A Review of Laser Cladding on Copper and Copper Alloys

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Laser cladding owns many advantages, such as high instantaneous heating temperature, fast cooling speed, metallurgical bonding between the coating and the substrate, small heat-affected zone and so on. Laser cladding has been used to improve the surface properties of copper and copper alloys for many years. This paper reviews the laser cladding on copper and copper alloys from the following three aspects: cladding materials, coating preparation process and functional coatings. The main problems and corresponding improvement measures for laser cladding on copper and copper alloys are summarized. Finally, the future research direction of laser cladding on copper and copper alloys are proposed.

1. INTRODUCTION

Copper and copper alloys own excellent thermal conductivity, electrical conductivity and corrosion resistance, which is widely used in electric power, electronics, communications, machinery, transportation, marine engineering, aerospace and so on[1-3]. With the rapid development of modern industrialization, the demand for the performance of copper alloy parts are getting higher. For example, continuous casting mold with high wear resistance and heat resistance[4, 5], propeller with high strength, wear resistance and corrosion resistance[6, 7], blast furnace tuyere with high temperature wear resistance and corrosion resistance[8]. Surface coating technology provides an effective way to improve the surface properties of copper. It can impart the surface of material special properties such as wear resistance, corrosion resistance and high temperature resistance without changing the composition of the matrix material and weakening the mechanical strength and performances of the matrix material. Common surface coating preparing processes such as electroplating[9, 10], and thermal spraying with flame[11],

arc and plasma[12] as heat sources have poor adhesion between the coating and the substrate, which can easily lead to coating spalling and failure. Laser cladding is a more advanced coating preparation process. And the coating prepared by high energy density laser has the characteristics of metallurgical combination of the coating and the substrate, fine coating structure, controllable thickness, small heat-affected zone[13-15].

Although laser cladding has many advantages in the preparation of surface coatings, there are few studies on laser cladding of copper and copper alloys surfaces. The main reason is that there are many difficulties in preparing coatings on copper and copper alloys. Firstly, copper has high thermal conductivity and high reflectivity to infrared and near-infrared light, which need enough energy density to melt the copper substrate and to form a stable molten pool. Secondly, the wettability between copper and many other metallic elements is poor. Thirdly, laser cladding has the characteristics of rapid heating and cooling, and the coating is prone to defects such as pores and cracks[16-18]. This paper summarizes the current situation of laser cladding on the surface of copper and copper alloys from three aspects, cladding materials, coating preparation process and functional coatings. The problems and corresponding solutions encountered when using laser cladding to prepare coatings on copper and copper alloys are clarified. Finally, the future research directions of laser cladding on copper and copper alloys are prospected.

2. CLADDING MATERIAL SYSTEM

According to existing studies, laser cladding materials that are suitable for copper and copper alloys mainly include metal alloy powder system, composite material system, high-entropy alloy system, and rare-earth oxide additive system.

Table 1. Cladding material system[19-24].

Type	Advantages	Disadvantages
Ni-based	Good wettability, high hardness, excellent corrosion resistance and wear resistance	Poor high temperature performance
Co-based	Good high temperature performance, excellent corrosion resistance and wear resistance	Expensive
Fe-based	High hardness, excellent wear resistance and low price	Poor oxidation resistance
Composite material	High hardness, excellent wear resistance and corrosion resistance	Clustered reinforcement materials are prone to pores and cracks
High-entropy alloy	Excellent properties and simple phase structure	Complex chemical composition
Rare-earth oxide additive	Refine grains and reduce cracks	Content is difficult to control

Among them, the metal powder system includes Ni-based, Co-based and Fe-based alloy powder system. The characteristics of these material systems are shown in Table 1.

2.1. Metal alloy powder system

Metal alloy powder system is the preferred material for laser cladding of copper alloys. Ni-based, Co-based and Fe-based alloy powder system are highly adaptable to laser cladding of copper alloys, and can prepare cladding layers with excellent performances. Ni-based alloy coating has good wettability with the substrate, high hardness, excellent wear resistance and corrosion resistance, and moderate price, which is suitable for wear-resistant, corrosion-resistant and fatigue-resistant parts. In the composition design of the Ni-based alloy powder system, the commonly used material are Ni-Cr[25], Ni-Cr-Si[18, 26, 27], Ni-Ti-Si[28], Ni-Mn-Si[16], Ni-Co[5] and the addition of Al, Fe, Mo, B, C and other elements[29-32] based on these material to form new material. The properties of the coating are improved by solid solution strengthening, precipitation strengthening of intermetallic compounds and grain boundary strengthening. Laser cladding of copper alloy is generally based on the above strengthening principle, but considering the performance requirements of the coating, the addition amount of each element is different. In terms of structural and thermophysical parameters of the metal elements, both Ni and Cu have a face-centered cubic structure, and the thermophysical parameters of atomic radius (Cu: 1.278 Å, Ni: 1.246Å,), density, melting point and linear expansion coefficient are similar, so Ni and Cu can be infinitely dissolved in each other and form a Ni-Cu solid solution[33, 34]. Zhang et al.[26] prepared three Ni-Cr-Si coatings on the surface of copper by laser cladding. The results showed that the phases of three coatings were $Cr_3Si+\gamma\text{-}Ni+Cu_{ss}$ (Coat 1, Ni-26Cr-29Si), $Cr_6Ni_{16}Si_7+Ni_2Si+Cu_{ss}$ (Coat 2, Ni-10Cr-30Si) and $Cr_3Ni_5Si_2+Cr_2Ni_3+Cu_{ss}$ (Coat 3, Ni-26Cr-16Si). The microhardness and friction coefficient of the three coatings are related to their phases. The microhardness of coating 1, 2 and 3 is $1050HV_{0.1}$, $900HV_{0.1}$, $400HV_{0.1}$, and the average friction coefficient is 0.45, 0.5 and 0.4, respectively. The phases of the coatings change with the content of the alloy powder, and the performance of the coatings change accordingly. Li et al.[32] used laser cladding to prepare Ni-based alloy coatings on the surface of pure copper to study the electrical conductivity and wear resistance of the coatings. The test results show that the hardness of the coating has increased, which depends on the hard phase CrB/Cr_3C_2 produced in the coating. The electrical conductivity of the coating decreases slightly. The higher the dilution rate of the substrate to the coating, the higher the conductivity of the coating, which is related to the conductivity of Cu and Ni.

