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Amorphous structure in a laser clad Ni-Cr-Al coating on Al-Si alloy[①]

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Abstract: A mixing microstructure containing Ni-based amorphous structures was observed by TEM in the laser clad zones. As the uniformity of chemical composition and temperature is poor in the laser cladding, the amorphous structure with some Ni_3Al crystals coexists in the cladding. The microhardness of the mixing amorphous structure is HV 600 ~ 800, which is lower than that of crystal phases in the coating. Differential thermal analysis (DTA) shows that Ni-based amorphous structure exhibits a higher initial crystallizing temperature (about 588 ℃), which is slightly higher than that of the eutectic temperature of Al-Si alloy. The wear test results indicate that there are some amorphous structures in the laser clad coating, which reduces the peeling of the granular phases from matrix, and improves the wear resistance.

Key words: laser surface treatment; aluminum alloy; amorphous structures **Document code:** A

1 INTRODUCTION

Recently, laser cladding and alloying of aluminum alloys have been investigated for the enhancement of wear and corrosion resistance[1~4]. For the purposes of modifying surface properties of aluminum alloys, some transition elements, such as Fe, Ni, Cr, are often used as coating materials in laser cladding or laser alloying treatment[5~7].

Many amorphous structures with high hardness were found in the laser clad Ni-Cr-B-Si coatings[8,9] on substrate of aluminum alloys. Although the group IIIA elements are capable of forming amorphous structure with metalloid elements, such as B and Si, cracks are often formed in the laser clad zone. However, the laser clad Ni-Cr-Al coating have higher microhardness and better surface quality on Al-Si alloys, and less cracks are found in the coatings. As aluminum possesses some properties of metalloid elements, it is possible to produce amorphous structure with transition elements Fe, Ni and Cr during rapid solidification. Up to now, few research was available on the amorphous structure in laser clad Ni-Cr-Al coatings[10], but the property of these amorphous structures is also not clear. As the amorphous structure exhibits high hardness and good corrosion resistance, it would be beneficial to improving the surface properties of aluminum alloys. In this paper, the morphologies and properties of an amorphous structure in the laser clad Ni-Cr-Al coating are reported.

2 EXPERIMENTAL PROCEDURE

The substrate was a cast Al-Si alloy containing (mass fraction) 8.23%Si, 0.057%Mg and 1.35% Cu. Samples were machined into 10 mm thick rectangular plates. After etching in hot NaOH solution and sandblasting, sample surface was sprayed with Ni-Cr-Al powder using a METCO 4HC plasma spraying device. For the Ni-Cr-Al sprayed powder, the chemical compositions (mass fraction, %) were: Cr 16.5, Al 8.0 and Ni the balance. The coating thickness was approximately 0.25 mm.

Laser cladding process was conducted with a 5 kW continuous-wave transverse-flow CO_2 laser. The laser beam diameter was 2.5 mm. The power density of the laser beam ranged from 32 kW/cm^2 to 44 kW/cm^2. The samples were manipulated by mounting them on an computer-controlled *X*-*Y* table. The samples were fed at 8 mm/s during laser cladding. The sample surface was protected by argon gas during the laser cladding.

A cross-section of the sample was taken perpendicular to the alloyed surface, and it was polished metallographically. A thin plate of about 0.5 mm in thickness was cut from the top of the laser melted zone. After mechanical thinning to 0.1 mm in thickness by grinding, TEM sample was prepared by electropolishing using a twin jet polisher. Observation of microstructure were performed on a S-2700 scanning electron microscope (SEM) and a JEM-200CX transmission electron microscope (TEM). The crystallization process was analyzed by differential thermal analysis (DTA). The DTA samples were prepared from several foils of the laser clad surface layer, which are about 0.1 mm thick. From these foils, materials in the substrate and the transition regions were removed as much as possible. The DTA was performed using a

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DuPont Type 2000 DTA equipment. The measurements were carried out with a wide temperature range (373 ~ 1 073 K) and the heating rate was 10 K/min under argon protecting. Microhardness was measured using a Vickers Hardness test with load of 0.5 N and loading time of 15 s. The sliding wear test was carried out on an M200 ring-on-block apparatus under oil lubricated condition. The upper sample is a laser clad block, and the lower sample is a gray iron ring.

3 RESULTS AND DISCUSSION

3.1 Microstructure of laser clad zone

There are three zones in a laser clad coating, namely the clad, the transition and the heat affected zones. The heat affected zone is mainly composed of the remelted substrate. Fig.1 shows the structure of the laser clad zone. Fig.1 (b) is a higher magnification micrograph in point *A* of Fig.1(a). From Fig.1, it is seen that the microstructure of the clad zone consists of granular structures and the surrounding white network-like structures.

