

Microstructure of nanometer Al_2O_3 dispersion strengthened Ni-based high-temperature protective coatings by laser cladding

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Abstract: The nanometer Al_2O_3 dispersion strengthened NiCoCrAlY high-temperature protective coatings by crosscurrent CO_2 laser on Ni-based superalloy GH4033 were produced. Microscopic morphologies, phase constitutions of cladding coatings and distribution of nano- Al_2O_3 particles were examined using SEM and XRD. The results show that the interface grains, after adding proper nano- Al_2O_3 , grow from epitaxial to non-epitaxial shape gradually, and the columnar dendrites become thinner and denser with cellular shape. Cracks in the substrate close to the interface are eliminated. Moreover, dispersive nano- Al_2O_3 particles mainly distribute around cellular substructure and on grain-boundaries, which prevents the diffusion of alloying elements and restrains the formation of new phase. There is a critical value of nano- Al_2O_3 addition, and the most suitable content of nano- Al_2O_3 is 1% (mass fraction) in this experimental conditions. The “nanometer effect” of nano- Al_2O_3 particles plays an important role in the improvement of coating microstructure.

Key words: high-temperature protective coating; laser cladding; nano- Al_2O_3 ; microstructure

1 Introduction

High-temperature protective coatings have been widely researched and applied in the aerospace, aviation, gas power generation, chemical industry, metallurgy and other fields[1–3]. MCrAlY (M=Fe, Ni, Co) high-temperature protective coatings are generally strengthened by solution and γ' -phase, nevertheless, these enhancement patterns will not work when the temperature is over 1 000 °C. The strength components of MCrAlY alloy play a decisive role in the growth speed, component, and integrality of thermal oxygenation layer and its bonding to and flaking off the base in the thermal cycles[3–4]. Therefore, the selection of strengthening component of MCrAlY alloy is highly important to the service performance of high-temperature protective coatings.

Some relevant researches show that nanometer structure coatings have many advantages in the strength, toughness, corrosion resistance, heat resistance and other

characteristics compared with the traditional coatings, owing to the nanometer effect of scaled phase in the coatings[4–10]. Furthermore, the nanometer scaled phase has a certain impact on the thermal expansion coefficient, thermal conductivity coefficient and other thermal parameters. Meanwhile, the laser cladding technology has been one of main technologies to prepare MCrAlY coatings with the development of laser technology. With introducing “nanometer effect” to laser cladding MCrAlY coatings technology, preparation of the nanometer oxide dispersion strengthened(NODS) MCrAlY coatings by laser cladding will further enhance the performance of MCrAlY coatings because of the cooperation of the “high-power and fast-cooling” of laser cladding and the “nanometer effect”.

Most researches on NODS MCrAlY laser cladding coatings are almost concentrated on the modification of ferrous alloys, and the research on NODS laser cladding coatings on superalloy is limited to the wear-resistant coatings of NiCrBSi series. The study of NODS MCrAlY high-temperature protective coatings on super-

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alloy by laser cladding technology has been less reported before[8–11].

The nanometer oxide Al_2O_3 dispersion strengthened NiCoCrAlY high-temperature protective coatings by A.C. CO_2 laser on Ni-based superalloy GH4033 were produced. This work aims to analyze the microscopic morphologies, distribution of nano- Al_2O_3 particles, cracks and phases of NODS NiCrAlY cladding coatings. The crystallization behavior of the coatings and the effects of nano- Al_2O_3 particles on the microstructure of the coatings are investigated, which lays a foundation for the analysis of the effects of nanometer particles on the properties of the coatings.

2 Experimental

The substrate material is Ni-base superalloy GH4033 and the cladding material is NiCoCrAlY powders with size of 40–100 μm , and their chemical compositions are listed in Table 1 and Table 2, respectively. The average size of nano- Al_2O_3 powders is 20 nm.

Table 1 Chemical compositions of GH4033 alloy (mass fraction, %)

C	Cr	Al	Ti
0.03–0.08	19–22	0.6–2.8	2.4–2.8
Ni	Fe	B	Si
Bal.	≤ 4	≤ 0.01	≤ 0.35

Table 2 Chemical compositions of NiCoCrAlY powders (mass fraction, %)

Cr	Al	Co	C	Y	Ni
18.64	3.39	2.60	0.55	1	Bal.