Another commonly used powder is Co-based alloy powder system, which is widely used in aerospace, petroleum and chemical industries due to its good high temperature performance, excellent wear resistance and corrosion resistance. However, since its price is more expensive than Ni-based alloy powder, it is relatively less used in laser cladding of copper alloys. Co element has a low melting point, it is easier to melt during heating and form new phases with other elements in the alloy during solidification, which is very beneficial to the enhancement of cladding layer. In the composition design of the Co-based alloy powder system, the commonly used materials are Co-Ni[5, 35], Co-Cr-Ni[3, 25], Co-Fe[36], Co-Ni-Fe[37]. To improve the wettability of the coating and the substrate and reduce the oxygen content in the coating, B and Si are often added to the powder to form a self-fluxing alloy powder. B and Si have the functions of deoxidation and slagging, and preferentially form low-melting borosilicate with oxygen and oxides, which can improve the process forming performance of the coating. Co has a high melting point (1495°C), and Co powder can be melted at a very high temperature. Therefore, Al is

often added to the powder to improve the fluidity of the molten pool. Yan et al.[3] laser cladding Co-based alloy powder on the surface of continuous casting crystallizer, and the results showed that the hardness of the coating was about 5 times that of the substrate, and the relative wear resistance was more than 15 times that of copper, which indicated that wear resistance of copper could be significantly improved. The improvement of coating performance is related to the Co-based solid solution and $Cr_{23}C_6$ hard phase produced in the coating. Since the wettability of Co with most elements is not as good as that of Ni, some scholars[5, 35, 38] have studied Ni-Co duplex layer or multi-layer coating, with Ni-based coating as the bottom layer and Co-based coating as the top layer. The purpose is that the Ni-based coating increases the bonding with the substrate and the Co-based coating maximizes the performance of the coating. Wang et al.[35] prepared a Ni-Co duplex coating on Cu-0.85Cr-0.25Zr (wt.%) alloy surface. First, pre-electrodepositing a $Ni/n-Al_2O_3$ coating on the substrate surface, and then a Co-based coating was deposited on it by laser cladding. The experimental results show that the coating has no defects, and the hardness of the coating reaches 845.2HV, which is 8.2 times that of the substrate. The friction loss of the coating is 3.5 times less than that of the substrate. Due to the low price and good wettability of Fe, Co-Fe duplex layer coatings have been studied. Xu et al.[36] prepared Co-Fe duplex coating by laser cladding on the surface of Cu-Cr-Zr alloy. The coating had good formability and free of defects. The Co-Fe layer showed higher hardness and better wear resistance, and the average wear amount was 19.8% of the substrate.

Fe-based alloy powder is suitable for parts that require partial wear resistance. The advantages are low cost and good wear resistance, but the disadvantages are poor oxidation resistance and poor corrosion resistance. Therefore, there are few studies on laser cladding Fe-based alloy powder on the surface of copper alloy. When designing Fe-based alloy powder, it is often matched with Ni-based and Co-based alloy powder, or reinforcement materials are added to improve the hardness and wear resistance of the coating. Zhou et al.[19] successfully fabricated carbon nanotube (CNT)- and Fe_p-reinforced copper-matrix composites on pure copper by laser induction hybrid rapid cladding. The experimental results showed that when the CNT content was 2.6wt.%, Fe_p and CNTs were uniformly embedded in the copper-rich matrix. The composites exhibited attractive properties including thermal conductivity and wear resistance.

In summary, laser cladding of copper alloy using Ni-based, Co-based and Fe-based alloy powders can effectively improve the performance of copper alloy parts. Among them, Ni-based alloy powder is widely used because of its excellent wear resistance and moderate price. Co-based alloy powder has excellent wear resistance and high temperature oxidation resistance, and can be used in high temperature and harsh conditions. Fe-based alloy powders, which are inexpensive, can be used selectively according to the conditions of use.

2.2. Composite material system

With the development of science and technology, the performance requirements of materials are getting higher and higher, and Ni-based, Co-based and Fe-based alloys cannot meet the requirements for use. Therefore, high melting point strengthening materials can be added to the above materials to make

Int. J. Electrochem. Sci., 17 (**2022**) Article Number: 220920

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composite material. Some achievements have been made in the preparation of laser cladding coating on copper alloy surface by composite material system. The composite material system consists of various reinforcing materials such as ceramic particles, short fibers and whiskers mixed with metal alloy powder. It combines the high hardness, excellent wear resistance and corrosion resistance of the reinforced material with the high strength and high toughness of the metal to form an alloy material with more excellent performance. In the laser cladding of copper alloys, the reinforcing materials that improve the wear resistance the cladding layer are carbide (such as Cr_3C_2[39], TiC[40], (Ti, W)C[4], WC[41], B_4C[42]), boride (such as TiB_2[43], ZrB_2), oxide (such as Al_2O_3[35]) and other ceramic particles, silicon carbide whiskers[44], carbon nanotubes[19], as shown in Table 2.

Table 2. Composite material system for the laser cladding of copper alloys.