3.2 Amorphous structure in laser clad zone

Fig.2 shows a series of TEM micrographs of a laser clad at the processing condition of laser power density of 32 kW/cm^2. A flake-like structure appears in Fig.2(a). Fig.2(b) is the electron diffraction pattern of Fig.2(a). It is clear that the structure of Fig.2(a) is amorphous structure.

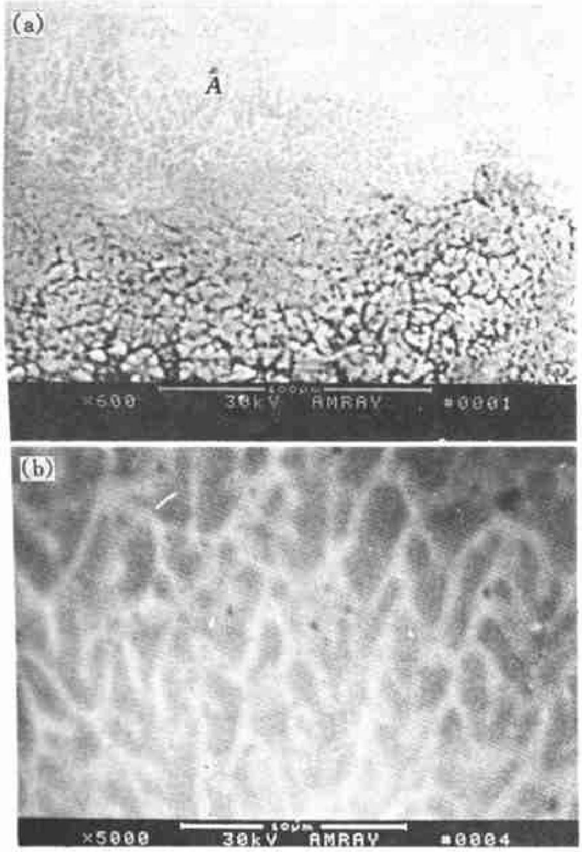

Fig.1 SEM micrographs of a laser clad with low (a) and higher (b) magnification

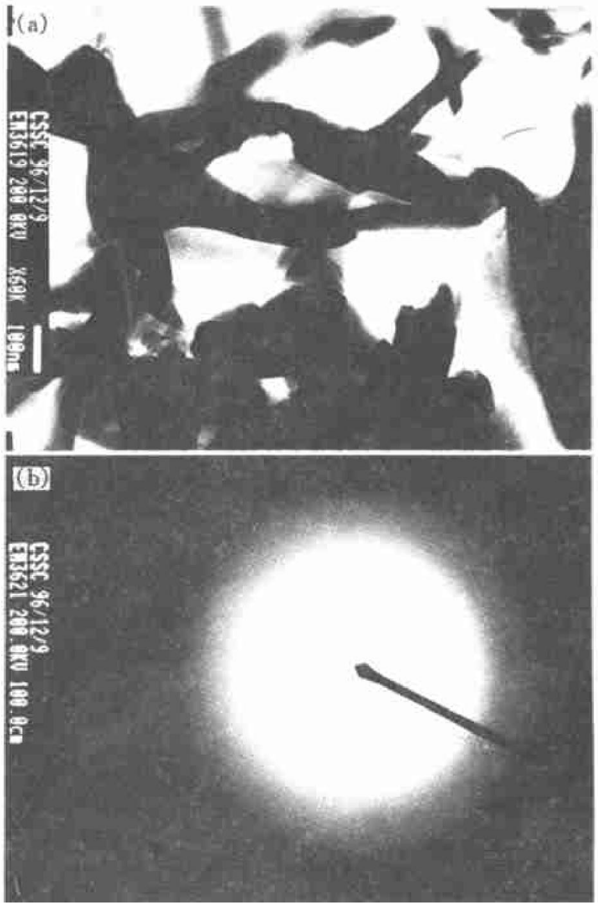

Fig.2 TEM micrographs of a laser clad zone with a laser power density of 32 kW/cm^2
(a) —Flake-like amorphous form;
(b) —Electron diffraction pattern

Fig.3 shows TEM micrographs of the laser clad zone at a laser power density of 44 kW/cm^2. Fig.3 (a) is a TEM bright field image. The structure of the laser clad zone appears to be in petaloid form. Fig.3 (b) is an electron diffraction pattern of Fig.3(a). It shows that this structure is still amorphous. Fig.3(c) is another TEM micrograph. There are two structures present in the Fig.3(c), denoted as *A* and *B*. Fig.3(d) is an electron diffraction pattern of structure *B* in Fig.3(c). The dendritic-like structure *A* has the same diffraction pattern as that shown in Fig.3(b). Therefore, it is amorphous too. Structure *B*, by the index, can be found to be crystal Ni_3Al.

