Article ID: 1003 - 6326(1999)03 - 0462 - 06

$Cu + Al_2O_3$ composite coating on AISI 1045 steel surface by laser cladding①

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Abstract: Perfect composite coatings have been successfully produced with preplaced mixture of $Cu + Al_2O_3$ (2% ~ 20%) on AISI 1045 steel substrate by using a 2 kW CO_2 laser. A suitable amount of Al_2O_3 in Cu as additive can improve the processing conditions of laser cladding. Fe-rich particles were observed in the clad layer during microstructural observation with SEM and chemical composition analysis by EDAX. The experimental results showed that microhardnesses of the coatings were over $150HV_{0.05}$ and the electric resistivities were about $4.0 \times 10^{-8} \sim 4.5 \times 10^{-8}$ Ω·m.

Key words: laser; cladding; conductive coating; microhardness tests; resistance **Document code: A**

1 INTRODUCTION

During past twenty years, composite coatings produced by laser cladding have shown great perspective in material surface hardening because of their high microhardness, excellent wear resistance and good corrosion resistance[1]. This kind of coatings is mostly formed with preplaced or injected powders including Ni-based, Co-based, Fe-based or Cu-based alloys as base metal and WC, BC, TiC, SiC, ZrO_2 or Al_2O_3 particles as reinforcement[2]. The application of laser cladding process on nonferrous metals has attracted increasing interest in recent years. Some investigators tried to produce SiC and SiC/Al coatings on aluminium alloy AA6061[3,4]. In order to reduce Ag consumption and pollution, Bruck once obtained Ag coating on Cu surface by using laser to produce electric contact material[5].

So far copper coating and particle reinforced copper matrix composite coatings have not been produced by laser cladding according to reported researches in spite of their wide applications in electricity-conductive materials. Alumina as additive in Cu can improve hardness and keep its electric conductivity at elevated temparature[6]. Therefore, mixture composed of pure Cu powder and Al_2O_3 powder was used to form Cu composite coatings on plain carbon steel AISI 1045 in the present work. The processing condition, microstructure and chemical composition of the above coatings were investigated, and then microhardness and electric resistivity were tested.

2 EXPERIMENTAL

AISI 1045 steel with the size of 40 mm × 30 mm × 8 mm was used as substrate material in the present experiment. The pure copper powder (99.9%, ~20 μm in size) was mixed with alumina(99.9%, ~20 μm in size) used as additive with mass fraction of 2%, 5%, 10% and 15% respectively. The mixture, with a thickness of about 1.0 ~ 1.5 mm(for overlapping), was preplaced on the surface of the substrate with a chemical binder.

The laser used in this experiment was HGL-81 CW CO_2 laser produced by Huazhong University of Science and Technology with a maximum output power of 2.2 kW. The main processing parameters were as follows: laser power P_l, 2.0 kW; beam spot diameter D, 3 mm; scanning

① Project 59581004 supported by the National Natural Science Foundation of China
Received Jul. 23, 1998; accepted Nov. 22, 1998

speed v_b, 3 ~ 13 mm/s; overlapping rate η, 1/3.

The track cross-sections were cut and polished by standard metallographic techniques. The polished samples were etched in a solution of 20 %$(NH_4)_2S_2O_3$-80 %H_2O for about 10 s. After specimens prepared, a JSM-35 C type scanning electron microscopy(SEM) with associated energy dispersion X-ray analysis(EDAX) was used to observe the microstructure and investigate the chemical composition. The hardness measurements were carried out with a Buehler III microhardness tester using 100 g and 50 g loads for single track cross section and overlapped track surface respectively. Electric resistivity was calculated from the result of the clad resistance tested by a digital ohmmeter with an accuracy of 0.001 Ω.

3 RESULTS AND DISCUSSION

3.1 Laser cladding process

Laser cladding technique can produce smooth, crack-free and pore-free clad coating with some superior properties. For a given material system, energy density in a certain period is the key factor to determine the clad quality. To evaluate energy density, specific energy E_s is defined as

$$E_s = \frac{P_l}{D \cdot v_b} \tag{1}$$

where P_l is the laser power, D is the beam spot diameter, and v_b is the laser scanning speed.

