Microstructure and Wear Resistance of 62Cu-38Zn Brass with Bionic Coupling Units Treated by Laser Cladding

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Abstract. In order to improve the wear resistance of 62Cu-38Zn brass, bionic coupling units were fabricated by laser cladding using Ni-based, Fe-based and Co-based self-fluxing alloy powders. The microstructures, chemical composition and mechanical properties of the units were studied in this paper. Wear resistance of samples was examined by dry sliding wear. Good metallurgical bonding between the unit and substrate was obtained, and fine dendritic microstructure was resulted in the unit zone, which proved marked availability of laser cladding on brass. Laser cladding treatments with different self-fluxing alloy powders were beneficial to reinforcing the surface of brass and then improved its wear resistance with various results. The Ni-based alloy powders led to the best wear resistance amongst the all samples.

1. Introduction

Copper and its alloys are widely used in metallurgical apparatus, electrical equipment and oceanographic engineering, due to their excellent electric and thermal conductivities as well as high combination of strength and ductility [1, 2]. In many cases, the method to improve the wear resistance is to fabricate a protective coating on metal surface. Therefore, several surface modification techniques, such as thermal spraying, electroplating, magnetron sputtering, casting infiltration and laser cladding, were used to improve properties of copper alloys [3-5]. In particular, among the mentioned methods, laser cladding could not only enhance wear resistance of the working surface, but also has some other advantages, such as narrow heat-affected zone, small deformation, strong bonding force and none pollution.

However, due to the high thermal conductivity and low absorptivity of copper alloys, previous studies showed that laser was not a preferential method to treat copper alloys [6]. CO₂ laser was once used to laser cladding on copper [7, 8], but the high power was needed. In addition, its sample surface must be blackened to better absorb power. Compared with CO₂ laser, Nd: YAG laser has quicker heating speed and higher metal absorptivity.

In bionics, Ren et al. [9-11] in Jilin University studied abrasion resistance to soil of some ground animals and insects such as dung beetle, pangolin, and cricket. Certain structures on their cuticles
called showed good wear resistance to soil, due to the coupling effect of non-smooth morphology, special physical structure, chemical compositions and so on. The previous studies presented that abrasion resistance of the sample with coupling units was obviously improved [12-14]. The above studies thus might provide a new way for modifying the surface of copper alloys.

It is worthwhile to note that, major focus is on copper, as presented by many studies [1-4, 15]. Less work has been carried out on brass. Brass alloys are widely used in manufacturing, shipbuilding and electronic industries, etc. So study on improving properties of brass alloy is essential.

The aim of this work is to study the effects of laser cladding on 62Cu-38Zn brass alloy, to analyze the related microstructure of processed samples with bionic coupling units by laser cladding, using Ni-based, Fe-based and Co-based self-fluxing alloy powders, and to further evaluate their wear resistance.

2. Experimental procedure

The chemical compositions of 62Cu-38Zn brass substrate material are given in table 1, and its microstructure (etched by a mixed solution of FeCl₃, HCl and absolute ethyl alcohol) was composed of α-phase and β-phase as shown in figure 1. The cladding materials are the commercial Ni-based (Ni45), Fe-based (Fe58) and Co-based (Co40) self-fluxing alloy powders with particle size from 33 to 61 μm. Their chemical compositions are listed in table 2.

| Compositions | Cu | Fe | Pb | Sb | Bi | P | Zn |
|--------------|----|----|----|----|----|---|----|
| Content      | 60.5-63.5 | ≤0.15 | ≤0.08 | ≤0.005 | ≤0.002 | ≤0.01 | Bal. |

| Compositions | C  | Cr | Si  | B  | Mn | Mo | Fe | Ni | W | Co |
|--------------|----|----|-----|----|----|----|----|----|---|----|
| Ni45         | 0.45 | 12 | 4   | 2.4 | 0.1 | -  | 10 | Bal. | - | -  |
| Co40         | 0.6–1.4 | 2–3 | 1–2 | -   | 1–2 | 1–2 | 3–6 | 2–5 | 6–9 | Bal. |
| Fe58         | 4–5 | 40–50 | 1–2 | 1–2 | -   | -  | Bal. | 8–12 | - | -  |

