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Effect of RE oxides on the microstructure of the coatings fabricated on titanium alloys by laser alloying technique

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Abstract

Composite coatings were fabricated on the surface of pure titanium and Ti–6Al–4V by laser alloying with boron and graphite powders. The results show that with the addition of Ce_2O_3 and Y_2O_3, not only the compounds but also the microstructures of the coatings are refined compared with that without rare earth (RE) oxides. The mechanism of the microstructural refinement by the addition of RE oxides is discussed in this paper.

Keywords: Rare earth oxides; Titanium alloy; Microstructural refinement

1. Introduction

Titanium alloys are increasingly used in aerospace, marine, medical devices, etc., mainly due to their excellent specific strength and outstanding corrosion resistance. However, they are currently restricted to non-tribological applications, owing to their poor friction and wear resistance and strong tendency to galling. Titanium alloys modified with ceramic compounds of high strength and stiffness are expected to have an appreciable improvement in strength, wear resistance and high temperature stability. Titanium borides and carbides, such as TiB, TiB_2 and TiC, are excellent reinforcements for titanium alloys because of their particular properties such as high hardness and wear resistance in many tribological systems, good thermal stability at high temperature, and high elastic modulus. In recent years, various surface modification techniques have been developed to improve the wear and corrosion resistance of titanium alloys. Among them, laser beams are increasingly used due to their high coherence and directionality [1–3]. Therefore, they provide the ability to precisely control the width and depth of processing, the ability to process specific areas of a component and the ability to process complex parts. However, laser surface alloying of titanium alloys with boron and carbon separately can easily form coarse titanium borides (see Fig. 2a and c) and carbides [4], which have a detrimental effect on the toughness of the coatings [5–8]. As is well known, rare earth (RE) oxides are effective in grain refinement of alloys such as steel, cast iron, aluminum and magnesium alloy and thus improve the mechanical properties [9–12]. Xia et al. [13–15] reported that the RE element Gd can significantly reduce the lamellar packet sizes in as-cast titanium aluminides. With an addition of 0.15 at.% Gd, Ti–44Al–1Mn–2.5Nb alloy exhibits a obviously lower creep rate than that of the alloy without Gd. The microstructural coarsening rate of Ti-1100 alloy modified with Y (0.1 at.%) is slower at high temperature (1060 °C) compared with that of Ti-1100 alloy without Y [16]. The experiment of modifying TiAl alloy with element Y demonstrated that with the increase of Y from none to 0.6 at.%, the grain size decreased from 100 to 30 μm [17,18]. In addition, the alloy modified with Y has higher ultimate tensile strength,

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elongation and oxidation resistance than the Y-free alloy. After oxidation for 350 h, the mass gains for Y-free and 0.6Y-added alloys are 29.0 and 10.3 g/m^2, respectively, reflecting a significant improvement in the oxidation resistance by Y addition.

So, in the present study the laser alloying technique is employed to melt the surface of titanium alloys. Boron and graphite powders are selected as alloying materials for the purpose of producing wear resistance coatings on the surface of titanium alloys and the effect of RE oxides, Y_2O_3 and Ce_2O_3, on the microstructure of the coatings is investigated.

2. Experimental procedures

Pure titanium and Ti–6Al–4V samples, of dimensions 10 mm × 10 mm × 12 mm, were polished with SiC grit paper prior to the coating operation. Fine boron, graphite, Ce_2O_3, Y_2O_3 and pure Ti powders, of about 10 μm in size, were blended with dilute sodium silicate solution and precoated on the surface of the samples to a thickness of about 0.5 mm and then dried. A 1.5 kW continuous wave CO_2 laser with a beam diameter of 3 mm and at a scanning velocity of 3.5 mm/s, was employed to melt the surface of the samples. During the process of laser surface alloying, the precoated powders were dissolved into the melted pool, leading to surface alloying of the samples. To protect the melted pool from oxidation during processing, an argon gas shield at a pressure of 0.3 MPa was fed through a nozzle which was coaxial with the laser beam. In addition, there was a side argon gas flow through a nozzle at an angle of 30° to the melted pool. The alloying powders used and their weight ratios are shown in Table 1.

