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Influence of laser re-melting and vacuum heat treatment on plasma-sprayed FeCoCrNiAl alloy coatings

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ABSTRACT

FeCoCrNiAl high entropy alloy coatings were prepared by supersonic air-plasma spraying. The coatings were post-treated by vacuum heat treatment at 600 and 900 ℃, and laser re-melting with 300 W, respectively, to study the influence of different treatments on the structure and properties of the coatings. The phase constitution, microstructure and microhardness of the coatings after treatments were investigated using X-ray diffraction, scanning electron microscopy and energy dispersive spectrometry. Results showed that the as-sprayed coatings consisted of pure metal and Fe-Cr. The $AlNi_3$ phase was obtained after the vacuum heat treatment process. A body-centered cubic structure with less $AlNi_3$ could be found in the coating after the laser re-melting process. The average hardness values of the as-sprayed coating and the coatings with two different temperature vacuum heat treatments and with laser re-melting were 177, 227, 266 and 682 HV, respectively. This suggests that the vacuum heat treatment promoted the alloying process of the coatings, and contributed to the enhancement of the coating wear resistance. The laser re-melted coating showed the best wear resistance.

1. Introduction

Yeh[1,2] first proposed the concept of high entropy alloys (HEAs) in 1995. Typically, HEAs consist of five or more, but less than 13, principal elements. The component of each element should be between 5% and 35%, and the character of HEAs is determined by the combined features of multiple elements[3,4]. For distinguishing HEAs and traditional alloys, the number of principal elements was defined as more than five. In a similar fashion, alloys with one principal element are considered as low entropy alloys. Middle entropy alloys are between these two kinds of alloys and commonly have two to four principal elements[5].

The structure of HEAs is unique and no complex intermetallic compound exists within it due to the high entropy in the alloy system. Thus, simple solid solutions, like body-centered cubic (BCC), face-centered cubic (FCC) and even hexagonal close-packed (HCP) structures, as proved recently, tend to form[6]. The high solid solubility or single phase contributes to the potential characters of HEAs[7-9], including high strength and hardness, good wear, heat[10] and corrosion resistance, good magnetism performance and even bulk metallic glass properties[11].

HEAs have wide application prospects as a result of their outstanding properties[12]. They are even considered as potential nuclear materials[13]. Therefore, the utilization of HEAs in the preparation of coatings is a vital orientation for their development.

The current most common method for preparing HEA coatings is using laser cladding, which has many advantages. For instance, the coatings after laser cladding have uniform microstructures and a strong combination with the substrate[14-16]. However, laser cladding provides a lower efficiency due to the small spot size and slow scanning speed. Furthermore, the thermal injection of laser cladding is so high that it usually produces deformations, grain growth and phase changes to the workpiece after several claddings, which can have a detrimental effect on the qualities of the workpieces. In addition, physical vapor deposition (PVD), like magnetron sputtering and electron-beam evaporation deposition, is also used to prepare HEA coatings, since

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the coating thickness can be well controlled. However, there are some drawbacks for PVD. The long production cycle time and expensive price have restricted its development. Thus, finding a new technology for the preparation of HEA coatings is a vital research interest.

Nowadays, plasma spraying is one of the most commonly used technologies for preparing coatings[17,18]. It is a kind of thermal spray technology that uses high temperature plasma as its heat source and is mainly used to spray powder. Typically, heat treatment or re-melting is required to achieve a high quality coating after the plasma spray process. Furthermore, the efficiency of plasma spray deposition is much higher than other methods and every corner of the workpiece can be reached.

