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ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 27, No. 6, Dec. 2009, p. 997
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Laser cladding in-situ carbide particle reinforced Fe-based composite coatings with rare earth oxide addition

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Received 18 February 2009; revised 27 March 2009

Abstract: Particulate reinforced metal matrix composite (PR-MMC) has excellent properties such as good wear resistance, corrosion resistance and high temperature properties. Laser cladding is usually used to form PR-MMC on metal surface with various volume fractions of ceramic particles. Recent literatures showed that laser melting of powder mixture containing carbon and carbide-forming elements, was favorable for the formation of in-situ synthesized carbide particles. In this paper, rare earth oxide (RE_2O_3) was added into the clad powder mixture to investigate the effects of RE_2O_3 on the in-situ carbide particle formation in Fe-based composite coatings. Through the analysis using scanning electron microscope (SEM), energy-dispersive spectroscopy (EDS) and transmission electron microscope (TEM), it was revealed that: (1) Adding RE_2O_3 to the Fe-based powder mixture could effectively reduce cracks and porosities and the coating surface was more smooth; (2) The solubility of carbon could be improved which increased the eutectic degree of the microstructure; (3) RE_2O_3 could promote the nucleation of the reinforcement particles as heterogeneous nuclei. During the precipitating process of the carbide particles, some RE_2O_3 powders still existed while others react with carbon in the melt to form rare earth carbides. Both of them acted as heterogeneous nuclei for the formation of particles.

Keywords: laser cladding; particle reinforced; rare earth oxide; nucleation; rare earth carbide

Rare earth (RE) elements possess excellent physical and chemical characteristics due to their particular atomic structure and outstanding chemical appetence. They have been applied successfully in many fields, such as metallurgy, electronics and chemical engineering[1]. One of their important applications is to modify the surface properties of engineering components, such as chemical treatment, flame spraying and electric plating[2–4].

In recent years, RE is gradually introduced to the area of laser surface treatments. Liu et al.[5] investigated the effects of the addition of La_2O_3 into NiCr-Cr_3C_2 precursor mixed powders on the microstructure and wear properties of laser cladding γ/Cr_7C_3/TiC composite coatings on γ-TiAl intermetallic alloy substrates. Coatings with good finishing, refined microstructure, reduced dilution and increased microhardness were obtained under an optimized La_2O_3 addition amount. The similar effects were reported by Wang et al.[6] when laser cladding a nickel-based alloy powder with addition of CeO_2 and La_2O_3. Zhao et al.[7] investigated microstructure evolution of laser cladding Ni/WC coatings with CeO_2 addition. The results showed that a small amount of CeO_2 could improve the dissolution of WC particles and thus the remained WC particles became smooth. CeO_2 could also spheroidize the eutectic structure of the coatings. Liu et al.[8] confirmed that the addition of Y_2O_3 could refine the grain size and improve the toughness of a gradient bioceramic coating by wide-band laser cladding.

Metal matrix composites (MMCs) are well known to have high hardness and outstanding wear resistance. Some carbide particles are often incorporated in the matrix to form particulate reinforced metal matrix composite (PR-MMC) to improve their high hardness even at elevated temperature. In-situ synthesis of the particles within the matrix has attracted more and more attention in recent years. The eminent advantage of the in-situ synthesis technology is that the reinforcements are much more compatible with the matrix and the interface between the reinforcements and the matrix is much stronger than the composites made by conventional methods such as the mechanical mixing. Recent literature reports on laser hardfacing show increasing interests in depositing composite coatings containing various volume fractions of hard particles in-situ synthesized[9–12]. Many re-

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DOI: 10.1016/S1002-0721(08)60377-4

searches have demonstrated that adding rare earth oxide (RE_2O_3) into the laser cladding powder mixture can refine the microstructure, however, little work was reported on the influence of RE_2O_3 addition on in-situ carbide particle nucleation especially in the field of laser producing PR-MMCs. This paper focused the effects of RE_2O_3 on the microstructure and nucleation of carbide particles in laser cladding Fe-based composite coatings.

