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Effect of Ni-to-Fe ratio on structure and properties of Ni–Fe–B–Si–Nb coatings fabricated by laser processing

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ABSTRACT

Ni–Fe–B–Si–Nb coatings have been deposited on mild steel substrates using high power laser cladding process followed by laser remelting. The influence of Ni-to-Fe concentration ratio in $(Ni_{100-x}Fe_x)_{62}B_{18}Si_{18}Nb_2$ (x = 55, 50, 45 and 40) powders on the phase composition and microstructure is analyzed by X-ray diffraction, scanning- and transmission-electron microscopies. The microhardness and corrosion resistance properties of the coatings are also measured. The results reveal that amorphous matrix layers are obtained for all coatings. The increase of the Ni-to-Fe ratio can promote the formation of γ(Fe–Ni) phase and decrease the formation of Fe_2B phase and α-Fe phase. The coating with 1:1 ratio of Ni-to-Fe exhibits the highest microhardness of 1200 $HV_{0.5}$ and superior corrosion resistance property due to its largest volume fraction of amorphous phase in the coating. Higher or lower than 1:1 ratio of Ni-to-Fe may result in lower amorphous forming ability. However, even that the coating with ratio of 3:2, shows a minimum of microhardness, it shows a better corrosion resistance than other two coatings.
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1. Introduction

Surface coating technology has been applied extensively to obtain wanted functional properties, such as excellent wear, corrosion and oxidation resistance. High power lasers have become increasingly accepted as tools for many applications from cutting to welding and surface modification. Laser cladding is one of laser surface modification techniques, by which beneficial alloy powder or pre-deposited materials are melted with a surface layer under laser irradiation, and then rapidly solidified to form an alloy coating that is metallurgically bonded to the substrate [1]. High power laser irradiation can cause a rapid localised heating and melting of material. If the radiation time is short, as it is the case for a specimen moving rapidly under the stationary laser beam, the substrate material at some depth below the surface will not be heated and will act as a self-quenching substrate. This will cause rapid solidification and possible metallic glass formation [2–5].

Most of bulk metallic glasses contain very expensive elements of zirconium, platinum and/or lanthanum groups, limiting their applications [6]. But Fe-based, Ni-based and Fe–Ni (or Ni–Fe) based bulk glassy alloys (BGAs) are of special interest among metal-based BGAs due to their excellent mechanical and physical properties, such as, high yield strength, good soft magnetic properties, high thermal stability, and good corrosion resistance and, at the same time, abundant natural resources and low material cost [7–9]. In the past, several attempts were made to obtain this kind of amorphous coating on bulk crystalline substrate [10–15]. However, up to now, the works on exploring the effect of Ni-to-Fe concentration ratio on the variation of coating hardness, together with that of electrochemical corrosion resistance, are still lacking, especially under laser processing condition.

The work in the present study is thus driven by a desire to form coatings of Ni–Fe based alloys using high power laser cladding process followed by laser remelting. We intend to investigate the effect of Ni-to-Fe concentration ratio on the structural, mechanical and corrosion resistance properties of Ni–Fe–Si–B–Nb alloy coatings. The alloy composition of Ni–Fe–Si–B–Nb was selected based on its glass forming ability (GFA), mechanical properties and our previous research [8,16].

2. Experimental procedures

Four types of Ni–Fe–B–Si–Nb powders with different Ni-to-Fe ratio were deposited onto mild steel substrates with dimensions of 150 mm × 100 mm × 8 mm. The atom contents of the four different powders were $(Ni_xFe_{100-x})_{62}B_{18}Si_{18}Nb_2$ (x = 45, 50, 55 and 60) defined as Ni45, Ni50, Ni55 and Ni60, respectively. The size of the powder particles was in the range of 75 μm to 150 μm. It is neces-

