Study of laser cladding Fe–Co duplex coating on copper substrate

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Abstract
Fe–Co duplex coating has been successfully deposited onto pure copper surface by Nd:YAG laser cladding. The morphology and microstructure were investigated by optical microscopy (OM), scanning electron microscopy (SEM) and x-ray diffraction (XRD). Mechanical properties of the samples have been evaluated by microhardness measurement and wear properties. Experimental results showed that the coating was free of cracks and voids, and good metallurgical bonded to the substrates. The surface of the Fe–Co duplex coating was mainly composed of α–Co solid solution, CoC2, Fe0.64Ni0.36 and a number of carbides. The microhardness of the Co-based coating reached 438.6 HV0.2, which was about 5 times of Cu substrate (90.5 HV0.2). The wear test showed the average wear rate of Fe–Co duplex coating was 19.8% of that of copper matrix. The hardness and wear resistance of the Fe-Co duplex coating was significantly improved.

1. Introduction
Copper is being widely used as crystallizer in continuous casting and rolling due to its excellent electrical and thermal conductivity [1–6]. However, the low strength and poor wear resistance limit its applications [2]. In recent years, it has become a new research hotspot to improve the wear resistance of copper by preparing surface coating. Many techniques, such as electroplating, infiltration and thermal spraying, have been utilized to solve the low physical performance of copper [3–5]. However, the coating is generally mechanically bonded with the matrix, which cannot meet the technical requirements under special conditions. In contrast, the advantage of laser cladding is metallurgical bonding with matrix structure, forming high performance coating with uniform and compact structure, low dilution and small heat-affected zone [6, 7]. Researchers have done a lot of work in this field [8–13]. Wang et al [8] prepared a layer of Ni-based alloy on the surface of thick plate by plasma spraying, and then clad the coating with YAG pulse laser, the wear test showed the laser cladding layer performed 14 times higher wear resistance compared to copper substrate. Zhang et al [9] deposited two overlapping Ni-based alloy coatings by laser cladding, which significantly improved the wear resistance of copper. Yin et al [10] prepared metal silicide based composite coating on pure copper substrate, and analyzed the mechanism of improving the properties of the coating through combining the phase composition.

Although Ni-based coating is widely used nowadays, its high temperature performance is poor [8, 11]. Co-based alloy coating has high hardness, good wear resistance and corrosion resistance at high temperature [12, 13]. The working layer of Co-based alloy prepared on the surface of mold copper plate can obviously improve its service life. However, in the process of laser cladding Co-based coating on copper substrate, cracks and other defects often appear due to different compositions and poor thermophysical properties.

In order to improve the bonding strength and reduce the crack sensitivity of copper substrate and Co-based coating, preparation of transition layers might act as a recipe [14–17]. For example, Liu et al [14] successfully prepared crack-free Ni-Co biphasic coating on copper substrates by continuous laser cladding of Ni-based and Co-based coatings. Chen et al [15] prepared Ni/Co based alloy coating with high wear resistance of gradient on the surface of copper alloy by YAG laser in situ induction reaction method.

Although it is well recognized that Ni-based alloy transition layer could play an important role in improvement of metallurgical bonding with matrix structure, few studies have been conducted on the Fe–Co
biphasic coating deposited on copper substrate. Therefore, the aim of this study is to investigate the effect of Fe-based alloy transition layer on copper substrate, optimizing the parameters of laser cladding Fe-based and Co-based coatings, investigating the corresponding mechanism for the improvement of wear resistance of working layer, thereby providing the theoretical basis for promoting the application of metallurgical industry.

2. Experimental

2.1. Material and sample preparation
In the present study, crystallizer plates (99.0%Cu:0.8%Cr:0.2%Zr) with dimensions of 100 mm × 30 mm × 15 mm were used as substrate for laser cladding. The substrates were sand blasted and cleaned to remove surface oxide before cladding. The chemical compositions of the alloy powders for preparing Fe/Co gradient coating are shown in Table 1. Before laser cladding, the powders were put into the heat insulation box for 30 min and the temperature was adjusted to 200 °C.

Laser cladding was applied by a Nd:YAG pulse laser (XL-800) with a wavelength of 1064 nm and a maximum power of 800 W. The cladding layer was prepared by side synchronous powder feeding method. The Laser cladding parameters for cladding coating are shown in Table 2.

2.2. Analysis methods
DPT-5 colored penetration flaw detection agent was used to nondestructively detect the surface cracks and voids of the cladding layer. In order to observe the microstructure, samples were cut in the size of 10 mm × 10 mm × 10 mm, and then the specimens were abraded using 1500 grit emery paper, degreased with acetone in an ultrasonic cleaner, washed with distilled water and dried in air before testing. Microstructures were examined by optical microscopy after polishing and etching with etchant solution (aqua regia), and the corrosion time was 30 s.