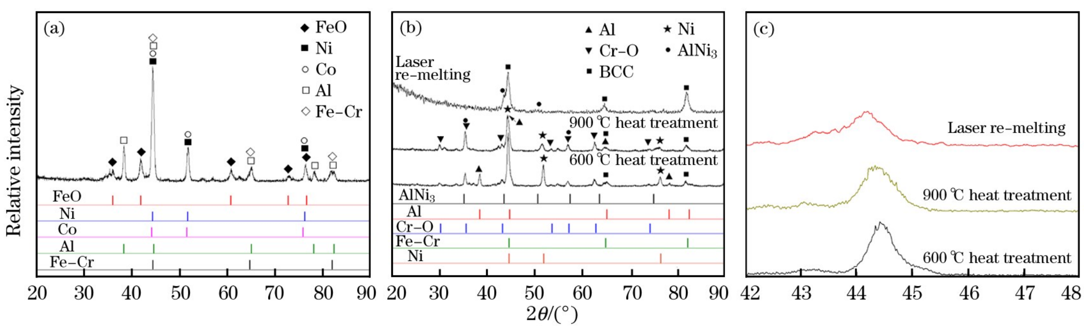
Thus, in this study, a plasma spray method combined with vacuum heat treatment and laser re-melting was used to prepare FeCoCrNiAl[19] HEA coatings.

2. Experimental Procedure

A 304 stainless steel was used in this experiment, and Fe, Co, Cr, Ni and Al powders of around 48 μm with more than 99% purity were mixed together at the same molar ratio. A planetary ball mill was used to mix the powders for 8 h. The ball material ratio (mass ratio) was 10 : 1 and the revolution rate was 200 r/min. A supersonic atmospheric plasma spraying system (3710 Praxair, USA) was used to spray the mixed powder at 500 A and 40 V. Part of the as-sprayed samples were heated in a high temperature vacuum tube (CVD, Hefei, China) for 10 h at 100 Pa. The other samples were re-melted using a semiconductor laser (FL-Dlight-1500, Xi'an, China) with a 300 W power, 3 mm×1 mm spot size and 3 mm/s scanning speed. The wear resistance of the coatings was tested using a universal wear tester (MMW-1) with a disk made of Cr12MoV as the counterpart with a 100 N load and a 100 r/min revolution rate for 15 min at room temperature. The structure and elemental distribution of the coatings were observed with a scanning electron microscope (Hitachi-S3400, Japan). The phase composition was analyzed with an X-ray diffractometer (Shimadzu 7000, Japan), with a scanning speed of 8 (°)/s and scan range of 20°-90°. The microhardness of the coatings was tested using a Vickers hardness tester (DHV-1000) with a 1.96 N load and dwell time of 10 s.

3. Results and Discussion

Fig. 1(a) shows the X-ray diffraction pattern of the as-sprayed coating. It can be seen that the as-sprayed coating mainly consists of pure metals, except for small quantities of Fe-Cr and FeO. The coating cannot be deemed a HEA coating, since no high entropy phase was obtained. After 600 and 900 ℃ heat treatment, and laser re-melting, as shown in Fig. 1(b), the composition in the coatings changed. After the 600 ℃ heat treatment, a BCC structure existed in the coating. Cr-O, $AlNi_3$ and pure metals, like Al and Ni, could also be detected. After the 900 ℃ heat treatment, the content of Cr-O increased and the content of pure metal decreased. After laser re-melting, BCC and $AlNi_3$ phases could be detected, similar to the conclusion of Chen et al. [20].



(a) As-sprayed coating; (b) Diffraction angles of 20°-90°; (c) Diffraction angles of 42°-48°.

Fig. 1. X-ray diffraction patterns.

According to the Gibbs free energy formula[21],

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

where, ΔH_{mix} represents the mixing enthalpy of the alloy system; T represents the thermodynamic temperature; ΔS_{mix} represents the mixing entropy of the alloy system; and ΔG_{mix} represents the Gibbs free energy. According to the Boltzmann entropy hypothesis, the mixing enthalpy of an alloy system can be represented as:

$$\Delta S_{mix} = -R[C_1 \ln C_1 + C_2 \ln C_2 + \cdots + C_n \ln C_n] \quad (2)$$

where, R represents the gas constant; and C_1, $C_2 \cdots C_n$ represents the mole fraction of each element. The diffusion phenomenon produced by heat treatment enhanced the system entropy according to Eq. (2). It is known that the mixing entropy of an alloy will increase with increasing treatment temperature. The