Clad coatings of different quality may be obtained by using different specific energy E_s. If specific energy E_s is too low, it is impossible to achieve good coating due to not completely melting of the mixture preplaced on the surface of the substrate. Minimum specific energy $E_{s\,min}$ is introduced to describe the minimum value of specific energy needed to form uniform, smooth and continuous clad coating. In the present experiment of laser-cladded Cu + Al_2O_3 mixture on AISI 1 045 steel substrate, minimum specific energy $E_{s\,min}$ is 43.0 ~ 52.0 J·mm^{-2}, varies with the content of Al_2O_3 in the mixture.

Particles such as Al_2O_3 in the mixture may have great influence on the processing condition of laser cladding. As can be seen from Table 1, the density of Al_2O_3 is much lower than that of Cu, and the mass fraction of Al_2O_3(represented by w) is quite different from its volume fraction (represented by φ). There exists the following equation:

$$\varphi = \frac{w/\rho_{Al_2O_3}}{w/\rho_{Al_2O_3} + (1 - w)/\rho_{Cu}} \tag{2}$$

Table 2 shows the relation of the two fractions and a conclusion may be drawn from it that the volume fraction is double mass fraction when the content of Al_2O_3 in the mixture is not very high. Absorptivity of the mixture to CO_2 laser (represented by α_m), which is mainly determined by the content of the mixture, is also given for every content of Al_2O_3 in Table 2. It is calculated according to volume fraction as

$$\alpha_m = \varphi \cdot \alpha_{Al_2O_3} + (1 - \varphi)\alpha_{Cu} \tag{3}$$

The specific energy needed for laser-cladded Cu + Al_2O_3 mixture decreases when the content of Al_2O_3 increases because of much higher absorptivity of Al_2O_3 to CO_2 laser compared with that of Cu. However, when the content of Al_2O_3 in the mixture reaches 15 % (nearly 30 % in volume fraction), laser cladding process becomes very difficult due to the appearance of many defects such as cracks and pores. In

Table 1 Thermophysical parameters of three substances[7]

Substance	Density ρ/(g·cm^{-3})	Melting point t_m/ ℃	Boiling point t_e/ ℃	Thermal conductivity λ/(W·m^{-1}·K^{-1})	Laser absorptivity(CO_2) α/ %
Al_2O_3	3.97	2 045	2 980	36.0	95.0
Cu	8.90	1 083	2 595	398.0	1.5
Fe	7.80	1 535	3 000	80.3	3.5

Table 2 Laser absorptivity of $Cu + Al_2O_3$ mixture α_m

$w(Al_2O_3)$ / %	$\varphi(Al_2O_3)$ / %	α_m
2	4.4	5.6
5	10.6	11.4
10	20.0	20.2
15	28.3	28.0

addition, a great amount of Al_2O_3 are lost when its temperature is higher than that of its boiling point during laser irradiation. Excellent clad coatings are obtained when the content of Al_2O_3 in the mixture is about 10%.

3.2 Microstructure and composition

3.2.1 Microstructure

Smooth and crack-free clad coatings were formed after the mixture of $Cu + Al_2O_3$ was melted and metallurgically bonded with the AISI 1045 steel substrate. Fig.1 shows the SEM micrographs of laser-cladded $Cu + 10\% Al_2O_3$ composite coating. Three regions of clad, heat-affected zone and AISI 1045 steel substrate may be seen in Fig.1 (a). The interface between the clad and heat-affected zone is not flat, but appears to be slightly higher in the center and lower on the side. Under the action of gravity and surface tension force, there is a strong convection loop of liquid metal in the molten pool on

