



Featured Letter

Synthesis of amorphous coating by laser cladding multi-layer Co-based self-fluxed alloy powder



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ABSTRACT

An amorphous coating was synthesized on low carbon steel by laser cladding Co-based self-fluxed alloy powder successfully. The microstructure, thermal stability property of the fabricated amorphous coating was investigated. The thickness of amorphous coating was 400 μm while the dendrite zone was only 10 μm height near the interface. The volume fraction of amorphous was 85.1% approximately. DSC curve showed that the glass transition temperature and the crystallization temperature were 298 $^{\circ}\text{C}$ and 342 $^{\circ}\text{C}$, respectively. The supercooling liquid region was 44 $^{\circ}\text{C}$ which ensured the high thermal stability of amorphous coating against crystallization.

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1. Introduction

Surface properties such as high microhardness, excellent wear, corrosion and oxidation resistance are rather important for those components under severe work conditions [1]. Advanced surface engineering technologies could help enhance surface properties [2] and the integral performances [3] of the substrate/surface systems. Laser cladding as a surface technique, which irradiates, melts and mixes preplaced or synchronous powders transported by argon gas and substrates, possesses characteristics such as metallurgical bonding between coatings and substrates, high accuracy, rapid melting and cooling process and so on. Due to its sufficiently rapid heating and cooling, the preplaced-powder coatings might be amorphous, and crystallization could be prevented. The metallic glasses formed with rapid solidification rate are promising materials in the field of surface coatings because of their unique mechanical, physical and chemical properties.

However, the powders utilized for preparing amorphous are mostly customized with expensive rare metal elements used simultaneously, which greatly limited the development and application of amorphous coatings. Ruifeng Li [4] and Y.Y. Zhu [5] successfully fabricated customized Ni-Fe-B-Si-Nb and Fe-Co-B-Si-C-Nb amorphous coatings by laser cladding process, respectively. X Wu [6] and T.M. Yue [7] both obtained amorphous coating with the help of element Zr. Jianran Lin [8] used a self-made Fe-based

cored wire (FeNiCrBSiNbW) with the diameter of 2 mm to research amorphous coatings by twin wires arc spraying process. Currently, there is few literature available about obtaining amorphous coatings from commercial self-fluxed alloy.

The presented paper had chosen a kind of commercial self-fluxed Co-based alloy powder to fabricate laser cladded coating which was justified to be amorphous. The microstructure, phase constitution and thermal stability of the coating was investigated systematically. The presented work should supply conclusive evidences of successfully obtaining amorphous coatings by laser cladding and appeal for further research on fabricating advanced coatings with sustainable and commercial raw materials rather than the customized materials. It is a very promising materials in strengthening and repairing the surface of expensive precision molds by laser cladding.

2. Experimental

Commercial FCo-06 Co-based self-fluxed alloy powders of which the size was 100–250 μm was preplaced on the surface of Q235 steel with dimensions of 200 mm \times 100 mm \times 6 mm for the subsequent laser cladding process. The thickness of the preplaced powder for each cladded layer was about 200 μm . Table 1 showed the chemical composition of the powder and the substrate. Prior to the laser cladding process, the substrate was polished mechanically with XKA714/F CNC milling machine, and washed by alcohol and water, neither dirt nor oil could be found. The powder was

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Table 1
Chemical composition of the substrate and clad powder (wt%).

	C	Mn	Si	S	P	Fe	
Substrate	≤ 0.22	≤ 1.4	≤ 0.35	≤ 0.05	≤ 0.045	bal	
	C	Si	B	Cr	Ni	Fe	Co
Powder	0.8–1	3.5–4.5	2.5–3.5	28–32	10–12	2–3	bal

dried by keeping in drying oven for 1 h at 100 °C. Laser cladding process was performed with the laser spot diameter of 2.5 mm and the defocusing distance of 15 mm. The substrate was put into a full-argon shielding box made of quartz while laser cladding process was carried out. The function of shielding box was to prevent samples from oxidation and protect lens from dirt, besides, the quartz materials could absorb few laser and decrease the laser energy loss. The optimized laser power of 467 W and scanning speed of 100 mm/min were used.

The samples were cut by wire cutting machine along the cross section before microstructure analysis. After polishing the face to be observed, the samples were etched by HCl:HNO₃=3:1 for 90 s and then cleaned by water and alcohol in sequence. The microstructure of the coating was observed by scanning electron microscope (SEM, ZEISS, Czech Republic) equipped with energy dispersive X-ray spectroscopy (EDS, EDAX, USA) unit and transmission electron microscope (TEM, JEOL-2100, Japan). The phases presented in the coating were identified with X-Ray diffractometer (XRD) (D/max 2500, Japan) using Cu-K α radiation and scanning within 2 θ =10°–90°. Differential scanning calorimetry (DSC, DSC-60, Japan) was utilized to evaluate the thermal stability property of sample by measuring the glass transition temperature (T_g) and crystallization temperature (T_x).

