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Rare-earth La_2O_3 modification of laser-clad coatings

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The effect of rare-earth La_2O_3 on laser-clad coatings has been studied. For this purpose, nickel-based alloy powders with different contents of La_2O_3 were laser-clad on to a steel substrate. The clad coatings were examined and tested for microstructural features, microhardness, inclusions and phase composition. The results are compared with those for coatings without La_2O_3. The comparison indicates that additions of La_2O_3 refine the microstructure of the clad, and the coating increases its microhardness. Moreover, the wear resistance and corrosion resistance of the clad coatings are also enhanced.

1. Introduction

One of the solutions to many problems of wear and corrosion is the use of coatings. There are many ways to prepare coatings on the substrate. Amongst them, laser cladding is an effective way of material processing that produces a surface layer having good wear and corrosion properties with minimal dilution [1, 2]. Owing to its unique advantage, laser cladding has developed rapidly in recent years.

Work on rare-earth elements (RE) have dealt mostly with metallurgy [3] and surface treatment [4–6]. The studies indicate the advantageous effect of RE. Previous research of RE on laser surface modification has concentrated on laser alloying [7]. Very little has been carried out on laser cladding, although some has been done on laser-clad coatings containing CeO_2 [8].

In the present work, the effect of RE lanthanum on laser-clad coatings was investigated. With the same processing parameters, the nickel-based alloy powder containing various contents of La_2O_3 was laser clad on the workpiece. The microstructure and properties of the clad coatings were studied to obtain an experimental basis for practical application of RE.

2. Experimental procedure

2.1. Preparation of laser-clad coatings

The substrate used was AISI 1045 steel. Nickel-based alloy powder was selected as the laser cladding material, whose chemical composition is shown in Table I. The size of the powder was $-140+320$ mesh. RE La_2O_3 was added to the nickel-based powder in different ratios (wt % = 0.4, 0.8, 4), then the powder with or without La_2O_3 was coated on to the substrate by flame spraying. The thickness of the sprayed layer was about 0.5 mm.

TABLE I Chemical composition (wt %) of nickel-based alloy powder

Composition					
Ni	Cr	B	Si	C	Fe
Bal.	8.0	2.0	2.5	0.2	$\leqslant 10$

TABLE II Parameters of wear tests

Sliding speed ($m\,s^{-1}$)	Sliding distance (m)	Time (min)	Load (kg)
0.314	280	15	20

Laser cladding was performed by using a continuous 2 kW CO_2 laser, operating at power level of 1.5 kW at the scanning speed $5\ mm\,s^{-1}$. The laser beam was defocused to 4 mm diameter. Nitrogen gas was used to minimize oxidation.

2.2. Microstructure observation

Optical microscopy and scanning electron microscopy (SEM) were used to observe the microstructure of the clad coatings. Inclusions in the coatings were analysed by an image system. A D/max-RB model X-ray diffractometer was used to determine the phase structure of the clad coatings. The microhardness of the coatings was measured on a microhardness tester under a load of 50 g.

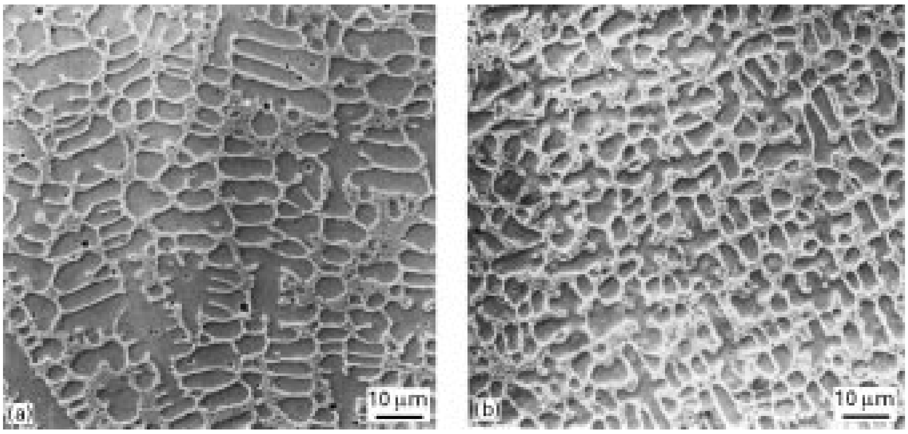

Figure 1 Microstructure of laser-clad coatings, (a) without La_2O_3, (b) with La_2O_3.