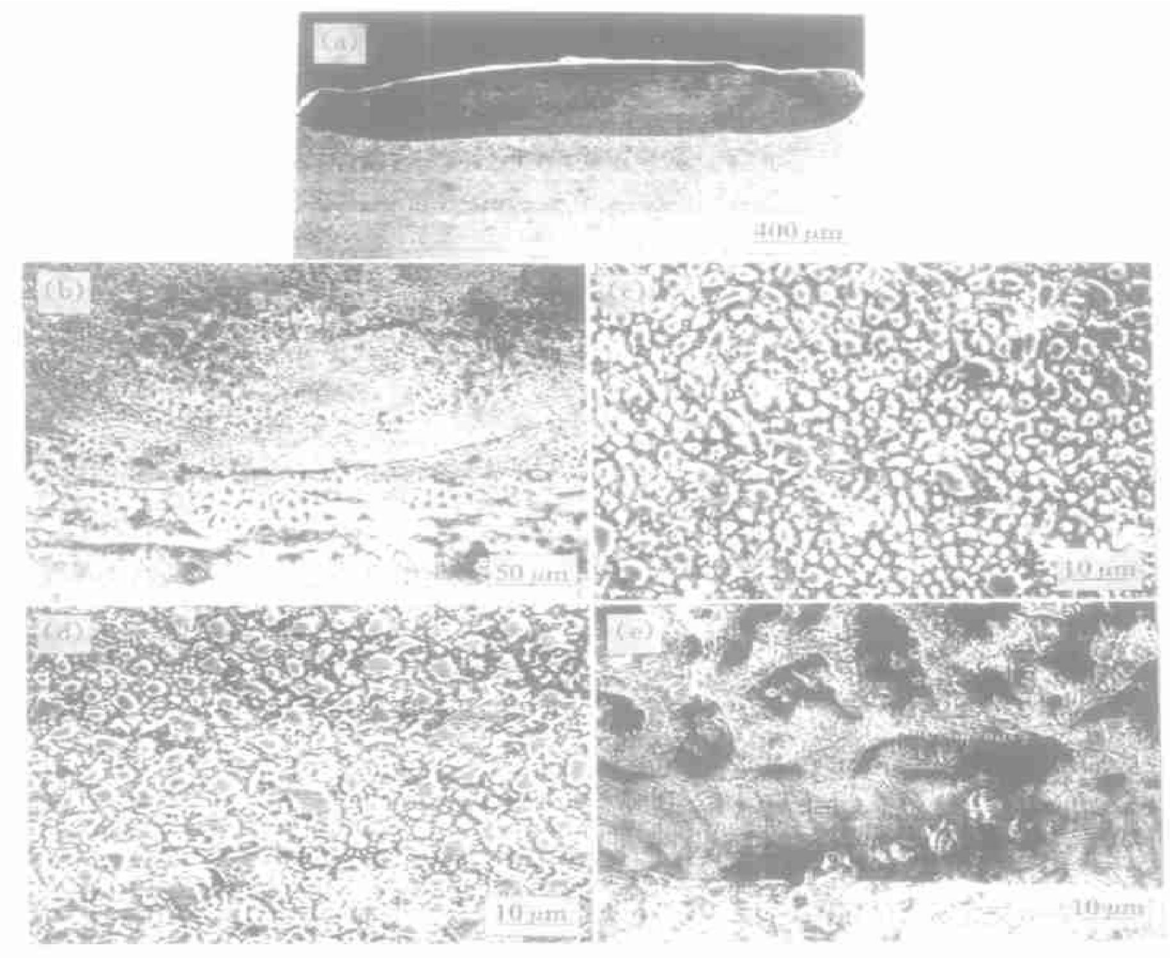

Fig.1 SEM micrographs of $Cu + 10\% Al_2O_3$ clad

(a) —Clad panorama; (b) —Three regions; (c) —Top region; (d) —Mid region; (e) —Bottom region each side during laser cladding, with upper liquid flowing to the side and lower liquid flowing to the center. The liquid convection loop improves heat transferring from the molten pool to the substrate, so the substrate under it may be heated to a higher temperature and melted. The interface is formed after more melted AISI 1045 steel substrate on the side was brought into the molten pool compared with that in the center.

Fig.1(b) shows microstructure of the clad coating with three typical morphologies as follows: black particles in the top region, bright particles in the mid region and black lumps in the bottom region. Magnified micrographs of these regions are given in Fig.1(c), (d) and (e). Particles in Fig.1(c) have spherical shape with a diameter of about 10 μm. Few bright particles with very fine size can also be seen in the same figure. Some particles in Fig.1(d) also have spherical shape, but the others are in cornuted shape. In addition, there are much more fine particles among those big ones in this region than that of Fig.1(c). The black lumps in Fig.1(e) have serrated side and fine separated particles in them. Obvious dendrites of Cu near the interface may also be seen in Fig.1(e).

3.2.2 Composition

Contents of main elements (Cu, Fe, Al and Si) in different regions in the depth direction of the clad are shown in Fig.2. The x axis represents the reduced distance calculated from the ratio of the distance (represented by d) from surface and the height of the clad (represented by H). It is noted that the above results are effective in spite of their possible errors due to the fact that the content of carbon and oxygen have not examined.