Composite material system		Substrate	Reinforced phase	Propertie	Year	Ref.
Ceramic	Metal					
WC	Ni-Cr-Fe	Brass	Ni-rich matrix+WC	CER	2002	[49]
SiC whiskers	Ni-Cu-Fe-B-Si	Cu-Cr-P alloy	SiC whiskers+Ni_3B	H	2009	[44]
TiB_2+CaF_2	Ni-Cr	Cu-Cr-Zr alloy	TiB_2+CaF_2	H and WR	2012	[43]
(Ti, W)C	Ni-30Cu	Cu-Cr-Zr alloy	$TiWC_2$	H and WR	2012	[4]
TiC+CaF_2	Co-based	Cu-Cr-Zr alloy	TiC+ CaF_2	H and WR	2013	[40]
carbon nanotubes	Cu-Fe-Ni-C	Pure copper	carbon nanotubes	H, WR and TC	2013	[19]
WC	Cu-Ni45/Ni60	H62 brass	WC+W_2C+$Cr_4Ni_{15}W$	H and WR	2014	[41]
Ni/Al_2O_3	Co-based	Cu-Cr-Zr alloy	Co-based soild soulution+Cr_7C_3+$(Fe,Ni)_{23}C_6$	H and WR	2016	[35]
Cr_3C_2	Co-based	Cu-Cr-Zr alloy	α-(Cu,Ni)+Cr_3C_2+$M_{23}C_6$+M_7C_3 （M=Cr, Co, Mo）	H and WR	2018	[39]
Ni@B_4C+ZrO_2	Cu-Al	Pure copper	ZrB_2+ZrC	H and WR	2020	[47]

Remarks: Hardness (H); Wear resistance (WR); Corrosion performance (CP); Thermal conductivity (TC); Cavitation erosion resistance (CER)

Although the addition of the strengthening materials can increase the performance of the substrate, the excessive addition or uneven distribution of strengthening materials will cause voids and cracks in the cladding layer, which will eventually lead to a decrease in the toughness of the coating. It is difficult to have both good wear resistance and excellent high temperature oxidation resistance for

parts such as continuous casting crystallizer. Therefore, high temperature self-lubricating wear resistant layer has received widespread attention. Researchers have found that adding solid lubricants to the metal-based can improve the wear resistance of the coating. CaF_2 is a well-known and widely noticed solid lubricant with a lubrication mechanism that is easy to shear along the basal plane of the hexagonal crystalline structures[45]. In addition, its lower hardness and slip plane structure make CaF_2 easily soften. And its chemical stability at elevated temperatures makes it difficult to react with other elements[46]. Yan et al.[40] successfully prepared Co-based alloy/TiC/CaF_2 self-lubricating claddings on the surface of Cr-Zr-Cu alloy by Nd:YAG laser cladding. The research results show that with the addition of CaF_2 content from zero to 20%, the microstructure of the coating changes from dendritic to granular, and the average microhardness of the coating is three times that of the pure Co-based alloy coating. The friction coefficient has also changed significantly. When the content of CaF_2 is 10%, the friction coefficient is the lowest with a value of 0.19. Therefore, with the continuous improvement of material performance requirements, composite materials reinforced by a single strengthening phase often cannot meet the requirements. There are two or more strengthening materials to strengthen a matrix material to meet the needs of different applications. For example, in order to improve the wear resistance of the coating, two reinforcing phases ZrB_2+ZrC[47], TiC+CaF_2[40, 46, 48], TiC+WC[4] are added to the coating.

To ensure that the cladding layer meets the required performance, the following principles should be considered when selecting materials. First, the mechanical and thermal properties of most reinforcing materials are not matched with the metal (coating base metal powder), especially the elastic modulus and the thermal expansion coefficient are not matched, it is easy to produce stress concentration at the interface, which leads to cracks or even interface delamination. Therefore, the selected reinforcement material and the metal have a small difference in expansion coefficient and specific heat capacity. Secondly, the atoms in the metal alloy are bonded by metal bonds, and the atoms in the reinforced material are bonded by ionic or covalent bonds. The wettability between the metal and the reinforced material is an important issue. Therefore, the selected metal alloys and reinforcing materials should have good wettability. Finally, the selected strengthening material can react with metal or alloy powder to enhance the bonding between the strengthening material and the coating.

2.3. High-entropy alloys system

In 2004, Ye et al.[50] formally proposed the concept of high-entropy alloys (HEAs) for the first time. They defined that multi-principal element high-entropy alloys generally consist of five or more main elements, and the main elements are composed of equal atomic ratio or close to equal atomic ratio. To broaden the range of alloy design, the content of each main element of the high-entropy alloy is 5%~35% (atomic fraction). High-entropy alloys have high-entropy effects in thermodynamics, slow diffusion effects in kinetics, lattice distortion effects in structure, cocktail effects in performance, and high-stability effects in structure. These five effects together promote the formation of single-phase solid solution structures in high-entropy alloys, and even amorphous and nano-phase structures. High-entropy alloys have opened new avenues for the development of new alloy systems, so it is getting more and

more attention. Laser cladding has the characteristics of rapid heating and rapid cooling, the nucleation rate of crystal grains is high, and the coating can obtain the fine structure[51]. The slow diffusion effect of high-entropy alloy makes the effect of cooling rate on the solidification of high-entropy alloy coating more obvious. At the same cooling rate, the grains of the high-entropy alloy coating are smaller than those of the traditional alloy coating, and the inhibition of other phases is more obvious. Therefore, laser cladding has great advantages in preparing high-entropy alloy coatings to obtain simple solid solutions, and the application of high-entropy alloy cladding coatings on alloy surfaces has attracted more and more attention.

