Research on microstructure of copper coatings on AlN ceramic surface by laser cladding and brazing

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Abstract
The preparation of Cu-based coatings on AlN ceramic surface was accomplished by laser cladding and brazing technology. The Cu-based coating was prepared by both copper powder and titanium powder on ceramic surface. The microstructure and properties were tested by x-ray diffraction, metallurgical microscope, scanning electron microscope, energy dispersive spectrometer and microhardness tester. The novelties of this paper in the method of laser cladding and brazing were used to prepare Cu-coating on ceramic surface and the addition of Ti could improve the properties of Cu-based coating. The addition of Ti improved the wettability of ceramic surface. According to the results of EDS, Ti could better get into the Cu-based coating and formed metallurgical bonding in the laser cladding. The microhardness of laser cladding was higher than brazing, which could be concluded that it was due to the rapid cooling rate during the laser cladding could restrain grain growth and element segregation.

1. Introduction
Ceramic material was a kind of inorganic nonmetallic material with excellent performances and possessing the advantages of high melting point, abrasion resistance and oxidation resistance [1]. At present, the ceramic materials with good properties mainly include AlN ceramic [2], Al2O3 ceramic [3], BeO ceramic [4] and diamond ceramic [5].

In the field of surface engineering, laser cladding technology had been widely used to enhance the material surface properties [6–8]. In addition, plasma spraying, plasma cladding and brazing [9–11] could also achieve the purpose of ceramic surface metallization. It had been concluded that ceramic metallization materials prepared by laser cladding conform to the properties of semiconductor materials and were suitable for the production of electronic components [12]. However, the original ceramic surface properties had been improved. Therefore, many researchers were using metal coating to improve the surface properties of ceramic materials. Uenishi et al [13] researched the formation of laser cladding Al3Ti surface layer and its compatibility with ceramics, and concluded that the formation of IMC improved the wear property of the substrate surface.

Fan et al [14] used Ni-Ti two-pulse current plating method, researched the effects of nano Al2O3 particles on the morphology and microstructure of copper-Al2O3 composite coating, and concluded that the composite coating gained good corrosion resistance. Because of the good affinity between copper and titanium, Shi et al [15] conducted brazing experiments on ZrC-SiC ceramics and TC4 alloy with AgCuTi alloy, researched the mechanical properties and microstructure of joints under different parameters, and the results indicated that...
with the increase of temperature or the extension of holding time, the dissolution of TC4 became strong and a large amount of Ti was dissolved into the brazing alloy. Metal matrix composite coating often adopted the addition of WC particles to enhance its composite coating [16, 17]. AlN ceramic were usually metallized with copper, and the methods of Metallization applied upon AlN surface mainly included thin film, thick film, direct copper (DBC) method and chemical coating method. As ceramic surface metallization could improve surface properties [13, 18], more and more researchers have been researching new welding methods in the recent years. In this paper, AlN ceramics was selected as the matrix material to prepare the Cu-based by laser cladding and brazing. It could be concluded that both laser cladding and brazing technology could prepare the metal coating. The microstructure of coatings and structural changes were systematically researched.

2. Experimental

The substrate was AlN-170 ceramic (10 mm × 10 mm × 1 mm), titanium powder and copper powder were the cladding materials. The chemical elements of copper powder and titanium powder were showed in tables 1 and 2. Coatings on the AlN-170 ceramic substrate were fabricated, respectively, using a laser cladding system (700 W RH-700 type Nd:YAG laser, China) and a vacuum brazing furnace (ZC-ZK/YL3). The schematic diagram of the laser cladding system was shown in figure 1, and Argon gas was pumped into the protective cover for 90 s before the experiment. According to the phase diagram of cu-ti binary alloy, which could be concluded that 1080 °C was a appropriate temperature. Figure 2 was the temperature curve of the vacuum brazing furnace. The parameters in the experiment were listed in table 3.

Different microstructure were obtained in the cladding layer and the metallographic samples were cut by internal circular slicer. The microhardness tester (TH701) was used to test the the microhardness of Cu-based coatings, the load and the load time were 200 g and 10 s, respectively. The optical microscope (OLYMPUS GX71) and the scanning electron microscope (HITACHI S-3400N) equipped with an energy dispersive spectrometer (EDS) analysis system were used to observe the microstructure, XRD (XRD, D/max 2500, Japan) was used to investigate the phase compositions of the cladding layer.

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**Table 1.** Chemical composition of copper powder (wt%).

| Cl | Si  | Fe | Mn | Mg | Zn | Cu |
|----|-----|----|----|----|----|----|
| 0.02 | 0.25 | 0.01 | 0.03 | 0.03 | 0.1 | bal |

**Table 2.** Titanium powder chemical composition (wt%).

| P   | Ni   | Si  | Fe  | Zn  | Ag | Ti |
|-----|------|-----|-----|-----|----|----|
| 0.07 | 0.02 | 0.04 | 0.08 | 0.09 | 0.1 | bal |
3. Results and discussion

3.1. Macroscopic observation of coating morphology

The wettability of pure copper powder on ceramic surface was relatively poor, and the addition of titanium powder could greatly improve its wettability. Figure 3(a) was the macroscopic morphology of laser cladding with process parameters of 170 A, 1.8 ms, 4 Hz and 350 mm min\(^{-1}\). The strength between copper powder and ceramic was obviously improved. And figure 3(b) was the macroscopic morphology of brazing sample, it could be found that copper powder could spread evenly on the ceramic surface and the Cu-based coating was formed.