TABLE III Dendrite spacing of laser-clad coatings

	La_2O_3 addition (wt %)			
	0	0.4	0.8	4
Dendrite space (μm)	4.30	3.33	3.70	4.25

2.3. Wear tests

Wear tests were carried out on a block-on-ring friction and wear tester. The specimens were cut to $20 \times 4 \times 5$ mm^3 pieces and the surface of 20×4 mm^2 was laser treated. The counterpart ring was made of AISI 1045 steel, quenched at 860 °C and tempered at

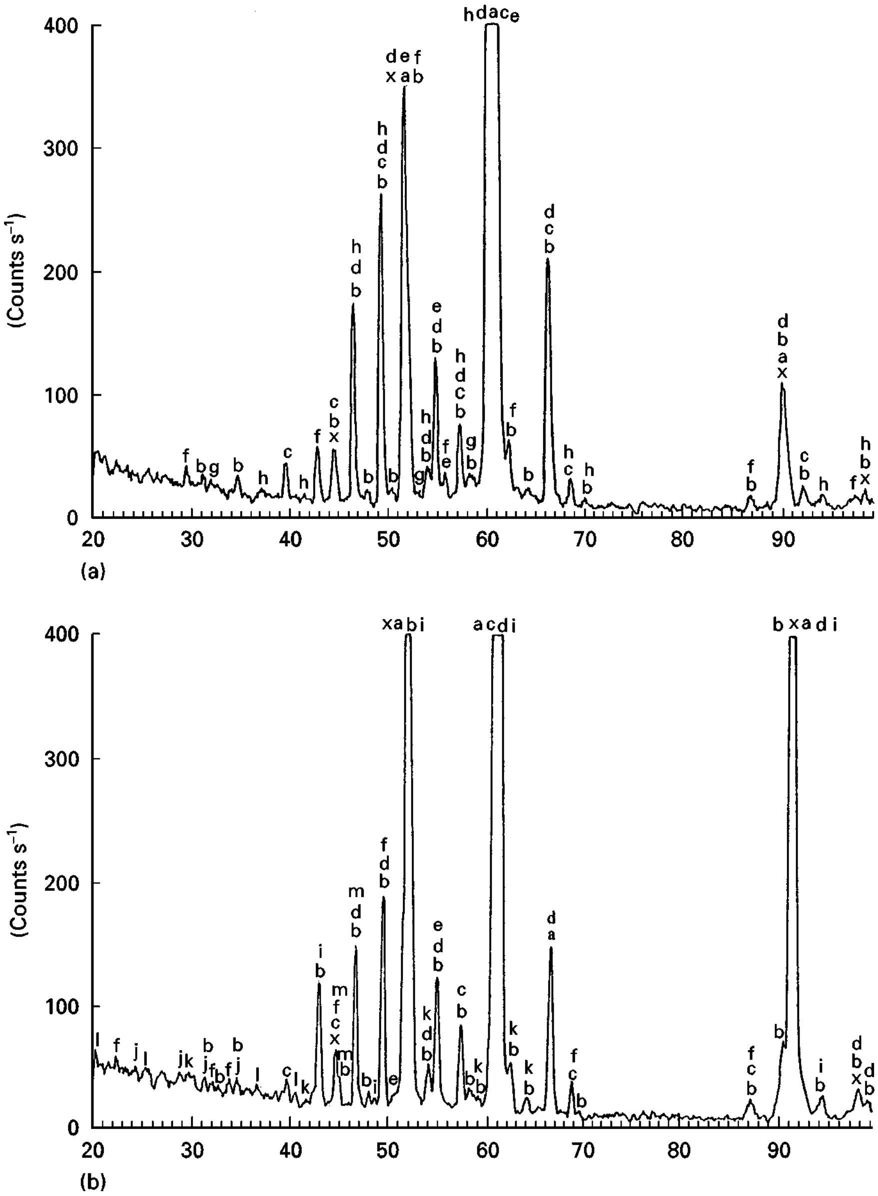

Figure 2 X-ray diffraction spectra of laser-clad coatings, (a) without La_2O_3, (b) with La_2O_3. ×, γ (Ni, Fe); a, Ni; b, Ni_3B; c, $(Fe, Ni)_{23}C_6$; d, σ-FeCr; e, Fe_3B; f, $C_3Ni_3B_6$; g, FeSi; h, $Ni_{16}Cr_6Si_7$; i, Cr_3Ni_2Si, C; j, La_2O_3; K, $LaCrO_4$; l, B_3LaO_6; m, $LaNi_8C_2$.