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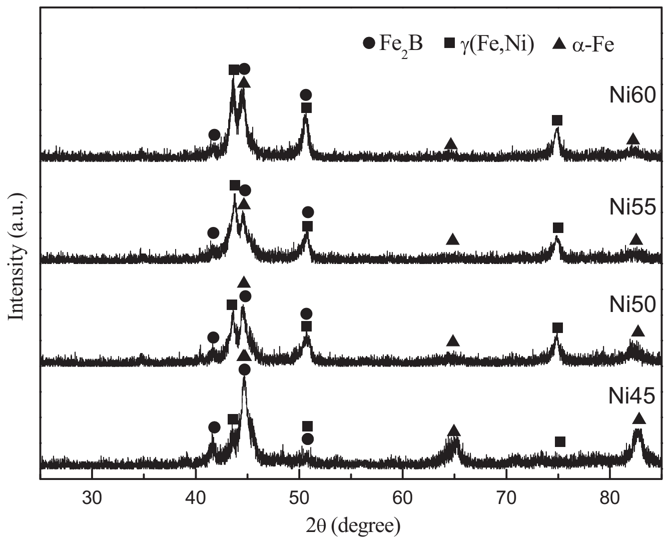

Fig. 1. XRD results of laser remelted layers for different laser cladded Ni–Fe–B–Si–Nb coatings.

sary to point out that the powders used in this study were industrial purity and the purity of the iron and nickel is 99 wt.%. The iron boron alloy contains 19.1 wt.% of B, 79.42 wt.% of Fe and other elements, such as aluminum, phosphorus and sulfur. The iron silicon alloy contains 44.3 wt.% of Si, 55.24 wt.% of Fe and other elements too. The columbium alloy contains 50.2 wt.% of Nb, 48.41 wt.% of Fe and other elements such as carbon, tantalum, titanium and tungsten. The powders were mixed in air by a ball mill for an hour. After that, the mixed powders were dried for half an hour at 200 °C.

The cladding experiment was conducted using a 15 kW continuous wave CO_2 laser (TRUMPF TLF15000) equipped with a lateral powder feeder. The processing was divided into two steps. Firstly, the alloys were deposited on the substrate by laser cladding. Laser power was 5.5 kW, scanning speed was 400 mm/min, powder feeding rate was 20 g/min and the diameter of laser beam was 5 mm. Then, the cladded coatings were remelted by laser at a higher speed. Laser power, scanning speed and laser beam diameter were 14 kW, 8000 mm/min and 4 mm, respectively. The argon was the atmosphere medium to feed powder in order to prohibit the alloy powders from oxidation during the process.

The phase evolution (identity and volume fraction) was studied by X-ray diffraction (XRD, D/max 2550VL/PC) using Cu Kα irradiation. The microstructure of coatings was characterized by JEOL scanning electron microscopy (SEM, JSM 6460) and transmission electron microscope (TEM, PHILIPS CM200) at 200 kV. Vickers hardness tester (HVS-10) was used to measure the microhardness of the coatings. The potentiodynamic polarization tests were conducted in 3.5 wt.% NaCl solutions at room temperature to obtain the corrosion resistance properties of the coatings and the substrate.

3. Results and discussion

Fig. 1 shows the XRD patterns of the remelted layers of the laser cladded Ni–Fe–B–Si–Nb coatings. It can be seen that the patterns exhibit broad halo peaks at diffraction angle of 44° (2θ) and diffraction peaks corresponding to some crystalline phases, implying partly amorphous phase layers are obtained. The amorphous phase fractions of the four remelted layers were calculated by the Verdon method [17], results show that the order of amorphous fraction in the remelted layer is Ni50(48%) > Ni55(44%) > Ni45(42%) > Ni60(36%). The crystalline peaks are identified as Fe_2B phase, face centered cubic γ(Fe, Ni) solid solution phase and body centered cubic α-Fe phase in all samples. The XRD results also reveal that the relative volume fractions of Fe_2B and α-Fe phases decreased gradually with the increasing Ni-to-Fe ratio, while the γ(Fe, Ni) content increased (as is evident from the difference in peak intensities).The XRD results exhibit no presence of oxide phase in the remelted layer. The reason may be the high Si content in the Ni–Fe–B–Si–Nb powder. Si is known as a deoxidation element due to its easy reaction with oxygen [18]. High amount of Si can also decrease the loss of other elements. In other words, the composition design with high amount of Si is an effective way to decrease the deviation from designed composition in the laser processing.