3.2. The analysis of microstructure

In order to research the formation of new phases in the laser cladding process. The phases in the cladding had a big difference in different environment. Figure 4(a) presented the XRD pattern of Cu-based coating without gas
protection. It could be seen that much oxides generated in the air environment, so that much oxides formed in the Cu-based coating. To some extent, the metallurgical bonding of the cladding was affected. Figure 4(b) was the XRD pattern of laser cladding under the gas protection. Compared to the environment without gas protection, it avoided much oxides formed in the cladding. It could be found that compounds containing Ti formed, which made the bonding strength higher and achieved the metallurgical bonding between the Cu-based coating and the ceramic surface.

Figure 5(a) was the micromorphology of the laser cladding layer, the upper part was Cu-based coating and the lower part was ceramic base. It could be seen that the defect of pore near the binding surface, which indicated that the cladding layer solidified so quickly that the gas could not escape during the process of laser melting metal powder, thus the porosity defect was formed. Figure 5(b) was the microstructure of the brazed Cu-based coating on the ceramic surface. A bright transition layer appeared between the ceramic and Cu-based coating. There were obvious crystal particles in the coating, and the structure with obvious grain boundary could be observed after corrosion.

Different electric currents also had great influence on the microstructure of cladding layer. Figure 6 were the microscopic images of cladding samples with current of 130A, 140A, 150A and 170A, respectively. The upper part was copper foundation and the lower part was AlN ceramic substrate. The Cu-based coating and ceramic substrate had been mutually diffused and formed a new phase. There was no transition layer when the current was 140A, and when the current was gradually increased to 150A, the transition layer between Cu-based coating and ceramic substrate was gradually enlarged. The quality of the coating was achieved better and no cracking formed on the surface of Cu-based coating.

3.3. The analysis of microhardness
Figure 7(a) depicted the dynamic hardness horizontal distribution of laser cladding coating. During the processing of laser cladding, the effect of metallurgical bonding between coating and ceramic was better. Due to the rapid cooling rate during the laser cladding, which could restrain grain growth and element segregation and
made the surface of Cu-based coating had a higher microhardness of 73 HV0.2. Figure 7(b) was the dynamic hardness horizontal distribution of brazing coating. In the high temperature brazing furnace, the cooling rate was so relatively slow that made a significant element segregation. Therefore, the metallurgical bonding was not better than laser cladding, which was indicated that the maximum microhardness was lower than the laser cladding coating. So that the effect of laser cladding was better than brazing.

**3.4. Discussion**

Figure 8(a) was the SEM image of the laser cladding layer Cu-based coating without gas protection. The left area was the ceramic and the right was the Cu-based coating. According to the result of EDS, which could be found that the transition layer mainly contained N, O, Al, Ti and Cu elements. It was indicated that metallurgical reaction took place in the transition layer and compound Ti3Al formed. Figure 8(b) was the SEM image of the laser cladding layer Cu-based coating under gas protection. Compared to the Cu-based coating without gas protection, the content of O decreased significantly. Meanwhile, the content of Cu in the cladding also increased a lot. Due to the presence of protective gas in the experiment, the influence of oxygen in the environment was reduced and the avoided excessive metal oxide formed. As a result, more copper got into the cladding, which meant a better metallurgical bonding formed in the process of experiment. According to the resulted of EDS, it could be concluded that gas protection played a role in the processing of laser cladding.

In order to further observe the element distribution of the Cu-base coating in the cladding layer. Figure 9 was the result of the line scan in the laser cladding layer under gas protection. The content of O was barely changed on the transition layer during the laser cladding process, and the effect of gas protection was better. Under the gas...
protection, the formation of part of the oxide was inhibited, so the oxygen content in the coating is reduced, and copper could better enter into the coating to form a metallurgical bond. Meanwhile, it could be found that the content of Ti increased first and then decreased around the transition layer, which could be concluded that Ti improved the wettability between Cu and ceramic.

Figure 10 (a) was the SEM image of the high-temperature brazed Cu-based coating. The left area was the ceramic and the right was the Cu-based coating. The distribution of ceramic particles was very clear around the coating. And figure 10(b) was the result of the spot scanning. It could be seen that the content of Ti was higher than that in the laser cladding layer. In the high temperature brazing furnace, the temperature cooling was so slow that the effect of element segregation was obvious. Therefore, Ti could better get into the Cu-based coating. Meanwhile, the content of N was 12.34%, which could be concluded that the N element in AlN ceramics spread to the Cu-based coating and improved the metallurgical reaction between Cu and Ti, and metallurgical combination formed.

According to the result of element distribution of laser cladding and brazing. Due to the rapid cooling rate of laser cladding, Cu could better get into the metal cladding. Laser cladding could restrain grain growth and element segregation, which was indicated that the effect of metallurgical bonding of laser cladding was better than brazing. The cooling rate of brazing was quite slower than laser cladding, thus the thickness of metal cladding was thicker than brazing.
4. Conclusions

In this experiment, Cu-based coatings were successfully prepared on ceramic surface by laser cladding and brazing. Due to the high laser power density, rapid cladding speed and short cladding time, the performance of the substrate was less affected. And Brazing was heated and held in a vacuum brazing furnace, and then cooled with the furnace, so that it could completely eliminate the influence of oxygen on the bonding surface of ceramic and Cu-based coatings.

According to the results of this experiment, it could be found that the addition of titanium powder could promote the diffusion effect of elements on the substrate surface to some extent. The different current will affect the segregation of the elements between the transition layers and affect the formation of the transition layer. The experimental results indicated that when the current was about 150A, the molding effect of the transition layer was better. And due to the rapid cooling rate during the laser cladding, which could restrain grain growth and element segregation. Thus the microhardness of laser cladding coating was higher than brazing. According to the results of EDS, the metallic oxide was reduced in the argon gas environment, which was beneficial to the formation of coating.

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Figure 10. The image of SEM, (a) the high-temperature brazing Cu-based coating, (b) the result of spot scanning.
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