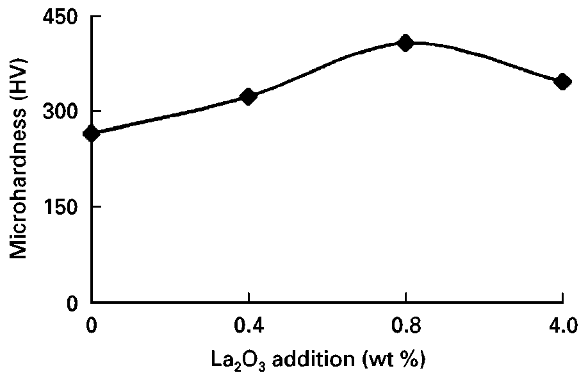

Figure 3 Microhardness of laser-clad coatings.

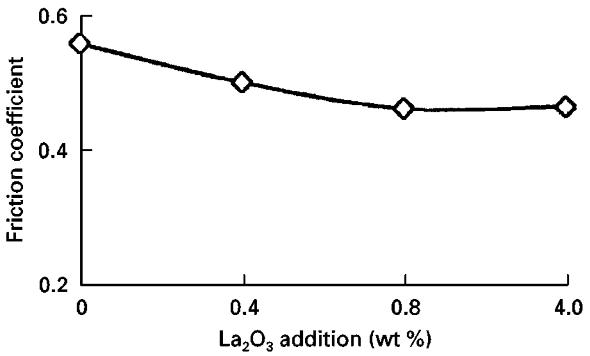

Figure 4 Friction coefficient of laser-clad coatings.

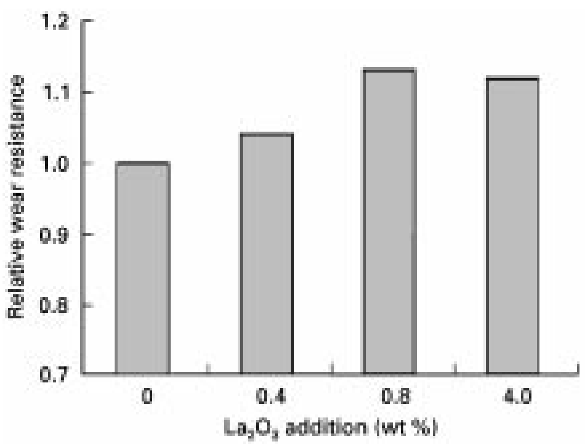

Figure 5 Relative wear resistance of laser-clad coatings.

180 °C, with a surface hardness of HRC 55. The diameter of the ring was 30 mm. Wear tests were performed without lubrication at room temperature. The parameters are shown in Table II.

The friction coefficient of the clad coatings can be obtained by calculating friction torque, and the relative wear resistance can be obtained from wear loss. The worn surface of the clad coatings was analysed by SEM.