When laser cladding is used to prepare high-entropy alloy coatings, alloy steel occupies most of the matrix, while Mg, Ti and Al alloys dominate the rest of the matrix[52]. However, there are few reports on the high-entropy alloy cladding layer based on copper alloy. On the one hand, because of the high reflectivity of copper to infrared and near-infrared lasers and the high thermal conductivity of copper, it is difficult for the copper alloy matrix to absorb laser energy to melt. On the other hand, due to the dilution of the coating by the copper substrate during the laser cladding process, a large amount of copper enters the coating. However, copper and other metal elements (such as Co, Cr, Mo, Fe) have a large positive mixing enthalpy[53], and the bonding force between them is weak. Therefore, the copper element is prone to segregate into the dendritic region or form copper-rich particles to form the second phase[54, 55]. Due to the low hardness of copper, the strength of the second phase is weakened to a certain extent. Wu et al[56]. used $FeCoCrAlCuNi_x$ (x=0.5, 1, 1.5) alloy powder to prepare laser alloyed coating on the surface of pure copper, with the purpose of improving the wear resistance and corrosion resistance of the coating. The results show that the crystal structure of the coating evolves from the BCC+FCC1+ordered FCC2 structure when x=0.5 and 0.1 to the FCC1+ordered FCC2 structure when x=1.5. After adding Ni, the microhardness of the coating was reduced from 636HV to 522HV, and the wear resistance and corrosion resistance were significantly improved. The increase in microhardness could be attributed to solid solution strengthening and the stronger p-d orbital bonding between Al and other transition metals. The Cu element has an FCC structure, which is beneficial to promote the formation of an FCC structure in the coating. Jiang et al.[48] prepared a high-entropy alloy $FeMnCoCr/TiC/CaF_2$ self-lubricating coating by laser cladding. The coating is composed of face-centered cubic and hexagonal close-packed solid solution phases. FeMnCoCr is spherical because it is insoluble in Cu, and the hardness of $FeMnCoCr/TiC/CaF_2$ coating is twice that of FeMnCoCr coating. Therefore, the main factor for the significantly improved performance is the presence of a supersaturated solid solution strengthening phase with lattice distortion in the coating, and the hard-strengthening phase produced in some alloy coatings. The conventional laser cladding method for preparing coatings can provide new ideas for the development of high-performance alloy systems used in extreme environments. So far, there have been many reports on the use of laser cladding to prepare high-entropy alloy coatings on engineering alloys. However, due to the particularity of copper (copper has high laser reflectivity and high thermal conductivity), the related results are still in the development stage.

The development of the composition system of high-entropy alloys is concentrated in two categories: one is Al and the fourth cycle Fe, Co, Ni, Cr, Cu, Mn, Ti and other low melting point elements as the main element, the other is such as Mo, Ti, V, Nb, Hf, Ta and other high melting point elements as main elements. At present, the research on high entropy alloy systems is concentrated on low melting

point alloy systems, and there is little research on high melting point alloy systems. However, high melting high entropy alloys have many excellent properties, such as high strength, wear resistance, temperature resistance and excellent oxidation resistance. Xu et al.[57] used higher laser power (2400w~2600w) to prepare high melting point $ZrNbHfTaTi_x$ and $ZrNbHfTaCu_x$ cladding layers on the surface of pure copper. The test results show that the higher the Ti content of the $ZrNbHfTaTi_x$ cladding layer, the lower the friction coefficient slightly，and the higher the Cu content of the $ZrNbHfTaCu_x$ cladding layer, the greater the wear rate.

2.4 Rare-earth oxide additive system

Laser cladding has the characteristics of rapid heating and rapid cooling, so there may be large thermal stress and phase transformation stress in the coating. In addition, the coating and the substrate are prone to cracks due to differences in thermal properties. Preheating the substrate, post-treatment, optimizing process parameters, and adding non-metal or non-metal oxides can reduce the cracking sensitivity of the coating to a certain extent. Studies have shown that adding an appropriate amount of rare-earth or rare-earth oxide to the cladding material can increase the fluidity of the molten pool, refine the structure and purify the structure, thereby improving the strength, toughness and cracking sensitivity of the coating. The rare-earth oxides commonly used in laser cladding include CeO_2[58], Y_2O_3[5], La_2O_3[59], etc. The rare-earth and rare-earth oxides are used more on titanium alloys and stainless steel, but less on copper alloys. This is mainly due to the high thermal conductivity of copper and the low absorption rate of infrared laser and near-infrared laser. Chen et al.[5] added 1wt.% Y_2O_3 to the Ni-Co based coating. Due to the presence of rare-earth oxides in the coating, the impurity and blocking tendency in the coating were reduced. Zhang et al.[60] prepared a Ni-based rare earth alloy coating on the Monel 400 alloy surface. Studies have shown that Y_2O_3 refines the structure of the coating. The average hardness of the coating reaches 9040MPa, and the cavitation resistance is 8.7 times that of Monel 400. The improvement of the cavitation resistance of the coating is due to the fine grain strengthening of the coating and the blocking grain boundary network structure produced during the cavitation etching process.

At present, the application of rare-earth elements or rare-earth oxides in cladding layers is mainly limited to the inability to effectively control the amount of rare-earth elements added. Although rare-earth elements can improve the strength and toughness of the material to a certain extent, the thermal stress generated when the coating is heated and quenched cannot fundamentally solve the problem. Therefore, it is necessary to select appropriate materials and laser process parameters according to the actual situation to effectively solve the cracking problem and improve the performance of the coating.

3. PREPARING PROCESS OF CLADDING LAYER

There are many laser cladding process parameters that affect the quality of copper alloy coatings. In addition to laser power, scanning speed, and dilution rate, the most important is the powder feeding

method. The common powder feeding methods for laser cladding of copper alloys are preset powder methods and synchronous powder feeding. The preset powder method is that the laser heats the pre-coated coating first, and then transfers the energy to the substrate by the heat conduction, as shown in Figure 1(a). The synchronous powder feeding method is that the laser transmits the energy to the cladding powder and the substrate at the same time, as shown in Figure 1(b). Due to copper's low absorption rate for infrared and near-infrared lasers and the high thermal conductivity of copper itself, when the laser is irradiated, the energy will be immediately reflected or scattered by the copper substrate. Therefore, when choosing different powder feeding methods, the absorption rate of the material varies greatly. Studies have shown that the reflectivity of the preset method to the laser is lower than that of the synchronous powder feeding method. When the synchronous powder feeding method is used, a high-energy density laser is required to obtain a coating that is metallurgically combined with the substrate[31].
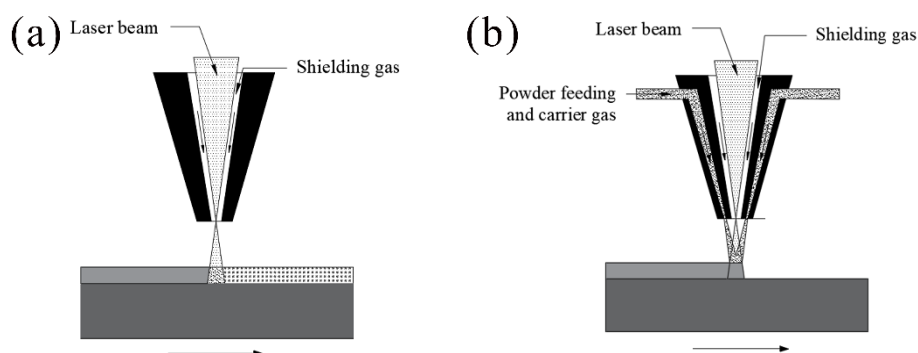

Figure 1. Schematic diagram of laser cladding of preset powder method (a) and synchronous powder feeding method.