High Fe content was detected in different region of the clad, which means that AISI 1045 steel substrate near the interface between the clad and substrate was melted and brought into the molten pool. From the fact that the contents of Cu and Fe in different regions are kept about 50%, it indicates that Cu liquid may be evenly mixed by Fe liquid brought into the molten pool. Due to heavily evaporating of Al_2O_3 after laser irradiation[8], the content of Al in the clad is about 2%, which is far lower than that of the

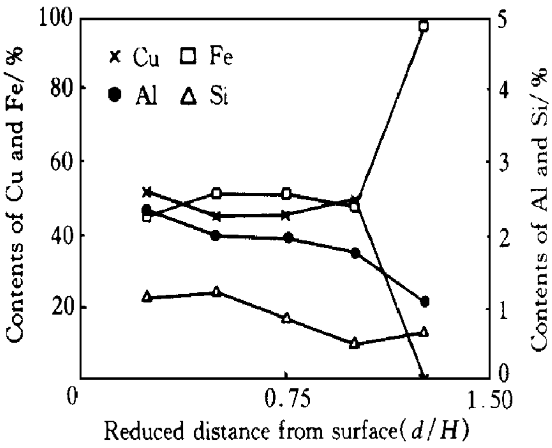

Fig.2 Composition in different regions along clad depth

Cu + Al_2O_3 mixture before laser treatment. With the increase of reduced distance, the content of Al slightly decreases due to the tendency for Al_2O_3 to float to the upper region in the molten pool because of its far lower density compared with Cu and Fe[9]. Like Fe, Si in the clad comes from AISI 1045 steel and has the same distribution.

Chemical compositions of different microstructures in the clad analyzed by EDAX are given in Table 3. It is obvious that the two kinds of particles are Fe-rich while the matrix around the particles is Cu-rich. Apparently, Fe element in the clad is originated from the AISI 1045 steel substrate melted near the Cu liquid. From the phase diagram of Cu-Fe binary alloy[10], it may be seen that Cu and Fe hardly dissolve in each other at a very wide temperature range. So liquid Fe brought into the molten pool did not completely dissolve in the clad and solidified into

Table 3 EDAX results of different microstructure (%)

Element	Cu	Fe	Al	Si
Particles in top region of the clad	14.32	82.45	2.17	1.06
Particles in bottom region of the clad	10.48	88.11	1.03	0.38
Matrix in bottom region of the clad	59.45	36.87	2.15	1.52

Fe-rich particles after the temperature fell down below its melting point. However, solubilities of Cu and Fe in each other have greatly increased due to high cooling rate during laser cladding.

3.3 Properties

3.3.1 Microhardness

Fig.3 shows the tested microhardnesses at different points in the depth direction of the clad cross section. With the increase of reduced distance from surface, the clad hardness decreased from 440 $HV_{0.1}$ to about 300 $HV_{0.1}$ and was relatively homogeneous when the laser scanning speed v_b was equal to 7 mm/s, however great heterogeneity was observed when the laser scanning speed was 5 mm/s. The hardness of the clad was mainly determined by its contents of Cu and Fe because of their obvious difference in hardness. Compositional homogeneity was obtained at $v_b = 7$ mm/s, which resulted in the homogenous distribution of hardness of the clad. When $v_b = 5$ mm/s, the heterogeneous distribution of hardness of the clad was resulted from the isolated existence of Cu and Fe, i.e. Cu in the top region and Fe in the bottom region.

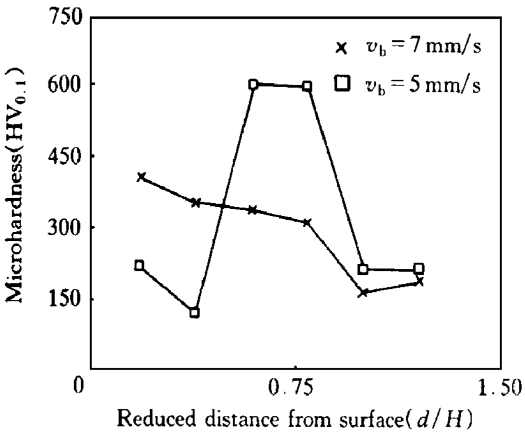

Fig.3 Hardness in different regions along clad depth

Clad coatings with large area of Cu + Al_2O_3 mixture may be produced through overlapping one track on another. The hardnesses in different regions on the overlapped surface may differ from each other. As can be seen from Fig.4, the hardness in the overlapped region is usually lower than that in the track center due to the reheating and remelting procedure of the overlapped area. Fig.4 also shows that with the increase of laser scanning speed v_b, the hardness of the clad decreases as a result of less Fe content in the clad owing to less substrate melted in spite of opposite effect of the increase of cooling rate.