Microstructure and interface bonding state of the cladding layer were observed by microscopy. Microstructural phases of the surface Co-based layer were determined by XRD with Cu Ka radiation, which was operated at 40 kV and 200 mA to generate monochromatic Cu Ka radiation with a wavelength of 1.5406 Å. A Rigaku rotating head anode diffractometer was used to scan the angular 2θ range from 30° to 100° at a scanning speed of 4 °/min. The microstructures and the surface morphology of the alloys were also characterized by SEM, equipped with EDS system for elemental analysis.

Hardness measurements were made in an HXD-1000TMC micro-hardness tester, with the test load of 1.96 N and the holding duration of 15 s. Each hardness value was determined by averaging at least 5 measurements at the same depth along the cross-section of the samples.

The wear tests were carried out on a Wear Test Machine under room temperature, samples were cut in the size of Φ6 mm × 10 mm for wear test. During the test, corundum sandpaper was used as abrasive material to grind through the positive and negative rotation of sandpaper and the back and forth axial movement of cantilever. The turntable rotated 300 cycles at 60 rpm speed and the wear distance was 420 meters. The test load was 1 N. The weight of the samples was measured by a balance accurate to 0.1 mg for calculating the weight loss.

### Table 1. Chemical compositions of gradient coating (wt%).

| Coating   | Fe  | C   | B   | Si  | W   | Ni  | Cr  | Mo  | Co  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| First layer | Bal | 1.1 | 0   | 1.4 | 0   | 21.8| 16.0| 3.0 | 0   |
| Second layer | 8   | 1.5 | 0.6 | 2.4 | 4.5 | 13.0| 23.0| 0   | Bal |

### Table 2. Technological parameters of laser cladding.

| Coating | Current intensity/A | Pulse frequency/Hz | Scanning speed/(mm min⁻¹) | Delivery rate/(g min⁻¹) | Spot diameter/mm | Lap rate/% |
|---------|---------------------|--------------------|-----------------------------|-------------------------|-------------------|------------|
| First layer | 250                | 22                 | 350                         | 8.8                     | 2.2               | 40         |
| Second layer | 250                | 22                 | 400                         | 11                      | 2.0               | 50         |
3. Results and analysis

3.1. Morphology and microstructure

The cross-sectional SEM image of the first Fe-based layer and the Cu alloy substrate is shown in figure 1(a). It can be observed that there were no cracks and voids on the interface, and a ‘white band’ structure was formed, which proved that a metallurgical connection was formed between the first layer and the base. After laser irradiation, there was a large temperature gradient in the bottom of the molten pool, however, the solidification rate was low. The cladding layer grew into the molten pool in a planar interface mode on the copper matrix, forming a planar crystal structure, which reacted as a ‘white band’ in morphology.

The micro-morphology of the middle area of the Fe-based coating is shown in figure 1(b). It can be observed that the predominant microstructures of the Fe-based layer were mainly composed of black dendrites (point B) and white eutectic structures (point A). During rapid remelting and solidifying process of laser cladding, heat always transferred from the surface of the coating to bulk cold substrate and dendrites solidify parallel with the direction of this thermal transmission, resulting in dendritic growth of the Fe-based cladding layer. The EDS of Fe-based coating is shown in figure 1(c). The results indicated that the layers were composed of Fe, Cr, Ni, Co, W and C. In order to define Fe-based layer, XRD analysis were conducted on the surface, and the results are shown in figure 1(d). The phases of the Fe-based layer were composed of (Fe, Ni) solid solution, Cu3.8Ni Intermetallic Compounds and Cr2Fe14C, MoC. These alloy phases in coating can improve the hardness of the Fe-based layer. The main function of the first Fe-based alloy layer was completed firstly, forming metallurgical interface to reduce cracks and improve the bonding strength of coating and copper substrate.

Based on the first Fe-based alloy layer, the second of Co-based alloy prepared by laser under optimized experimental parameters. The macroscopical photo and the results of surface nondestructive testing of the sample are shown in figure 2. It can be seen that there were no cracks and voids on the surface of gradient cladding layer.

The cross-sectional micrograph of the gradient coating after laser cladding is shown in figure 3. It can be observed that the thicknesses of Fe-based coating and Co-based coating were about 700 and 600 μm, respectively (figure 3(a)). The interface of Fe-based coating and Co-based were dendrites crystal with obvious orientation and a number of fine non-directional dendrites microstructures (figure 3(c)). During the preparation of Co-based coating layer, the very thin Fe-based layer was melted, partially mixed with the coating, and then solidified. During solidification, liquid metal grew into dendrites in the molten pool by continuous epitaxy, and the growth
direction was almost perpendicular to the Interface due to the combination of the temperature gradient direction and the preferred orientation of the crystal.

The microstructures of Fe-based coating and Co-based coating were dendritic crystal regions (figure 3(b) and (d)). During the rapid solidifying process of laser cladding, heat transfer was always from melted coating to cold substrate, which determines the dendritic crystal parallel to this heat transfer direction, forming dendritic microstructural growth of Fe-based and Co-based coating, respectively. These characteristics were determined by the local solidification conditions and were typical for laser clad coating.