3. Results and discussion

3.1. Microstructure and phase constitution

Fig. 1 presented the X-ray diffraction pattern of Co-based self-fluxed alloy coating. It could be seen clearly that a broad diffraction halo appeared at 45°. A thin crystalline diffraction peak which was shown to be (Co, Fe) solid solution was observed as well clearly. The volume percent of amorphous phase in the coatings was calculated up to 85.1% by Pseudo-Voigt function fitting with the method of Verdon, meaning the coating was mainly consisted of amorphous structure.

Fig. 2 showed typical SEM images of Co-based coating of which the thickness was 400 μ m approximately (Fig. 2(a)). The coating metallurgically bonded the substrate through the interface as the root of dendrites as shown in Fig. 2(c). Fig. 2(b) was the enlarged image of the area showing amorphous characteristics. From the EDS result shown in Fig. 2(b), the amorphous phase was mainly composed of Co, Cr, Fe and C. Fig. 2(c) was the magnified image of the interface in the Co-based coating, of which a few interesting results can be gained. Near the interface, the coating exhibited different structure morphologies, amorphous structure and dendritic structure from top to bottom of Fig. 2(c), respectively. The thickness of dendrites area was around 10 μ m, so the zone constituted of amorphous phase was pretty large. Fig. 2(d) exhibited details of the dendritic structure in Fig. 2(c). It was indicated that precipitates uniformly distributed in the interdendritic structure could be carbides and borides, the dendrites could be cobalt-based solid solution according to previous reference [9].

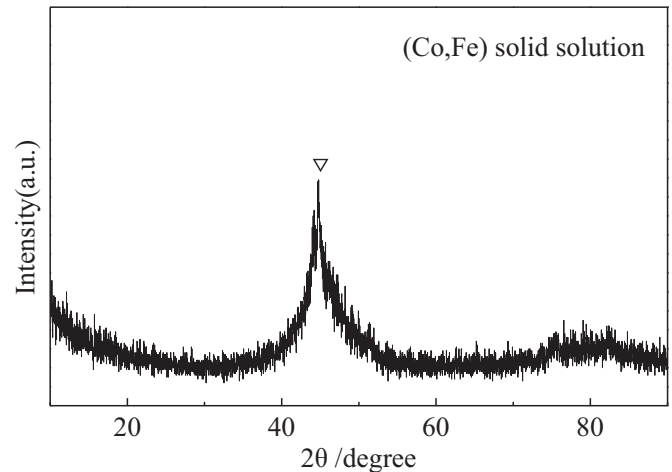


Fig. 1. XRD pattern of Co-based coating.

In order to avoid the disturbance of the dendrite layer, raw slices with the thickness of 200 μ m were obtained from the amorphous zone by wire-electrode cutting along the direction parallel to the substrate. Then the slices were prepared for TEM tests. TEM images shown in Fig. 4 were introduced to explain more detailed information about the microstructure of the coating. A bright field TEM image of the coating was exhibited in Fig. 3(a) and the selected area electron diffraction (SAED) pattern was shown in Fig. 3(b). It was obvious that a typical amorphous phase electron diffraction pattern appeared. It could be concluded that the Co-based coating was mainly composed of amorphous phase while a few dendrites and precipitates were sandwiched between the amorphous phase and the coating/substrate interface.

3.2. Thermal stability property evaluation

Fig. 4 showed the DSC curve of the Co-based coating. It could be seen that the glass transition temperature (T_g) and the onset temperature of crystallization (T_x) were 298 °C and 342 °C, respectively. A very important kinetic parameter activation energy indicates the degree of difficulty for phase transformation. The following Kissinger [10] equation is used to estimate activation energy.

$$\frac{E\beta}{RT_x^2} = Ae^{-\frac{E}{RT_x}} \quad (1)$$

where E is the activation energy, β is the heating rate, R is the molar gas constant, T_x is the crystallization temperature, A is the pre-exponential factor. Through the Eq. (1) deduction, the crystallization temperature T_x becomes:

$$T_x = \frac{E}{R \left(\ln \frac{RA}{E\beta} + 2 \ln T_x \right)} \quad (2)$$

300 K $\leq T_x \leq$ 800 K \rightarrow 5.7 $\leq \ln T_x \leq$ 6.9. Consequently, the crystallization temperature T_x becomes:

$$T_x \approx \frac{E}{R \left(\ln \frac{RA}{E\beta} + 12 \right)} \quad (3)$$

Because the denominator is positive, the crystallization temperature increases with the increasing of activation energy. Different chemical compositions of materials system causes different

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