Fig. 2 shows the SEM microstructures of remelted layers for different Ni–Fe–Si–B–Nb laser cladded coatings. It can be seen that all layers are dense and pore-free. Due to the large cooling rate, the solidification microstructures are mainly fine-grained non-directional equiaxicrystals. The variations of the ratio of Ni-to-Fe in powders changed the solidification microstructures. For Ni45, Ni50 and Ni55 powders, the layers consist of deep gray flower-like phase and light gray matrix as shown in Fig. 1, and Ni50 powder has the highest light gray phase volume fraction than the other two powders. The compositions of the deep gray phase and light gray phase in Fig. 2(b) as determined by SEM EDS analysis are (at.%): 48.4Fe, 19.4Ni, 7.1Si, 24.9B, 0.2Nb, and 37.4Fe, 38.1Ni, 7.3Si, 13.4B, 3.8Nb, respectively. As for Ni60 powder, the microstructure varies with the other three powders, is main γ(Fe, Ni) austenite phase. This is attributed to the highest Ni-to-Fe ratio in the coating. Studies have been shown that a small increase in the Ni content could lead to a large increase of austenite phase volume fraction [19,20].

The formation of amorphous phase in the remelted layer was further confirmed by TEM as shown in Fig. 3. When TEM investigation was implemented, a large portion of the sample could be found to be amorphous. The bright-field image as shown in Fig. 3(a) reveals a typical amorphous matrix and some black/gray nano-sized crystalline phases embedded within the matrix. The selected-area diffraction pattern (SADP) of featureless region A is shown in Fig. 3(b). The broad diffraction halo indicates that the phase in this region was amorphous. The composition of the spot A as determined by TEM EDS analysis is (at.%): 37.3Fe, 36.2Ni, 7.8Si, 14.5B, and 4.2Nb. It can be seen that the composition of this amorphous phase is almost the same with the composition of the light gray phase in Fig. 2. This indicates that the light gray phase is mainly composed of amorphous phase. The SADP of the black phase B in Fig. 2(a) is identified as γ(Fe, Ni) phase (Fig. 3(c)). This related well to the crystalline phase found in the XRD examination results (Fig. 1).

Based on the above structural and phase analysis, for the Ni–Fe–Si–B–Nb alloy system, it can be concluded that an amorphous matrix layer could be obtained using high power laser cladding process followed by laser remelting. During the solidification after the remelting process, the grain growth was ceased, and then the remaining liquid was frozen into amorphous phase. As shown in Fig. 2, the deep gray flower-like phase growth was ceased, and the remaining liquid was frozen into light gray amorphous phase. In addition, ratio of Ni-to-Fe in 1:1 might be a critical composition for formation of amorphous phase in our experiment condition, higher and lower than this Ni-to-Fe may result in lower amorphous forming ability. As a criterion in predicting of GFA, deep eutectic compositions are very helpful to improve the GFA [21]. Several studies have been shown that the eutectic point of Ni–Fe–B–Si alloy system is near 1:1 for Ni-to-Fe concentration ratio [22,23].

Fig. 4 gives the measured microhardness for obtained amorphous matrix coatings along the cross-section from the substrate to the remelted layer. The hardness of cladding layer and remelted layer are all much higher than that of the mild steel substrate; and the highest hardness all happen in the remelted layer. This is attributed to the formation of amorphous phase and the fine microstructure in it. For the ratio of Ni-to-Fe in 1:1 of Ni50 coat-

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