The content profile of Fe, Co, Ni, Cr and W from the interface between first layer and the second layer are shown in figure 4. From Fe-based coating to Co-based coating, the distribution of Fe content decreased gradually, while the content of Co element increased. As far as Cr and Ni were concerned, their contents did not change significantly. The Fe-based layer contains a certain amount of Co, which proved the mutual diffusion of

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**Figure 2.** The macroscopical photo (a) and surface nondestructive test results diagram (b).

**Figure 3.** Microstructure of the cross-section of Fe–Co duplex coating.
elements occurs between neighbouring layers. The element content in some areas fluctuated greatly due to the phenomenon of element segregation.

Figure 5 shows SEM morphology and EDS spectra of Co-based coating. It can be observed that different morphological tissues were divided into white eutectic structure (point A) and black dendrites (point B). To check the elementary composition of the different microstructures, EDS analyses were conducted. The results revealed that the main elements of the point A were C, Cr and Co (figure 5(b)), the main chemical compositions of point B were Co and Cr (figure 5(c)). So, dendrites were identified to be $\alpha$-Co solid solution rich in Co, while the interdendritic area was eutectic structure composed of $\text{Cr}_2\text{C}_6$ and $\alpha$-Co which was rich in Cr and Co. The EDS of Co-based coating is shown in figure 5(d). The results indicated that the layers were composed of C, Cr,
Ni, Mo, Si, Fe and W. The contents of Fe and Ni were increased compared with the design composition of the working layer, which verifies that the transition layer diluted the work layer.

The XRD pattern of the Co-based layer is shown in figure 6. It is found that the Co-based alloy working layer consists of α-Co (face-centered cubic structure), CoCx, Fe0.64Ni0.36, Cr23C6, and W2C. A small amount of Cr, Ni, and Fe was dissolved into α-Co and Cr23C6, which generated metastable phases possessing complicated centered structure.

3.2. Microhardness and wear resistance

Microhardness profile along the depth of Fe–Co duplex coating is shown in figure 7. From the copper matrix to the working layer, the microhardness increases with a gradient along the depth direction, which weakens the crack tendency of the cladding layer. The average microhardness of the working layer reaches 438.6HV0.2, which was four times higher than that of the matrix.

The high hardness of Co-based coating was mainly benefited from the hard intermetallic compounds and carbide phases, such as Fe0.64Ni0.36, CoCx, Cr23C6, W2C (figure 6). In addition, during laser processing, the metal melts and cools quickly, and the grains formed were very fine (figure 5(a)). According to Hall-petch relation theory, the fine grains are conducive to improve the hardness of coating. At the same time, there were many alloying elements in the solid solution of Co, such as Cr, Fe and W (figure 5(d)), which have the effect of

![Figure 6. The XRD pattern of the Co-based layer.](image1)

![Figure 7. Microhardness profile along the depth of Fe–Co duplex coating.](image2)
solid solution strengthening. Therefore, the hardness of copper substrate surface was significantly improved by laser cladding Co-based coating.

The SEM images of the worn surfaces of copper substrate and Fe-Co composite layer is shown in figure 8. The plough groove formed by copper matrix in abrasive wear test was deep, and accompanied by severe micro-cutting, as shown in figure 8(a). The cladding layer was slightly ploughed and the wear surface was relatively smooth, which greatly reduces the wear and has good wear resistance, as shown in figure 8(b). The wear medium of cladding layer was pressed shallowly, which was mainly benefited from the carbide formed in cladding layer (figure 6) effectively weakens the micro-cutting effect of abrasive particles.

Table 3 shows the average wear amount of the copper matrix and working layer. The average wear amount of the working layer of the sample was only 19.8% of that of the copper matrix. It can be attributed to the fact that, the Co-based coating has a dense and uniform microstructure (figure 5(a)) and a high microhardness (figure 7), thereby leading the relatively stable and low friction coefficient during the wear test.

### 4. Conclusions

(1) Fe-Co duplex coating was successfully fabricated by using multi-channel cladding layer of Fe-based alloy as transition layer. The cladding layer had good formability and no defect. The transition layer had good metallurgical bonding with the substrate and working layer.

(2) The microstructures of Co-based alloy layer and Fe-based alloy layer were mainly composed of dendrite and eutectic structure. The surface of the Fe–Co duplex coating was mainly composed of α-Co solid solution, CoC₀ₓ, Fe₀.₆₄Ni₀.₃₆ and a number of carbides.

(3) The microhardness of the cross section of the gradient cladding layer was distribution of gradient. The average microhardness of the working layer reached 438.6HV₀.₂, which was four times higher than that of the matrix. During wear tests, the average wear amount was 19.8% of the matrix. In the wear morphology of cladding layer, plough grooves decrease, and micro-cutting effect decreases. The Fe–Co composite layer showed higher hardness and better wear resistance.

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