Composite powders for cladding with 0.5%, 1.0%, and 1.5% nano- Al_2O_3 (mass fraction) were prepared with the method presented by WANG et al[12]. The morphology of composite powders reinforced by 1.0% nano- Al_2O_3 is shown in Fig.1. The sample surface was polished with sand papers and cleaned up with acetone. The cladding powders were coated onto the substrate surface by the squash presenting method[13]. The thickness of the presenting layer was 0.4 mm. The single channel laser cladding experiments were carried out by 2 kW cross-current CO_2 laser with nitrogen protection. The laser power was 1 kW and the spot diameter was 2 mm. The scanning speed was kept as 5 mm/s. The metallographic specimens were polished, and then etched with aqua regia. The microscopic morphologies of cladding coatings were observed on the scanning electron microscope (JSM-7001F type). The phases of

cladding coatings were analyzed by the X-ray diffractometer (D/max 2500PC type).

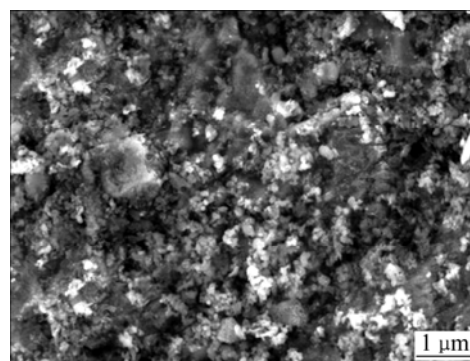


Fig.1 SEM morphology of NiCoCrAlY powders reinforced by 1.0% nanometer Al_2O_3

3 Results and discussion

3.1 Microscopic morphologies of cladding coatings

The cross-sectional SEM morphologies of cladding interface are shown in Fig.2. It can be seen that the solidification microstructure at the interface of cladding coatings without nano- Al_2O_3 appears in thin, directional and epitaxial dendrites perpendicular to the bottom of molten pool. This phenomenon is consistent with another related report[3]. After adding nano- Al_2O_3 , the columnar dendrites change in a cellular trend and the crystal morphology at the interface also changes. With the increase of additional nano- Al_2O_3 , the dendrites become thinner and denser. The crystal morphology at the interface translates from epitaxial growth (as shown in Fig.2(a)) to partially-epitaxial growth (as shown in Fig.2(b)), and then translates to non-epitaxial growth (as shown in Figs.2(c) and 2(d)).

With the proper addition of nano- Al_2O_3 , tiny nano- Al_2O_3 particles distribute dispersedly and uniformly in liquid metal. Lots of tiny and homogeneous nano- Al_2O_3 particles in the molten pool will be cores of heterogeneous nucleation, which promote the simultaneous nucleation of liquid metal in a large area and break the continuity of dendrite growth. Meanwhile, attached to the liquid/solid interface, nano-particles with large specific surface area hinder the growth of grains. From the above analysis, it can be seen that the effects of nano- Al_2O_3 on microscopic morphologies of laser cladding coatings are related with great-area heterogeneous nucleation of nano- Al_2O_3 particles and their action of hindering grain growth.

3.2 Distribution of nano- Al_2O_3 in cladding coatings

The distribution of nano- Al_2O_3 in cladding layer is shown in Fig.3. It can be seen from Fig.3 that there are