2.4. Corrosion tests

Two types of corrosion test were used for evaluation of the clad coatings: (i) anodic polarization in four solutions: (1N HNO_3, 1N H_2SO_4, 1N HCl and 3% NaCl); (ii) weight-loss method in 1N HNO_3. The surface morphology after the corrosion tests was also studied by SEM.

3. Results and discussion

3.1. Microstructural observation

Fig. 1 shows microstructures of the clad coatings. It has been found that addition of La_2O_3 refines the microstructure of the coatings and reduces the secondary dendrite spacing. Table III shows the relationship between the addition of La_2O_3 and the secondary dendrite spacing in the clad coatings. Inclusion analysis shows that additions of La_2O_3 decrease the amount of inclusions in the clad coatings from 1.52% to 0.35%.

The effect of La_2O_3 on the microstructure of clad coatings is due mainly to the properties of RE. The surface activity of RE attributes to the reduction of surface tension and facilitates the formation of nuclei of the critical size. RE could also reduce the crystalline growth velocity. Both account for the refining effect of La_2O_3. On the other hand, the chemical activity of RE results in the formation of some high melting point compounds between RE and oxygen, sulphur and silicon during the cladding process. These compounds will form slag on the surface of the clad layer, thus decreasing the inclusion content within the coatings.

3.2. X-ray diffraction results of laser-clad coatings

The results of X-ray diffraction are shown in Fig. 2. As can be seen, the addition of La_2O_3 results in the formation of such compounds as $LaCrO_4$, B_3LaO_6 and $LaNi_8C_2$ in the clad coatings.

3.3. Microhardness of laser-clad coatings

The relationship between the addition of La_2O_3 and microhardness of the clad coatings is presented in Fig. 3. La_2O_3 additions increase microhardness of the coatings. As can be seen from comparison of Fig. 3 and Table III, the increase in microhardness correlates well with the refinement of microstructure, namely, the finer the grain, the higher the microhardness.

3.4. Wear tests

The friction coefficients of various clad coatings are shown in Fig. 4. It can be seen that La_2O_3 additions decrease the friction coefficient thus improving friction properties of laser-clad coatings. Such a modification may result from an increased microhardness of the clad coatings.

Fig. 5 illustrates the relative wear resistance of different clad coatings under the load of 20 kg. It is clear that La_2O_3 additions improve the relative wear resistance of the clad coatings by about 10%.

The morphology of worn surfaces, as observed by SEM, is shown in Fig. 6. The worn surface of the coating with the addition of La_2O_3 is smoother and more regular in appearance.

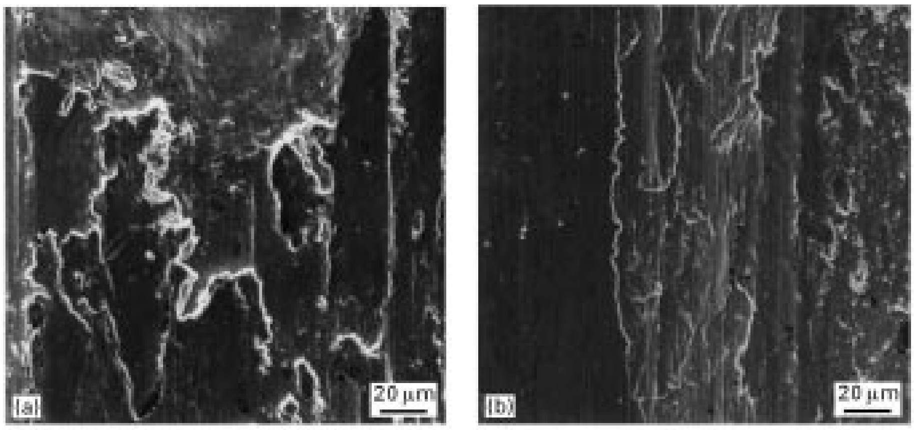

Figure 6 Morphology of the worn surfaces of laser-clad coatings, (a) without La_2O_3, (b) with La_2O_3.