3.1. The preset powder methods

At present, there are two commonly used the preset powder methods for preparing coatings on copper alloy surfaces by using laser cladding, one is the prefabricated powder method, and the other is the prefabricated coating method. One is to fully mix the cladding powder and the binder and spread it on the surface of the substrate, and then perform laser cladding. The other is to pre-deposits a certain thickness of the coating by various surface techniques such as electroplating, plasma spraying, and flame spraying before laser cladding. The combination of the prefabricated layer and the substrate is mechanical bonding, and the combination of the coating and the substrate after laser cladding is metallurgical bonding.

The commonly used binders are a mixture of diacetone alcohol and cellulose acetate[26], PVA[61], 502 glue[5], phenolic resin[42], water glass[62] and so on. Yan Hua and Zhang et al.[3, 16, 43] mixed diacetone alcohol and 5% cellulose acetate as a binder and coated copper alloy with coating powder. After laser cladding, the cladding layer that is metallurgically combined with the substrate can be obtained. Chen et al.[5] used 502 glue as a binder and mixed it with powder. The mixing ratio was

7:2 for alloy powder and 502 glue, and the preset coating thickness was 0.5mm. After laser cladding, the hardness and wear resistance of the coating have been improved. The method of prefabricating the coating with the binder has simple process and high utilization rate of laser energy. This is because the pre-coating is a porous structure, and its thermal conductivity is much smaller than that of the entire coating, and more energy reaches the coating under the same laser energy. Although the use of adhesives can solve the problem of copper's high reflectivity to the laser, it also has disadvantages. For example, when a binder is added, the binder burns and decomposes into carbon black products under laser irradiation, which may cause the alloy powder on the coating to overflow and regularly shield the laser[63]. In addition, most of the added binders are organic binders. If the gas generated by thermal decomposition does not come out, it is easy to produce defects such as pores in the coating.

The pre-deposited layer with various surface technologies can not only alleviate the sudden change in physical and mechanical properties between the substrate and the coating during laser cladding process, but also avoid the generation of internal stress by good wettability between the deposited layer and the substrate[25, 35, 49]. Wang et al.[35] prepared Co-based coatings on copper substrates by preheating and electroplating the η-Al2O3/Ni intermediate layer. The microhardness of the coatings was 8.2 times of that of the substrates. The volume loss of copper substrate in 60 minutes wear resistance test was 7.5 times of that of Ni-Co duplex coatings. Liu et al.[21] pre-coated a nickel-based alloy on the copper substrate by plasma spraying, and then used the laser plasma arc effect generated by a low-order mode to laser cladding the pre-coated substrate. After laser cladding, the costing quality are greatly improved, and the bonding method between the coating and the copper substrate has changed from mechanical inlay to metallurgical bonding. The quality of the cladding layer prepared by this method is better than the addition of a binder, but additional equipment is required to prepare the coating. Additional equipment such as electroplating may also cause pollution to the environment. Therefore, it is necessary to develop new processes to prepare coatings on the surface of copper alloys.

3.2. The synchronous powder feeding method

Copper has a low absorption rate for infrared and near-infrared lasers, and copper has a high thermal conductivity. Therefore, if the synchronous powder feeding method is used to directly perform laser cladding on the surface of the copper alloy, the laser energy is often insufficient to melt the molten pool. In order to achieve sufficient energy for the copper matrix to melt and form a molten pool, the following methods are often used: (1) adding an intermediate layer that has little difference in thermal properties from the copper matrix and has a higher absorption rate for lasers; (2) in order to reduce the energy of the substrate is dissipated to pre-heat and post-heat the substrate; (3) use high-power lasers, or use pulsed lasers to obtain higher laser energy.

Ng et al[64] laser cladding molybdenum on copper substrate to obtain an excellent wear resistant coating. To overcome the difference in thermodynamic properties and low miscibility between Cu and Mo, a nickel-based intermediate layer was introduced to form a Mo/Ni/Cu sandwich structure. The results show that there are no cracks and pores between the cladding layer and the substrate, and the wear resistance of the cladding layer is 7 times higher than that of the substrate. To improve the

deposition efficiency of the coating and reduce the cracks in the coating, Wang et al.[65] uses pulsed laser and preheating the substrate to prepare the cladding layer. Several preheating temperatures (room temperature, 600°C, 750°C and 850°C) were designed to observe the cracks of $Cr_{13}Ni_5Si_2$ based metal silicide coatings, the SEM image is shown in Figure 2. Studies have shown that the coating has cracks at room temperature and at a preheating temperature of 600°C. When the preheating temperature is 850°C, the coating with good deposition efficiency and forming quality can be obtained, and defects such as cracks and pores completely disappear. Therefore, when the synchronous powder feeding method is used to prepare the cladding layer, to overcome the difference in thermal properties such as melting point and linear expansion coefficient between the cladding material and the substrate, and reduce the generation of thermal stress of the coating, the method of preheating the substrate can be used to increase the quality of the coating. The above method is considered from the perspective of the substrate and the laser energy, and the metallurgical bonding coating is prepared on the surface of the copper alloy by the synchronous powder feeding method. For powders such as Cu and Al with high reflectivity, when the synchronous powder feeding method is used for laser cladding, most of the laser energy is reflected by the powder, and only a small part of the laser energy is absorbed by the powder and melted into the molten pool. Therefore, we modified the surface of Cu powder with high reflectivity, and prepared a layer of nano-Al_2O_3 and C on the surface of Cu particles (Cu-Al_2O_3-C alloy powder). The micro morphology is shown in Figure 2(a), and the principle diagram of powder absorption is shown in Figure 2(b). As Al_2O_3 and C increase the surface roughness of Cu particles, the energy that enters the copper during laser irradiation increases. In addition, the absorption rate of C element to the near-infrared laser is relatively high, and the absorption rate of the alloy powder to the laser is increased.
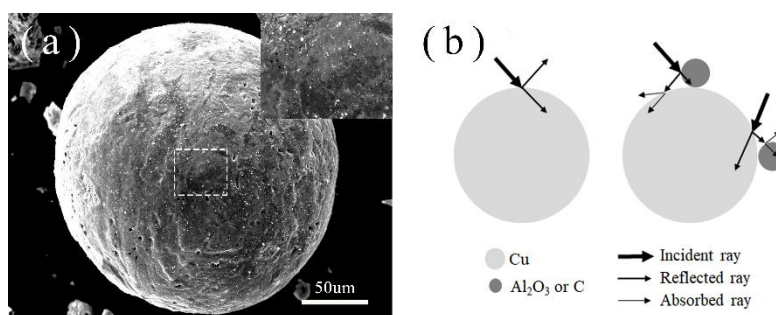