1 Experimental

A medium carbon steel plate (0.45 wt.% C) with a dimension of 200 mm×50 mm×15 mm was used as substrate. Fe-based alloy powders (6.1 wt.% of C, 2 wt.%–5 wt.% Si, B, Ni, Mo and Co, balance of Fe) with particle size in the range of 74–100 μm were used. The Fe-based alloy powder was mixed with the mixture powders of Zr, Ti and WC powders (refer to "M") to form "MC" type carbide particles. Different mass percents of RE_2O_3 (mixed rare earth oxide with composition listed in Table 1) were added into the mixed powders. The mass percents of M and RE_2O_3 are listed in Table 2. The density of the carbide particles was calculated under the condition of 3 wt.%M with the change of RE_2O_3 contents (2%, 4%, 6%, 8% and 10%). When the content of M was increased to 15 wt.%, lager particles were obtained and the formation course of particles was investigated. The powder mixtures with different ratios were pre-placed on the steel plate surface with an organic binder. The thickness of the pre-placed layers was controlled to about 2 mm.

Laser cladding was performed using a 3 kW continuous CO_2 laser. The laser cladding parameters are laser power of 1500–2000 W, laser beam diameter of 3 mm and scanning speed of 3 mm/s. Argon was used as a protective gas against oxidation.

The clad samples were sectioned, mounted and polished. The density of the carbide particles ($D=N\text{p}/S$) was evaluated, where "S" is the area of the longitudinal section of the coating in the observation field and "Np" is the number of the

Table 1 Composition of RE_2O_3

w (RE_2O_3)/(%, mass fraction)				w (impurity)/(%, mass fraction)				
CeO_2	La_2O_3	Pr_6O_{11}	Nd_2O_3	Fe_2O_3	CaO	MgO	Cl^-	F
>58	27–33	4–7	<5	<0.05	<0.3	<0.01	<0.4	<0.1

Table 2 Additions of cladding powders

No.	w(M)/wt.%	w(RE_2O_3)/wt.%
1	3	0
2	3	2–10
3	15	0
4	15	5

particles. The data are the average calculated values from five typical back-scattered-electron (BSE) images in the middle part of the cladding layers.

The clad samples were then etched with a solution of HF, HNO_3 and H_2O for metallographic examination. The microstructural characteristics of the coatings and the particles were analyzed with scanning electron microscope (SEM) equipped with an energy-dispersive spectroscopy (EDS). The microstructure was further analyzed using JEM-200CX transmission electron microscope (TEM). All of the thin TEM slices, 0.5 mm in thickness, were taken from the cladding surface at a distance of 0.5 mm away from the top surface of the coatings using a linear cutting machine. The slices were polished into a 50 μm film and cut into disks with 3 mm in diameter using an ultrasonic disk cutter. The disks were subsequently ion milled.

2 Results and discussion

2.1 Microstructure

Fig. 1 shows that the thickness of the coatings after laser processing is in the range of 1.0–1.5 mm and it is uniform. An excellent metallurgical bond forms between the substrate and the coatings. However, cracks and porosities were observed in some coatings dependent on the different RE_2O_3 contents (Fig. 1(a)). A penetrating crack occurs in the coating without RE_2O_3 addition. Cracks disappear when RE_2O_3 is added into the clad powders. But porosities still appear in the layers with 2 wt.% and 4 wt.% RE_2O_3 addition respectively. When 6 wt.%–10 wt.% RE_2O_3 is added, the coatings are free of porosities and cracks. Laser cladding is a rapid heating and rapid solidification process, which may induce stress in the clad layers especially when the substrate and the cladding materials are rather different in physical properties. As a result, cracks and shedding occur easily. With addition of RE_2O_3 into the cladding powders, the RE_2O_3 is decomposed within the melt pool induced by the irradiation of high-energy laser beam. Parts of RE elements react with harmful elements like S, P and Si. It is known that REs have the effects of removing gas and slag, purifying microstructure and eliminating pores and cracks[13]. Therefore, adding RE to the powder mixture can effectively reduce the cracking and porosity and also improve the surface smoothness of the cladding coating.

Fig. 1(b) shows that the coatings have a typically hypoeutectic microstructure, which consists of primary austenite (γ) dendrites/cells, interdendritic ledeburite (Le) and dispersed carbide particles in-situ synthesized. A large amount of ultrafine particles exist and their distribution is homogenous. Most of the dispersed particles are in γ dendrite and