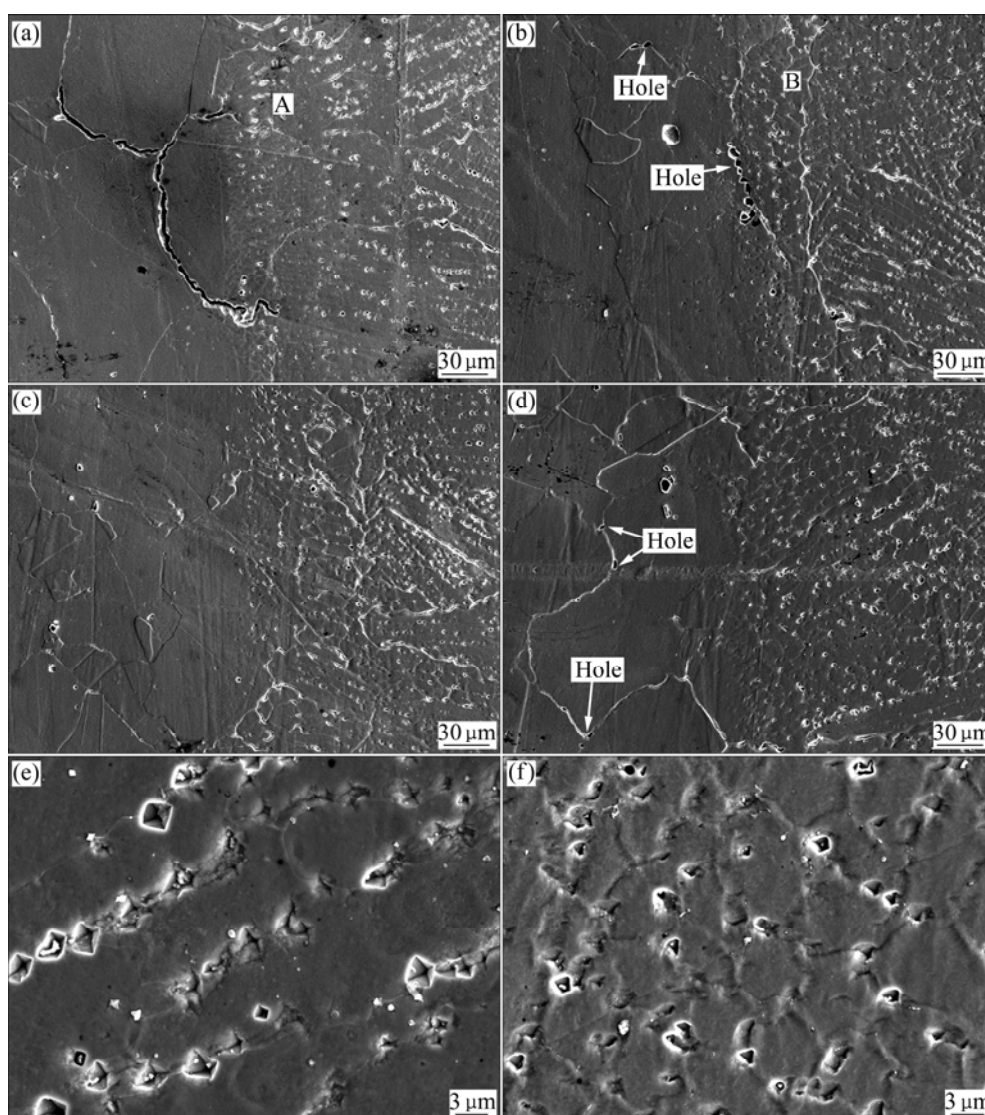


Fig.2 Cross-sectional SEM morphologies of cladding coatings: (a) Without Al_2O_3 ; (b) 0.5% Al_2O_3 ; (c) 1.0% Al_2O_3 ; (d) 1.5% Al_2O_3 ; (e) Local amplification of area A; (f) Local amplification of area B

lots of nanometer particles in the grain which mainly distribute around cellular substructure (as shown in Fig.3(a)) and on grain-boundary (as shown in Fig.3(b)), and the quantity of intragranular particles is more than that on grain-boundary. The particles on grain-boundaries of cladding layer without nano- Al_2O_3 (Fig.3(d)) are less and bigger than those of cladding layer with nano- Al_2O_3 (Fig.3(c)). Thus, it can be determined that tiny particles are the additional nano- Al_2O_3 besides a little of precipitates. Combined with cross-sectional SEM morphologies in Fig.2, although nano- Al_2O_3 particles aggregate around cellular substructure and on grain-boundaries, on the whole, the distribution of nano- Al_2O_3 particles in cladding layer is uniform because the size of intragranular cellular substructure is only 10 μm or so.