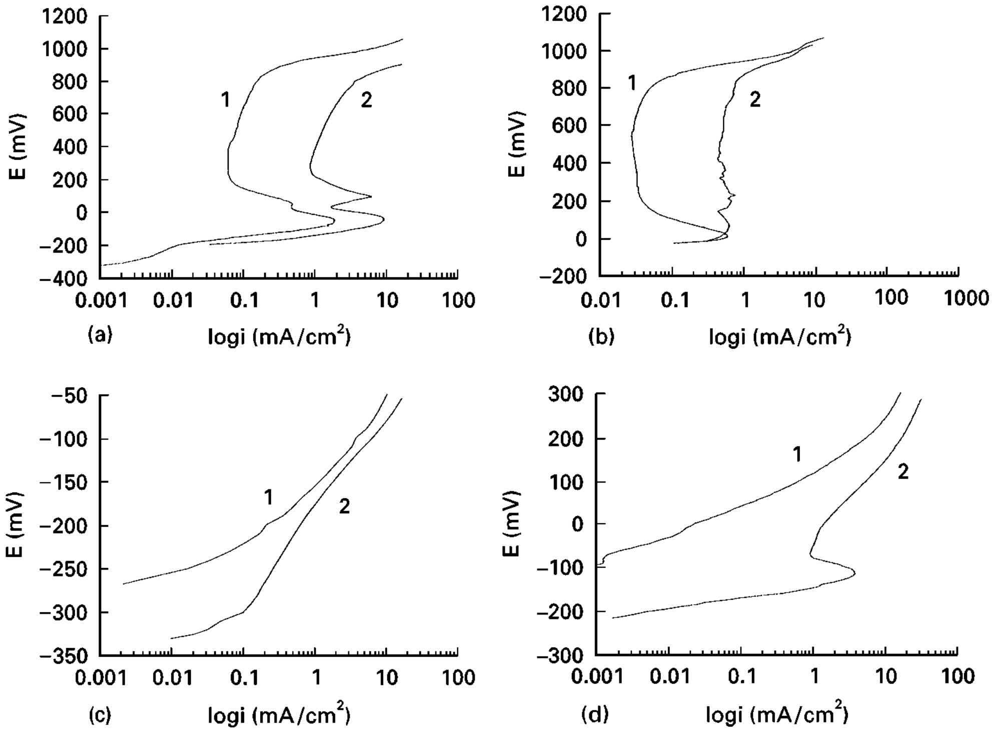

Figure 7 Anodic polarization curves of the clad coatings, (1) with La_2O_3, (2) without La_2O_3. (a) H_2SO_4, (b) HNO_3, (c) HCl, (d) NaCl.

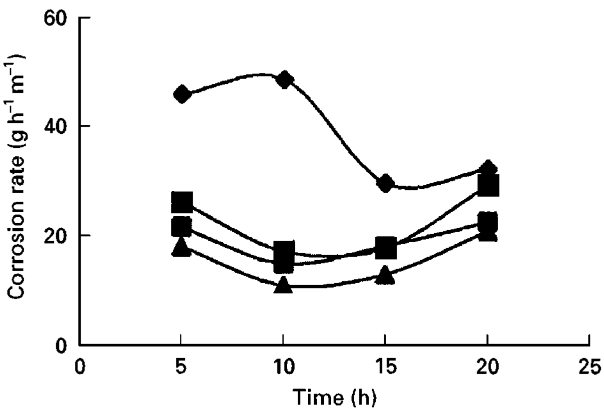

Figure 8 Corrosion rate of laser-clad coatings: (◆) Ni, (■) Ni + 0.4% La_2O_3, (▲) Ni + 0.8% La_2O_3, (■) Ni + 4.0% La_2O_3.

The effect of La_2O_3 on the friction and wear behaviour of the clad coatings can be explained in the following way. First, the addition of La_2O_3 increases microhardness and therefore helps to improve the wear resistance and lower the friction coefficient. Secondly, there are some new phases in the clad coatings containing La_2O_3. These hard particles dispersed in the coatings form a wear-resistant microstructure.