Figure 2. (a) SEM image of Cu-Al_2O_3-C composite powder (The upper right corner is an enlarged view of the white dashed frame in the figure) and (b) Cu-Al_2O_3-C composite powder laser absorption principle diagram

4. FUNCTIONAL COATINGS

Copper alloy has the advantages of good plasticity, thermal conductivity, electrical conductivity and excellent corrosion resistance. It is widely used in aerospace, marine, electric power and electronics industries. However, copper has low hardness, poor high temperature oxidation resistance, and poor wear resistance, which seriously affects the service life of copper alloy parts and easily causes waste of resources and environmental pollution. Therefore, researchers prepared a series of functional coatings

for different working conditions of copper alloys, with the purpose of reducing the failure of copper alloy parts.

4.1. Wear resistance coatings

The wear resistance of the cladding layer mainly depends on the type, quantity and distribution of the reinforcing phase. The reinforcing phase comes from the externally added high melting point ceramic particles and the in-situ self-generated reinforcing phase. The reinforcing phases commonly used to improve the surface wear resistance of copper alloys include carbide (ZrC[47], WC[4, 41, 49], TiC[48], B_4C[48]), borides (ZrB_2[47]), and metal silicide. Lv et al.[47] used laser cladding and self-propagating high-temperature synthesis reaction to synthesize ZrB_2-ZrC coating in situ on the copper substrate. The cladding powder is Cu, Al, Ni, ZrO_2 and Ni-Coated B_4C. The chemical reaction equation is:

$$4Al + 3ZrO_2 + B_4C \rightarrow 2Al_2O_3 + 2ZrB_2 + ZrC \qquad (1)$$
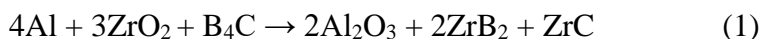
The results show that the in-situ ZrB_2 ceramic has a needle-like morphology and is covered by Ni dendrites. Ni forms an intermediate transition layer between the ceramic and the metal matrix. ZrC has a rectangular shape with a side length of 500 nm. The ceramic fibers and particles synthesized in situ are uniformly dispersed in the metal matrix to improve the mechanical properties of the coating. The wear mechanism of the coating is a combination of abrasive wear and adhesive wear, and the wear loss is about 85% lower than that of the uncoated substrate. Therefore, if the added reinforcing phase can react with other metal elements, it will increase the binding force between the reinforcing phase and the metal elements, and reduce the holes or cracks between them due to poor wettability.

Binary metal silicide (such as $MoSi_2$, Ti_5Si_3, Cr_3Si, Fe_2Si) are high-temperature resistant structural materials with good mechanical properties, but its low room temperature brittleness hinders their industrial application range. Therefore, the researchers developed the ternary metal silicide Ni-M-Si (M=Mn[16], Ti[28], Cr[27, 29], etc.), which has the characteristics of high melting point, low density, high wear resistance and good creep resistance. This new type of wear resistant material has great potential in the aviation, electrical and electronic industries. The performance of ternary metal silicide varies greatly with its composition and content. Zhang et al.[16] used laser cladding to prepare three different Ni-Mn-Si coatings. Coating 1 is Ni(40at.%)-Mn(20at.%)-Si(40at.%), and coating 2 is Ni(40at.%)-Mn(30at.%)-Si(30at.%), coating 3 is Ni(40at.%)-Mn(40at.%)-Si(20at.%). The results showed that Ni_2Si, Ni_3Si, Mn_5Si_2, Mn_3Ni_2Si phases were formed in coating 1, Ni_2Si, Mn_5Si_2, Mn_3Si, $Mn_6Ni_{16}Si_7$ phases were formed in coating 2, and Mn_5Si_2, Mn_5Si_3, Mn_3Si, and $Mn_6Ni_{16}Si_7$ phases were formed in coating 3. The hardness of the three coatings is higher than that of the substrate. The reason for the increase in hardness is the presence of metal silicide hard phases (Ni-Si phase and Mn-Si phase) in the coating. Since the main phase in coating 1 is Ni-Si phase (Ni_3Si) and the main phase in coatings 2 and 3 is Mn-Si phase, the hardness of coating 1 is higher than that of coatings 2 and 3. Yin et al.[27] used laser induction composite cladding technology to laser cladding Ni, Cr, Si composite powders (Ni: 39.9 at.%, Cr: 46.67 at.%, Si: 13.43 at.%) on pure copper. The same powder and process parameters are used to prepare a four-layer coating. Research shows that the coating consists of three different phases,