As shown in Fig.3(e), there are some deep colour

bands namely segregation zone of nano- Al_2O_3 particles in the cladding layer when the addition of nano- Al_2O_3 reaches 1.5%. It can be seen from Fig.3(f) that nano- Al_2O_3 particles in the segregation zone present in the flower-like form and the quantity of nano- Al_2O_3 particles around cellular substructure decreases significantly. The nano- Al_2O_3 segregation zone not only decreases the distribution uniformity of nano- Al_2O_3 particles, but also weakens the cellular tendency of dendrite, resulting in obvious dendrite characteristic and coarse microstructure (Fig.2(d) and Fig.3(e)). From above analyses, after excessive nano- Al_2O_3 particles are added, the size of micro-aggregates existing in micro/nano-powders will increase, and it will be further increased by attracting active monodisperse particles around it because the churning action of molten pool is limited in the course of laser cladding. With the increase

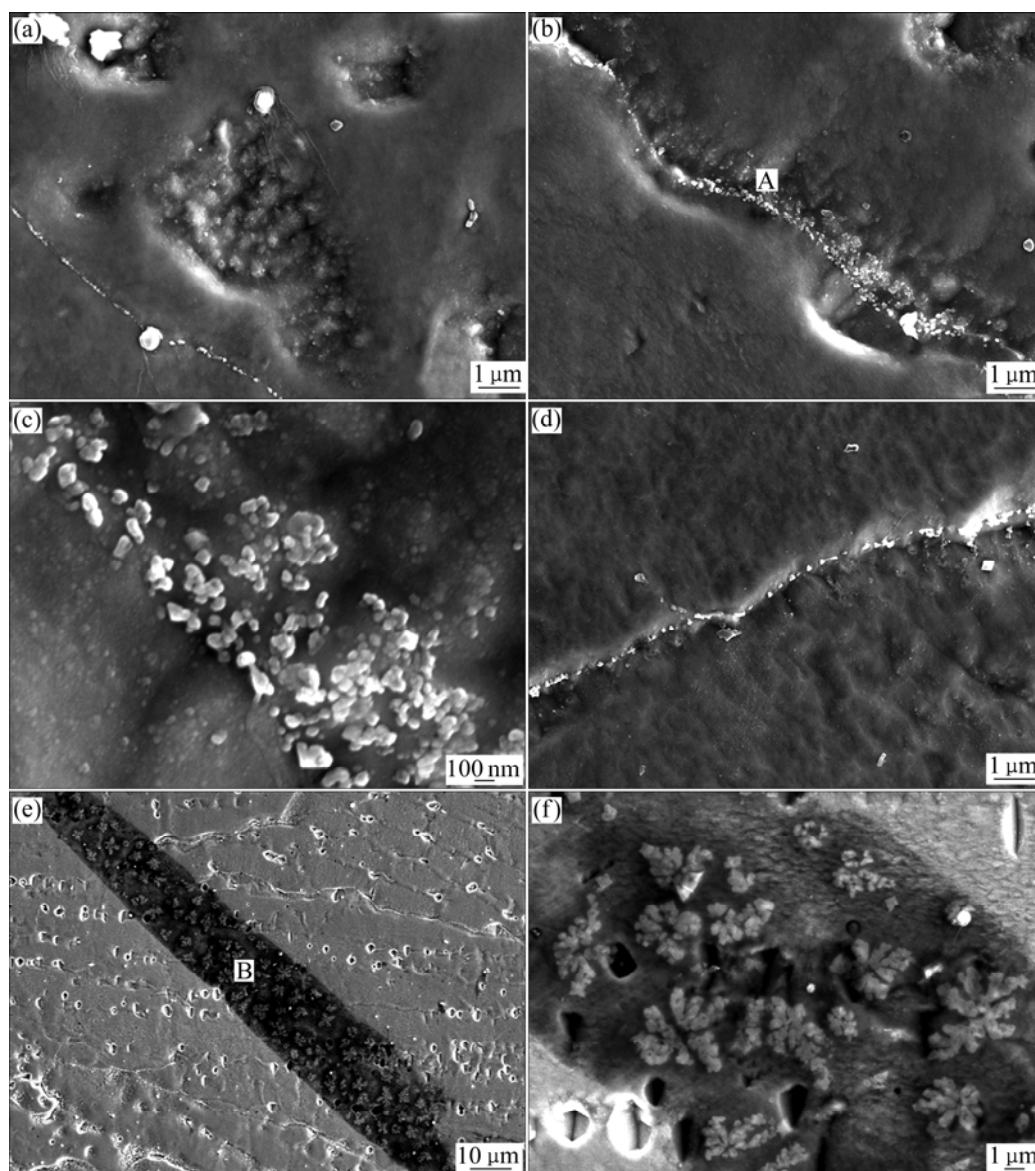


Fig.3 Distributions of nano- Al_2O_3 in cladding layer: (a) Grain interior; (b) Grain boundary; (c) Local amplification of area A; (d) Precipitates in cladding coatings without nano- Al_2O_3 ; (e) Aggregation of nano- Al_2O_3 in cladding coatings with 1.5% nano- Al_2O_3 ; (f) Local amplification of area B

of micro-aggregate size, the dispersive distribution of nano- Al_2O_3 particles is weakened. Aggregated nano- Al_2O_3 particles could not flow freely and float in some zone of the molten pool because of the “high-power and fast-cooling” of laser cladding. Therefore, the segregation zones of nano- Al_2O_3 particles appear regularly in the cladding layer with excessive nano- Al_2O_3 addition.

3.3 Effects of nano- Al_2O_3 on cracks

It can be seen from Fig.2 that there are obvious intergranular cracks in the substrate close to interface between coatings and substrate without nano- Al_2O_3 , and they extend to the bonding interface. There are some holes in the interface region and the substrate close to

interface when 0.5% nano- Al_2O_3 is added. The cracks disappear completely when 1.0% nano- Al_2O_3 is added. Some small holes appear once again in the substrate close to interface when the content of nano- Al_2O_3 reaches 1.5%. Moreover, the cracks of coatings are formed by the extension of some defects on grain-boundary such as holes and inclusions under the action of stress. From the above results, it is shown that the addition of nano- Al_2O_3 has certain inhibiting effect on cracks. However, there is an optimum value of nano- Al_2O_3 addition, and the most suitable content of nano- Al_2O_3 is 1.0% in this experimental conditions.