3.5. Corrosion tests

Electrochemical experiments were carried out by recording anodic polarization curves of the clad coatings in four solutions. The following conclusions can be drawn from the results shown in Fig. 7.

1. In H_2SO_4 and HNO_3 solutions (a, b) the passive property of laser-clad coatings is good. The coatings have a clear passive zone and the passive current is rather small. The addition of La_2O_3 decreases the passive current greatly. It also reduces the critical current and enlarges the passive zone to some degree.

2. In HCl and NaCl solutions (c, d) the passive effect of laser-clad coatings is weak and no clear passive zone is observed. However, the addition of La_2O_3 results in a reduction of the corrosion current density

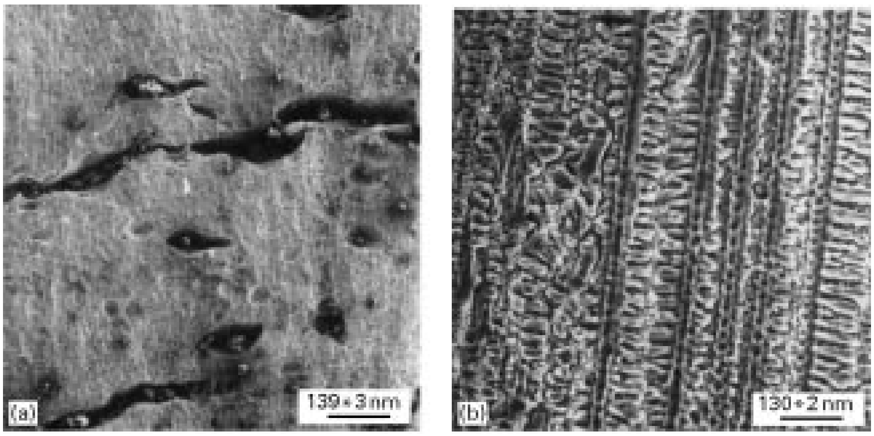

Figure 9 Morphology of the corrosion specimens of laser-clad coatings, (a) without La_2O_3, (b) with La_2O_3.

in laser clad coatings, thus indicating a lower corrosion rate and an improvement in corrosion resistance.

As can be seen from the above, additions of La_2O_3 modify the electrochemical corrosion behaviour of the clad coatings in different solutions.

The curves in Fig. 8 show the relationship between the corrosion rate of different clad coatings and corrosion time in 1N HNO_3 solution. The corrosion rate was evaluated by measuring the weight loss over 20 h at 5 h intervals. The addition of La_2O_3 leads to a great reduction in corrosion rate.

The surface morphology of coatings exposed to 1N HNO_3 solution is presented in Fig. 9. Some cracks are observed on the surface of the clad coatings without La_2O_3 (a), even after 10 h exposure, while the surface of the clad coatings containing La_2O_3 remained uniform when the specimens had been in HNO_3 for 20 h (b). The morphology illustrates that La_2O_3 could offer a lower corrosion rate and better corrosion resistance of laser-clad coatings.

The effect of La_2O_3 on the corrosion behaviour of the clad coatings can be ascribed to microstructure refinement of the clad coatings. The amount of inclusions is also diminished. The refining and purifying effect of La_2O_3 makes the microstructure more compact. Then the surface potential tends to be more homogeneous and it becomes more difficult for corrosion to occur.

4. Conclusions

Additions of RE La_2O_3 to laser-clad nickel-based alloy coatings results in the following changes.

1. The microstructure of the clad coatings is refined and the secondary dendrite spacing becomes smaller. The amount of inclusions in the coatings is decreased.
2. Some new phases are formed in the coatings.
3. Microhardness of the clad coatings is increased.
4. The friction and wear behaviour are modified. There is a reduction in friction coefficient and an increase in the relative wear resistance of the coatings with the addition of La_2O_3.
5. The corrosion resistance of the coatings is improved. The addition of La_2O_3 modifies the electrochemical corrosion behaviour. The corrosion rate of the coatings in HNO_3 solution is decreased.

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