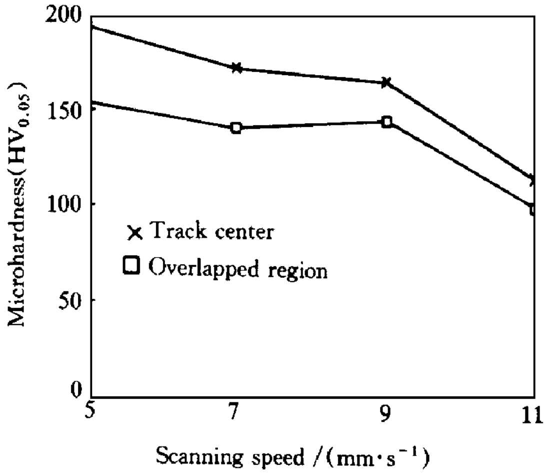

Fig.4 Hardness of overlapped clad under different scanning speeds

3.3.2 Electric resistivity

The tested electric resistances of some overlapped clad coatings produced under different laser scanning speeds are shown in Fig.5. Electric resistivities calculated from related resistance are also given in the same figure. It indicates that electric resistivities of the clad coatings were tested to be about $4.0 \times 10^{-8} \sim 4.5 \times 10^{-5}$ $\Omega\cdot$m, which shows very good electric conductivity. The calculated electric resistivities of the clad coatings are between those of pure Cu(1.69×10^{-5} $\Omega\cdot$ m) and pure Fe(9.78×10^{-5} $\Omega\cdot$ m), which is in consistence with the fact that the clad composition was mainly composed of Cu and Fe.

4 CONCLUSIONS

(1) Smooth and crack-free clad coatings have been successfully produced by preplacing

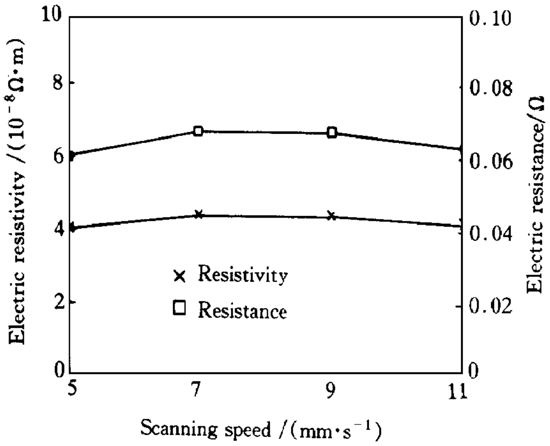

Fig.5 Resistivity and resistance of overlapped clad under different scanning speeds

$Cu + Al_2O_3$ mixture on AISI 1045 steel. The laser cladding process becomes easier by the additon of Al_2O_3 because of its high absorptivity to CO_2 laser. Excellent clad coatings can be achieved when the content of Al_2O_3 in the mixture is 10 %.

(2) The results of SEM observation and EDAX analysis show that Fe-rich particles appear in the clad coatings. These Fe-rich particles come from the melted substrate moving into the molten pool and completely mixed with Cu liquid during laser heating, so the contents of main element in the clad are homogeneous. The content of Al_2O_3 in the top region is found to be more than that in the bottom region of the clad coatings due to its lower density comparing with Cu and Fe.

(3) The microhardnesses of the clad are over 150 $HV_{0.05}$, far more than that of pure Cu, and vary with the content of Fe in the clad coating. The electric resistivities of the overlapped clad coatings are tested to be about 4.0×10^{-8} ~ 4.5×10^{-8} $\Omega\cdot m$, which is between those of pure Cu and pure Fe.

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(Edited by He Xuefeng)