Samples of brass alloys were cut in the size of 25×25×6 mm₃ for laser cladding treatment, and then their surface was finished. Seven parallel rectangular grooves with the spacing of 2 mm and the size of 1×0.4 mm² were carved on the surface of samples shown in figure 2. After cleaning the grooves with acetone, cladding powders were put into the grooves to 0.8 mm higher than the sample surface. A solid state Nd:YAG laser with 1.06 μm wavelength was used for laser cladding treatment, and the laser parameters used were presented in table 3.

| Alloy powder | Energy (J) | Pulse duration (ms) | Frequency (Hz) | Defocusing amount (mm) | Scanning speed (mm/s) |
|--------------|------------|---------------------|----------------|------------------------|-----------------------|
| Ni45         | 20.9       | 14                  | 11             | 4.5                    | 3.5                   |
| Co40         | 13.62      | 6                   | 15             | 4.5                    | 3.5                   |
| Fe58         | 9.1        | 4                   | 15             | 4.5                    | 3.5                   |

After laser cladding, the specimens were sectioned along the direction of the laser trace, and were then prepared by conventional metallographic techniques. Ni-based and Fe-based cladding specimens
were etched in a solution of FeCl₃, HCl and absolute ethyl alcohol, but Co-based cladding specimen was etched by aqua regia (HNO₃: HCl=1:3) due to its own excellent erosion resistance. Microstructure was characterized by an EVO 18 scanning electronic microscope (SEM) (Zeiss, Germany) under the 20.0KV voltage and second electron condition. Composition profile along the depth of brass substrate to Ni-based, Fe-based or Co-based biotic units was acquired by energy dispersive spectrometry (EDS, accessory to SEM). The XRD analysis was carried out using a DX-2700 X-ray diffractometer (Dandong Fangyuan, China) with Cu Kα diffraction generated at 40 kV and 30 mA, and a scan rate of 3.6°/min. The microhardness was measured using 402MVD Vickers microhardness instrument (Buehler, America) at a load of 200 g for a loading time of 10 s. Dry sliding wear tests were conducted on a MG-2000 friction and wear testing machine (Materials Tester Company, Xuanhua, China) at room temperature and loading of 40 N. A fixed rotating speed of 200 rpm was used and tests were performed for 20 min. The sliding disk (H13 die steel, hardness of 49 HRC) with 70 mm in diameter was used as counter-sliding material.

3. Results and discussion

3.1. Microstructural characterization

Figure 3(a)-5(a) show the SEM micrographs of Ni-based, Fe-based and Co-based unit respectively. In general, the treated surface was composed of coupling unit, transition zone and the substrate. There are no cracks in the unit zone, which indicates that the laser parameters are suitable for cladding treatment on the sample surface. Figure 3(b)-5(b) give microstructural details of transition zone in the white rectangular-looped areas marked as A-C in figure 3(a)-5(a) respectively. It can be seen that all the units are metallurgical bonded with the substrate.
The SEM cross-sectional microstructures in units of all treated samples are presented in figure 6(a)-(c), respectively. There are mainly two types of microstructures in the unit: the dendrite and cellular structure. Dendrite is a major constituent in the microstructure. However, noting that from the surface to the internal part, the size of the dendrite was slightly increased. High G/R (G is temperature gradient and R is solidification speed of crystal) is the driving force of the dendrite formation, due to the simultaneous effects of heating down from the internal part and cooling from the surface\cite{2,16}. As the cooling speed reached a critical value, the dendritic crystal growth was triggered\cite{17}.

Figure 5. SEM micrograph taken from the Co-based unit: (a) interface microstructure and (b) transition zone microstructure.

Figure 6. SEM morphology of microstructure in the middle of cross-section of units: (a) Ni-based unit, (b) Fe-based unit and (c) Co-based unit.

Figure 7. EDS analysis on chemical compositions of the Ni-based bionic sample across the interface.

Figure 8. EDS analysis on chemical compositions of the Fe-based bionic sample across the interface.
Figure 7-9 show the EDS analysis of the interfaces between the substrate and the units of Ni-based sample (figure 7), Fe-based sample (figure 8) and Co-based sample (figure 9). Such as the figure 7, it can be seen that a small amount of Ni and Cr exist in the substrate, which indicated a low dilution of unit. Compared with Fe-based and Co-based samples, Cu element content in interface between Ni-based unit and the substrate was the most. It is due to Cu and Ni being all face-centered cubic crystal structure and they can be infinitely miscible \cite{18,19}. The infinite mutual solubility between the Ni from the unit and the brass substrate is important for the sound bonding \cite{1}. In the role of high-power laser beam, a small part of Cu particles diffuse into the unit at the same time.