The residual stress of cladding layer is

$$\sigma = E\Delta\alpha\Delta T / (1-\nu) \quad (1)$$

where E and ν are elastic modulus and Poisson ratio of

cladding layer, respectively; $\Delta\alpha$ is the difference of thermal expansion coefficient of substrate and cladding layer, ΔT is the difference of cladding temperature and room temperature[14].

It can be seen that main reasons causing hot-stress are the temperature gradient in the process of laser cladding and thermal expansion coefficient difference between cladding layer and substrate. The appearance of cracks in the substrate close to the interface indicates that the difference of thermal expansion coefficient, $\Delta\alpha$, is negative, so the substrate bears tensile stress. Both substrate and cladding layer belong to Ni-based superalloys, and their thermal expansion coefficients are almost the same. Thus, the value of residual stress of the coating is mainly determined by the temperature gradient.

After adding proper nano- Al_2O_3 , the “nanometer effect” of particles can increase latent heat of fusion, decrease liquidus temperature and improve solidus temperature, resulting in the decrease of the melting point of cladding layer and the reduction of the solidification temperature range. Because of the above reasons, the temperature gradient in the cladding process decreases, and the wettability of molten pool to the substrate is improved because the fluidity of molten pool increases. Therefore, the tensile stress of substrate is reduced, and the formation of holes and cracks is inhibited.

The research of CHEN et al[15] showed that the less the size of grain is, the bigger the area of grain-boundary is, and the less the thermal conductivity of coatings is. When the content of nano- Al_2O_3 reaches 1.5%, the appearance of holes in substrate close to the interface may be related with obvious dendrite characteristic and coarse microstructure of cladding layer resulted from the segregation of nano- Al_2O_3 . The coarse microstructure causes the increase of thermal conductivity of coatings, which results in the increase of temperature gradient and residual tensile stress. Therefore, the defects, such as holes, are caused again in substrate close to the interface.

