(b) with RE

Fig. 7 Morphology of the corrosion specimens of laser clad coatings at 1N H₂SO₄ solution after 20 days

4. Discussion

The refining effect of RE on microstructure of clad coatings is due mainly to the characteristics of RE. RE is surface active element with rather large atomic radius. The atomic radius of cerium is 0.1824nm. RE is easy to react with other elements and stable compounds can be formed. It can increase the number of crystal nuclei during crystallization of laser remelted zone. The greater the number of crystal nuclei, the finer the grains [10]. thus the microstructure of the coatings can be refined. On the other hand, since the atomic radius of RE is rather large, the existence of RE within solid solution would surely cause great distortion of lattice, which would increase the energy of the system. In order to retain the lowest Helmholtz free energy, an enrichment of RE over the grain boundary, where the atomic arrangement is irregular, would be required. Thus RE in a clad coating distributes mostly over the grain boundary. When the grains grow the RE atoms and compounds over the grain boundary would make a dragging effect on the movement of grain boundary and the growth

of grain will be suppressed. Therefore the grain size is further refined

The chemical activity of RE results in the formation of some high melting-point compounds between RE and O, S, N and so on during cladding process. Some compounds would float off liquid phase before solidification and slag may occur on the surface of clad layer. Therefore the inclusion content within the coatings is decreased and the coatings are purified by deoxidation and desulfuration.

However, if the content of RE is too much, the compound with RE formed during cladding process would get the condition of accumulation and growth which would result in the reduction of the number of practical crystal nuclei. The microstructure of the coating can't be effectively refined.

As stated above, RE has obvious effects of refining grain size, reducing secondary dendrite spacing, purifying clad coatings.

In a corrosion medium the existence of active sites over the surface result in the inhomogeneity of the surface potential. Many microcells will be formed, and electrochemical corrosion will occur. In acetic solution it is usually hydrogen evolution that controls corrosion procedure. The cathode reaction (hydrogen evolution) occurs mainly over the inclusion, which has a low hydrogen overpotential [11-12]. Since the addition of RE could purify the clad coating and decrease the inclusion percentage, the area of active cathode is lessened, the surface potential tends to be uniform, and the amount of active sites and microcells are reduced with the addition of RE. As a result, in clad coatings containing RE, the cathode process is restrained, the corrosion rate is lowered, and the corrosion resistance is improved.

5. Conclusions

- (1) CeO₂ refines the microstructure of laser clad coatings. The secondary dendrite spacing is decreased and the microstructure becomes more compact.
- (2) The inclusion percentage in the coatings is deduced.
- (3) The corrosion property of the clad coatings is improved. The corrosion rate is decreased significantly.

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