It can be seen that there some Ni-based amorphous structures in the clad region, which partly exist isolated and coexist with the Ni_3Al phases. Referring to Fig.1, it can be found that those amorphous structures which appeared as flake-like and petaloid structures are formed by granular squeezing during grain growth. Therefore, they exist in the network-like structure surrounding the granular

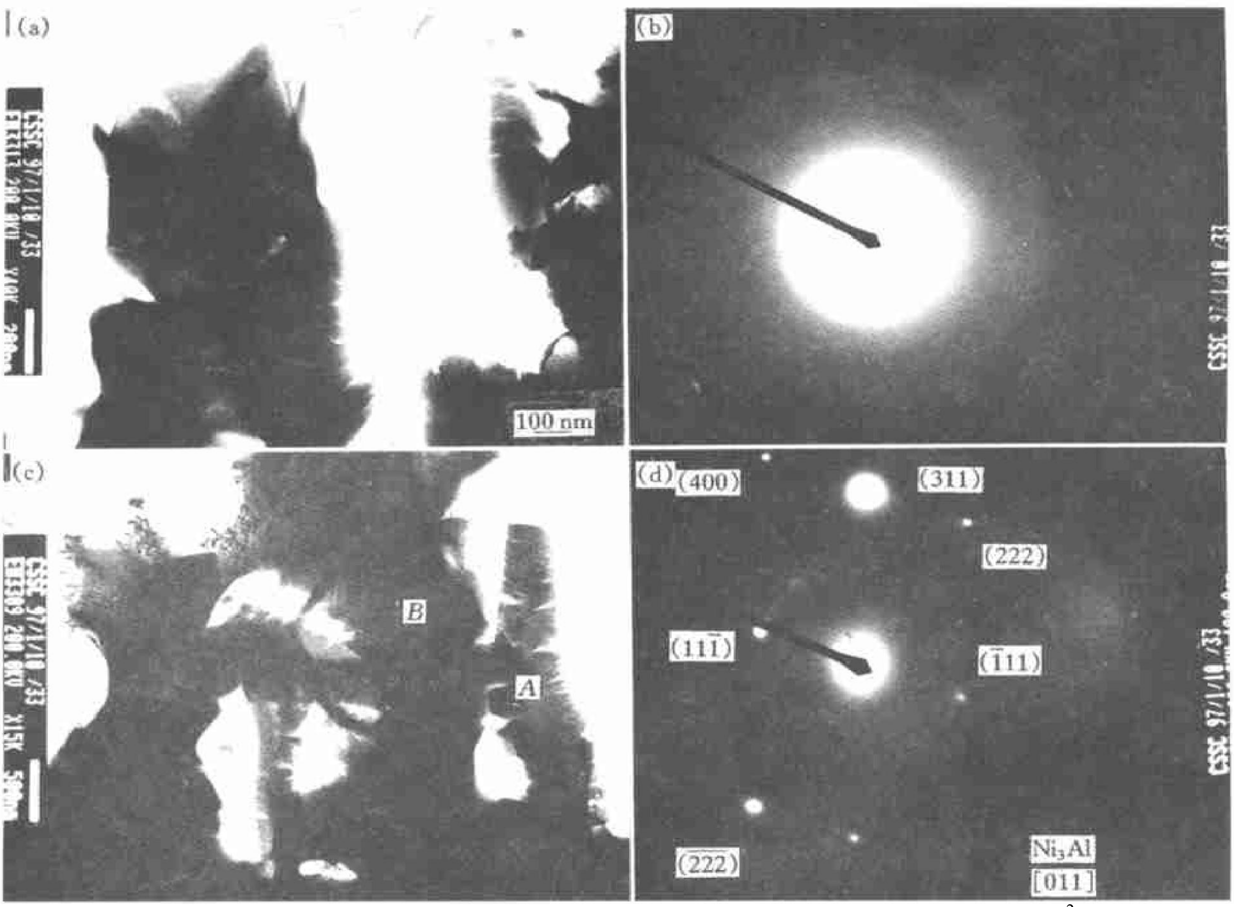

Fig.3 TEM micrographs of laser melted zone under laser power of 44 kW/cm^2

(a) —Bright field image; (b) —Electron diffraction pattern of Fig.3 (a);
(c) —Bright field image; (d) —Electron diffraction pattern of structure *B*

structure. The dendritic-like amorphous structure was formed because the crystal was etched out during the preparation of TEM samples. As it exists together with the crystal, it should occur in the granular structure. The TEM test also shows that the amorphous structure mainly exists in the surface cladding region, i.e. the granular structure and surrounding networklike boundaries. Moreover, the granular in the subsurface is Ni_3Al.