3.4 Effects of nano- Al_2O_3 on phase constitutions

The XRD patterns of cladding coatings are shown in Fig.4. It can be seen that main phases of the coatings without nano- Al_2O_3 are γ -Ni, β -NiAl, γ' - Ni_3Al and α -Cr, and main phases of the coatings with nano- Al_2O_3 are γ -Ni, β -NiAl and γ' - Ni_3Al . There is no Al_2O_3 phase or new phase formed by Al_2O_3 , which may be related with the little addition of nano- Al_2O_3 .

The basic phase γ -Ni will present ex-solution and react with β -NiAl to form γ' - Ni_3Al and α -Cr, which is given by Eq.(2)[15]:

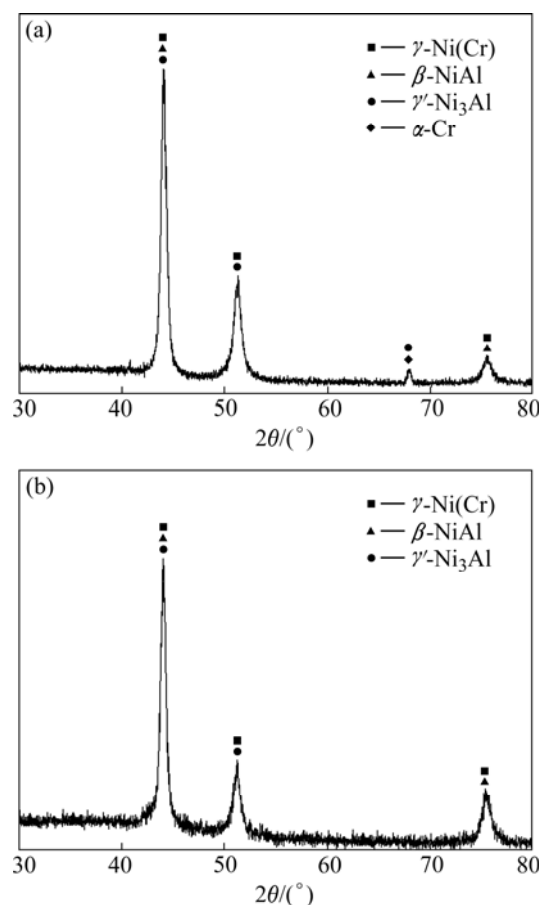


Fig.4 XRD patterns of nano- Al_2O_3 strengthened NiCoCrAlY coating: (a) Without Al_2O_3 , (b) 1% Al_2O_3



After adding nano- Al_2O_3 , nanometer oxides could hinder the dispersion of alloying elements, decrease the activity of Ni element and increase the dissolution of Cr element, which makes more Cr solid-solve into Ni substrate and inhibit the reaction of Eq.(2) to a certain extent. So, α -Cr phase disappears and the content of γ' phase also reduces. There is a very large volume change in the course of reaction, and the cracks appear because of the thermal expansion mismatch between coating and substrate. The reaction of Eq.(2) is inhibited after adding nano- Al_2O_3 , which has positive effect on reducing the trend of forming cracks. The cross-sectional SEM morphologies in Fig.2 also confirm this opinion.

4 Conclusions

1) After adding proper content of nano- Al_2O_3 , the interface grains grow from epitaxial to non-epitaxial mode. Columnar dendrites become thinner and denser with cellular shape. The cracks in the substrate close to the interface are inhibited.

2) The less addition of nano- Al_2O_3 will bring about

the inadequate modification on microstructure, but the excessive addition of nano- Al_2O_3 will reduce the improvement of nano- Al_2O_3 on microstructure. Thus, there is an optimum content of additional nano- Al_2O_3 , and the most suitable content of nano- Al_2O_3 is 1.0% in this experimental conditions.

3) The dispersive nano- Al_2O_3 particles mainly distribute around cellular substructure and on grain-boundaries, which prevents the diffusion of alloying elements and restrains the formation of new phase.

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