$Cr_{13}Ni_5Si2$ (point A), $Cr_3Ni_5Si_2$ (point B) and Cu_{ss} (point C). Among them, the phase with the highest hardness is $Cr_{13}Ni_5Si_2$. As shown in Figure 3, the wear surface morphology of 1Cr18Ni9Ti and the coating at 600°C, the wear mechanism of 1Cr18Ni9Ti is adhesive wear and abrasive wear, and the wear mechanism of the coating is fatigue wear. The wear resistance of the coating is 21.9 times that of 1Cr18Ni9Ti. The improvement in wear resistance is due to the synergistic effect of the hard phase $Cr_{13}Ni_5Si_2$ and the tough phase $Cr_3Ni_5Si_2/Cu_{ss}$.
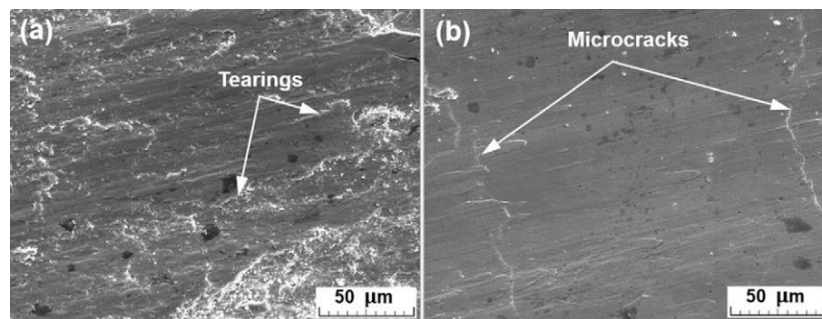

Figure 3. Wear surface morphologies of the (a) 1Cr18Ni9Ti and (b) composite coatings.

In summary, the application of laser cladding in the preparation of wear resistant coatings on the surface of copper alloys has become more and more extensive, and most of the research aims to improve the wear resistance by increasing the hardness and strength of the coating.

4.2 Corrosion resistance coatings

The corrosion resistance of copper alloys is very important in marine engineering. The corrosion rate in seawater is controlled by the cathode process and the surface passivation film. The initial stage of the corrosion is controlled by the cathode reaction, and the later stage is controlled by the stability of the surface oxide film[66]. Aluminum bronze undergoes dealumination corrosion in seawater. The α phase in the alloy basically does not undergo dealumination corrosion; when the second phase is β or γ_2 phase, the second phase is preferentially dissolved[67]. Copper-nickel alloys have excellent corrosion resistance in seawater and are often used to improve the corrosion resistance of aluminum bronze. Xu Jianlin et al.[68] used laser cladding to prepare Cu-Ni alloy coating on the surface of QAl9-4 aluminum bronze, and studied the corrosion behavior of the substrate and coating in 3.5% NaCl solution. The results show that the self-corrosion potential of the Cu-Ni alloy coating is higher than that of the substrate, indicating that the layer effectively improves the corrosion resistance of the material. The QAl9-4 aluminum bronze matrix has undergone dealumination corrosion. The corrosion mechanism is that there is a potential difference between Cu and Al. And the potential of Al is -0.6V and the potential of Cu is +0.05v. When the substrate is in 3.5% NaCl solution, Al is the anode and Cu is the cathode, forming a corrosion micro-battery. Al is corroded due to the loss of electrons. The corrosion process of the coating is mainly decomposition corrosion caused by the preferential dissolution of Cu element. In

3.5% NaCl solution, the potential of Ni is -0.02V and Cu is +0.05V, and a corrosion couple is formed between the two. However, Ni is a thermodynamically unstable element, it has a higher passivation tendency than copper, which can form a dense passivation film on the coating surface to form copper removal corrosion. Feng et al.[69] used laser cladding to prepare nickel aluminum bronze coatings under water and air respectively. The matrix materials and the coating materials are identical, and they are all nickel aluminum bronze. The experimental results show that the cladding layer coated with the protective layer has a better forming quality than the cladding layer without the protective layer under water within 10mm. The coating in water has an ordered solid solution and a twin structure. The collapse of the bubbles generates in the water causes the coating to produce more twin structures and dislocations, resulting in a further refinement of the coating structure and better corrosion resistance than the original substrate. As shown in Figure 4, the electrochemical test study in 3.5% NaCl solution shows that the open circuit voltage of the coating in the air, underwater and the substrate are -260mV, -249mV and -250mV, respectively. The corrosion tendency of the coating in the air and underwater is smaller than that of the substrate. According to the polarization curve, the underwater coating has the lowest corrosion current value and the least corrosion tendency. The reason is that the grain size of the underwater coating is the smallest, and there are Ti and F elements on the top of the coating. Ti has good corrosion resistance, and it is easy to make the coating form a dense oxide film when it is corroded.
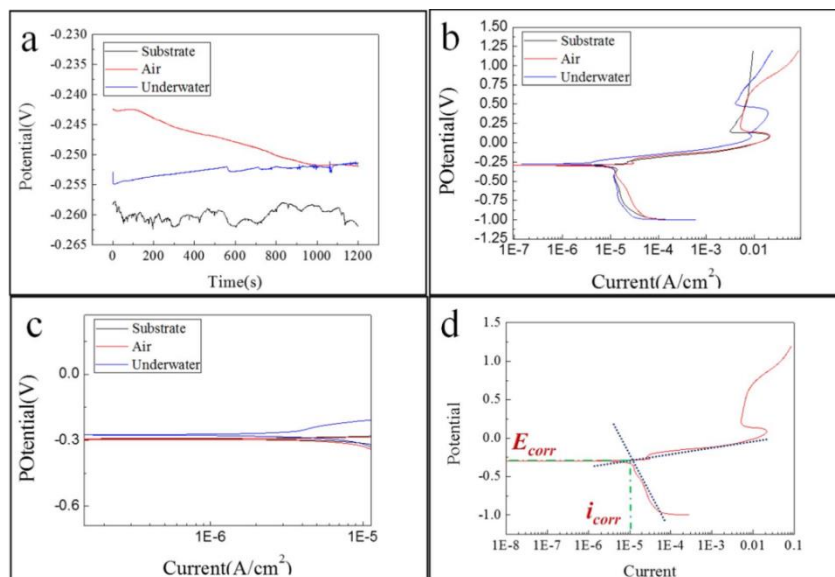

Figure 4. (a) Open-circuit potentials, (b) polarization curve and (c) higher magnification of polarization curves of substrate, NAB coating fabricated in the air and fabricated underwater and (d) schematic illustration of Tafel extrapolation fits to extract the parameters from polarization curves