3.2. Phase identification

Figure 10 shows the X-ray diffraction results of the all units. Ni-based unit (figure 10(a)) was composed of Ni solid solution, FeNi$_3$, Cr$_3$Ni$_2$, and Cr$_2$Ni$_6$, M-C$_4$, Cr$_5$B$_3$ hard phases. The diffraction peak for nickel was moved somewhat toward small angle due to the solution of Cr and Mn. XRD pattern of Fe-based unit is shown in figure 10(b). It revealed that the unit was mainly composed of Fe-Cr, (Fe, Ni) solid solution and M$_7$C$_3$ carbide. In addition, besides the strengthening phases as above mentioned, FeB$_4$ boride was also detected. Figure 10(c) shows XRD pattern of Co-based unit. It can be observed that Fe$_3$Ni$_2$ and Ni-Cr-Co-Mo were the major constituents, and moreover M$_7$C$_3$ carbide and NiCoCr intermetallic compound were formed in the Co-based unit.

3.3. Microhardness

Figure 11 presents the cross-sectional microhardness profiles of the treated surfaces. The microhardness of the treated surface was greatly higher than that of the internal material. An abrupt increase in microhardness was characterized in the transition zone. The average hardness of Ni-based, Fe-based and Co-based units was about HV$_{0.2545}$, 569 and 372, respectively, much higher than that of the brass substrate, HV$_{0.2113}$. In comparison, the microhardness of Co-based unit is 3 times that of the substrate, while the microhardness of Ni-based and Fe-based units is 5 times that of the substrate. The slightly lower microhardness in Co-based unit may be attributed to less Cr and the absence of B in Co-based self-fluxing alloy powder.
3.4. Wear resistance
Wear resistances of the as-received, Ni-based, Fe-based and Co-based samples are all shown in figure 12. The weight losses of the Ni-based and Fe-based bionic samples after the 20 min wear test are 4 times lower than that of the as-received sample. However, the weight loss of the Co-based bionic sample is only 1.5 times lower than that of the as-received sample. It is thereby concluded that the units can significantly improve the wear resistance. It is consistent with the microhardness of the all samples.

Worn surface morphologies of samples are presented in figure 13. The surfaces of the unit zones are much smoother than that of the substrate. It is noteworthy that the surface of the as-received sample was severely damaged by wear as shown in figure 13(d), which is characterized of deep grooves on the plowed surface. Due to protection from units, the hard structure withstood wear on the surface and it played an important role in supporting the wear loads in the wear contact area. Thereby less material was removed from the surface of samples. The brass surface treated by laser cladding with different self-fluxing alloys exhibited lower wear rate and high wear resistance with corresponding results.

Figure 11. The cross-section microhardness profiles of different bionic samples.
Figure 12. Weight loss of Ni-based sample, Fe-based sample, Co-based sample and pure brass sample in wear test.

Figure 13. SEM morphologies showing the worn surface of (a) Ni-based sample, (b) Fe-based sample, (c) Co-based sample and (d) as-received sample.

4. Conclusions
Ni-based, Fe-based and Co-based units were well fabricated by laser cladding on brass surface using pulsed Nd: YAG laser. A good metallurgical bonded interface was thus obtained between the units and
the substrate. The microstructures of three types of units were characterized of fine dendrites as well as partly cellular crystalline precipitates of intermetallic compounds.

The microhardness of the units was varied due to different chemical elements in the all treated samples. Average microhardness of Ni-based and Fe-based units are HV$_{0.2545}$ and HV$_{0.2569}$, respectively, which are 5 times that of the substrate (HV$_{0.2113}$). The Co-based unit has the microhardness obviously lower than that of Ni-based and Fe-based counterparts yet still much higher than that of the substrate.

Wear resistance of treated samples is higher than that of as-received sample. It is in good accordance with the microhardness profiles of the all four samples. Amongst all treated samples, Ni-based bionic sample has the best wear resistance.

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