Metallographic samples were prepared using standard mechanical polishing procedures and then etched in a solution of HF, HNO_3 and H_2O in a volume ratio of 2:1:47 to reveal the growth morphology of the compounds in the coatings. The phase composition of the coatings were identified using a D/max-rC X-ray diffractometer with CuKα radiation operated at a voltage of 40 kV, a current of 40 mA, and a scanning rate of 5°/min. The microstructure and the chemical composition of the coatings were characterized using a JXA-8800R electron probe microanalyser (EPMA) and EPMA-energy dispersive spectroscope (EDS).

Table 1
The weight ratio of the powders

Sample	Powder				
	B	Graphite	Ce_2O_3	Y_2O_3	Ti
(1) Ti–6Al–4V	1				1
(2) Ti–6Al–4V	2		1	1	4
(3) Pure Ti	1				1
(4) Pure Ti	2		1	1	4
(5) Ti–6Al–4V	1	1			2
(6) Ti–6Al–4V	1	1	1	1	4

3. Results and discussion

Fig. 1 shows XRD spectra of the samples 1 and 5. Clearly, the boron and graphite powders have dissolved into the melt leading to the formation of titanium borides and carbides in the coatings. Comparing (a) with (b), (c) with (d), (e) with (f) in Fig. 2 and (a) with (b) in Fig. 3, it is seen that with the addition of Ce_2O_3 and Y_2O_3, not only the compounds but also the microstructures of the coatings are refined. The mechanism of microstructural refinement can be explained as following.

When irradiated by high energy density laser beam, a large proportion of added Ce_2O_3 and Y_2O_3 decompose and release atomic Ce and Y:

$$2Ce_2O_3 \rightarrow 4Ce + 3O_2 \uparrow$$
$$2Y_2O_3 \rightarrow 4Y + 3O_2 \uparrow$$

The refining effect of Ce and Y on the microstructure of the coatings is mainly due to the characteristics of Ce and Y.

Firstly, they are surface-active elements and thus reduce the surface tension and the interfacial energy between the crystal nucleus and the melt during the process of solidification. Reducing the surface tension results in increasing the wetting properties and decreasing the contact angle between the melt and a substrate. The surface activity of RE elements had been confirmed by a number experiments.

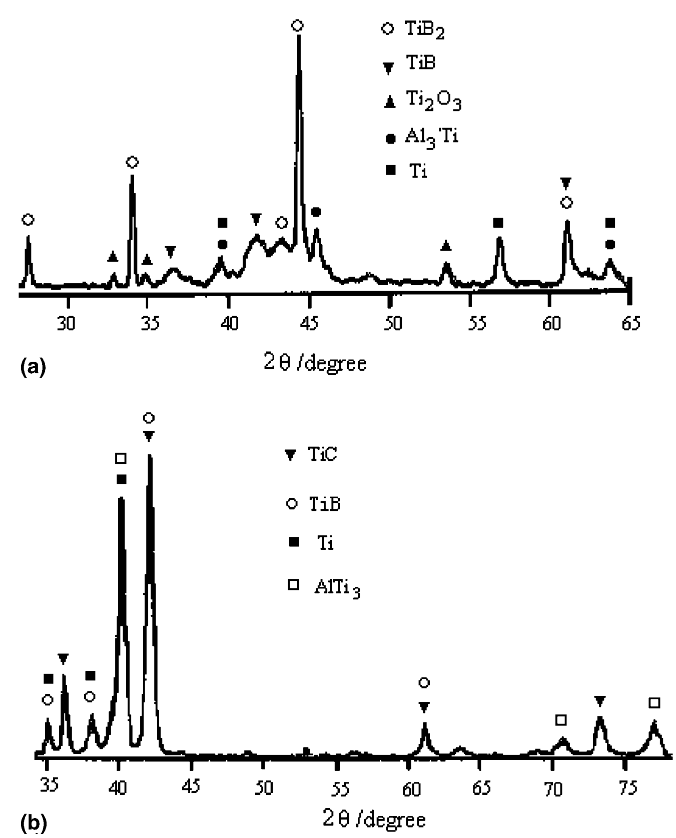

Fig. 1. XRD spectra of the samples: (a) No. 1; (b) No. 5.