3.3 DTA analysis

Fig.4 shows the DTA results of the laser clad region at a laser power density of 32 kW/cm^2. The upward direction shows exothermic reaction in this figure. It can be seen that there are an endothermic valley (*afb*) and an exothermic peak (*bpc*). It is seen that the endothermic valley is in the field of the eutectic temperature of Al-Si alloys so that the endothermic valley was caused by the melt of remained aluminum alloy. The exothermic peak was produced by crystallization of the amorphous structure. Some critical temperatures at various samples of laser power on the curves are listed in Table 1. T_b is the initial temperature of crystallization process. T_p is the temperature at the maximum transformation rate, and T_c

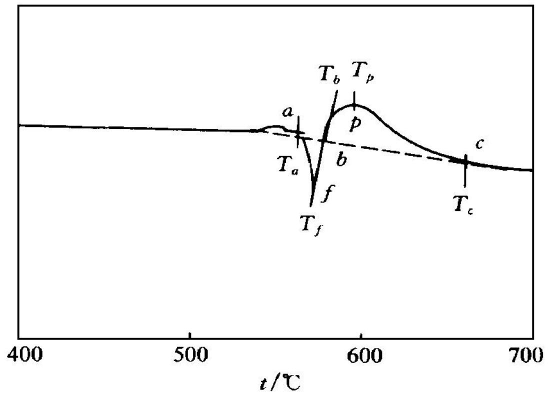

Fig.4 DTA curve of laser clad layer (32 kW/cm^2)

Table 1 Some critical temperatures on DTA curve at different power densities

Power density /(kW·cm^{-2})	T_a	T_f	T_b	T_p	T_c
32	561	573	589	615	652
36	562	576	592	619	646
40	562	573	586	612	675
44	560	572	585	617	656

is the temperature of the end of transformation. According to the DTA results, it is found that the crystallization temperature of every sample is quite high (higher than the substrate melting temperature). This characteristic can therefore be used to facilitate the application of laser clad aluminum alloy in industry.

3.4 Properties of amorphous structure

The microhardness of the laser clad coating in Fig.1 is listed in Table 2. The hardness of the amorphous mixture is HV 600 ~ 800, which is lower than that of the crystal phase. A wear test was conducted using a sample (laser power density 36 kW/cm^2) containing amorphous structure and one almost without amorphous structure (which was annealed at 520 ℃ for 6 h). After wear sliding of distance 5 km, the volume loss of the sample containing amorphous structure is only 6.2×10^{-2} mm^2, and the sample without is 0.224 mm^2.

Table 2 Microhardness of different region in laser clad zone at different power densities (HV)

Laser power density /(kW·cm^{-2})	Amorphous mixture region	Separated granular region
32	672	893
36	671	889
40	685	845
44	690	853

Fig.5 shows the SEM micrographs of the cross-section of the wear sample, one contains structure (Fig.5(a)) and another without amorphous (Fig.5(b)). It is found that some amorphous structures existing in the laser cladding can reduce the peeling of the granular phase from matrix, so it can improve its wear resistance.

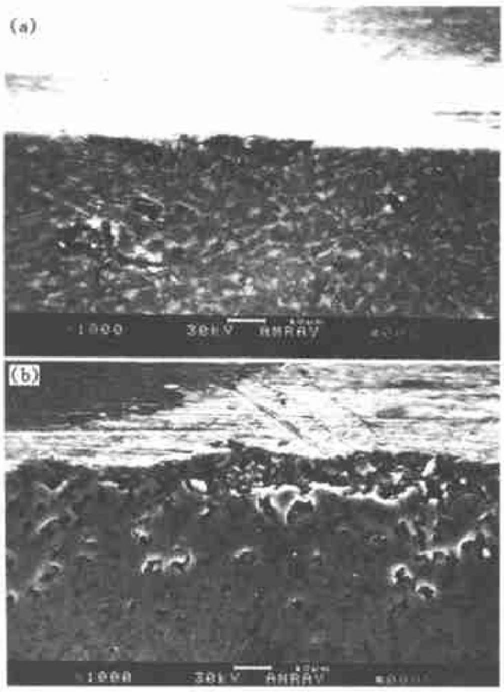

Fig.5 SEM micrographs of cross-section of samples
(a) —Containing amorphous structure; (b) —Without amorphous structure, at an angle of 38° with worn surface

4 CONCLUSION

Some Ni-rich amorphous structures exist in the laser clad Ni-Cr-Al coating on aluminum alloys. They exist in the network-like structure around granular structure and coexists with Ni_3Al phase in the granules. This amorphous structure has exhibited a high crystallizing temperature (about 588 ℃). The hardness of the amorphous mixture is HV 600 ~ 800, which is lower than that of the crystal phase. Some amorphous structures exist in the laser cladding can reduce the peeling of the granular phase from matrix.

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