There are many types of brass, and their seawater corrosion resistance varies greatly. There is no dezincification sensitivity when the Zn content is about 15%, and there is a tendency for dezincification corrosion in seawater when the Zn content is greater than 15%. The mechanism of the dezincification corrosion of brass is that the standard potential of Zn is relatively negative relative to that of copper, and

selective dissolution of Zn occurs when it contacts with seawater. The corroded Zn is compensated by the diffusion of Zn atoms on the alloy lattice, and Zn is selectively eroded at the front of active dezincification. This front moves continuously inside the phase, and finally leaves a porous copper framework. At this time, the mechanical strength of the alloy has almost dropped to zero[66]. To improve the surface properties of brass, Tam et al.[29] used a high-power continuous-wave Nd-YAG laser to perform surface alloying treatment on the brass surface with Ni-Cr-Si-B powder. The corrosion resistance and cavitation corrosion resistance of the coating in 3.5wt.% NaCl solution under different process parameters were studied. Studies have shown that the corrosion resistance of the coating is improved, and the pitting potential moves in the noble direction. The cavitation corrosion resistance of the coating is 6.10 ~ 9.06 times that of brass, and the cavitation corrosion resistance of the coating is related to the hardness of the coating. As the hardness of the coating increases, the pitting resistance increases. The results of this study are consistent with most studies. As the hardness of the coating increases, the pitting resistance increases, and the results are consistent with Munsterer.[70].

When a hard phase is added to the material, it is difficult to improve the wear resistance and corrosion resistance of the coating at the same time. During corrosion, corrosion galvanic cells are often formed between the base material of the coating and the hard phase, and the corrosion starts around the hard phase[71, 72]. Therefore, the improvement of the corrosion resistance of the coating is not only related to the nature of the added elements and the protective oxide film formed. More importantly, the consistency of the coating phase and the compactness and integrity of the protective oxide film play a decisive role in the wear resistance of the coating.

4.3 Cavitation corrosion resistance coatings

Cavitation resistance is particularly important in the flow passage components of ocean engineering. The propeller is a common copper alloy flow-through component, which will cause cavitation damage when moving relatively in seawater. Cavitation generation and collapse are related to local pressure changes caused by fluid flow or vibration[73, 74]. When the cavitation collapses on the solid surface, it will generate a strong pulse on the surface of the material, and the continuous pulse force cause the material to fatigue, fracture and even fail. Because of the unique attack mode of cavitation, the cavitation erosion of materials is regarded as its own independent property[61]. Gu et al.[75] laser cladding Ni60A alloy powder on the surface of nickel-aluminum bronze. The results showed that after 5 hours of cavitation in distilled water and 3.5wt.% NaCl solution, the surface was work hardened, and the weight loss of the substrate was 1.45 and 1.27 times that of the coating, respectively. This is because during the cavitation erosion process, the generation and collapse of cavitation will cause impact on the surface of the substrate and coating. For the matrix, the impact stress causes the lower stacking faults in the matrix to form dislocation plugging, and the surface is peeled off along the pores or loose under the cavitation effect of the ultrasonic negative pressure. For the coating, the increase in grain boundaries hinders dislocation slip and the resistance to plastic deformation increases, so the cavitation resistance of the coating is improved. To further improve the anti-cavitation corrosion performance, some scholars use ceramic particle-reinforced metal matrix composites to prepare coatings. Tam et al.[49] used Ni-Cr-

Fe-WC ceramic alloy powder to prepare a coating on the surface of brass, and studied the cavitation corrosion resistance of the coating. Studies have shown that the cavitation resistance of the coating is increased by 9.1 times. This increase is attributed to the formation of Ni-rich reinforced by precipitated carbides and tightly bound WC particles. Tang et al.[61] used laser alloying method to prepare alloying layer on MAB (Mn-Ni-Al bronze). The alloy powder with different proportions of Al powders can be coated without pore and crack by optimizing process parameters. The cavitation of the alloying layer is nearly 30 times higher than that of the original substrate. Figure 5 is the surface morphology of the substrate and coating at different erosion times. As shown in Figure 5(a), the k phase is separated from the α phase to form a large cavity. As shown in Figure 5(b)-(f), the corrosion damage starts from the grain boundary and the three joints. And as time evolved, the corrosion damage moves towards the grain boundary interior. As shown in Figure 5(a) and (g), the improvement of the cavitation resistance of the coatings is due to the higher hardness of β phase formed in the coatings than the α phase in the matrix.
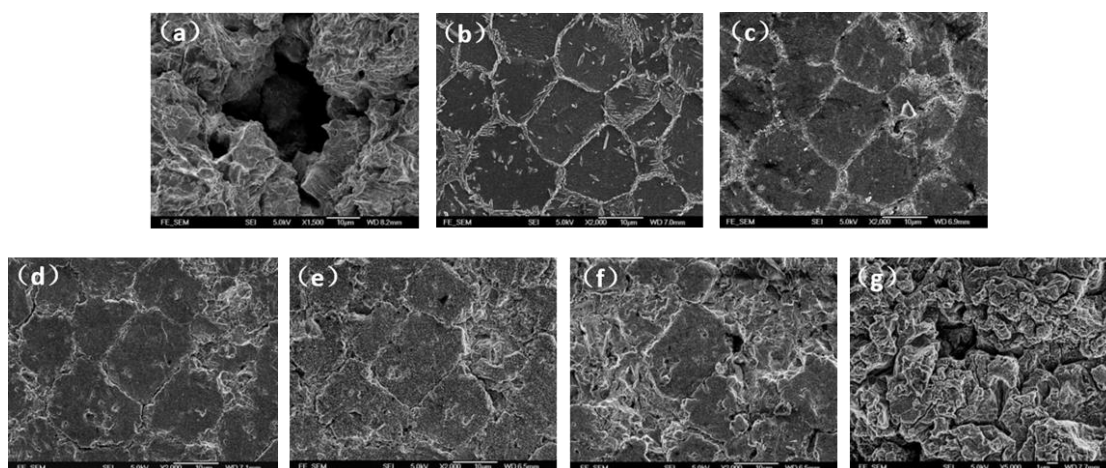

Figure 5. SEM micrographs surface after different erosion times: (a) as-received MAB, 8 h, MAB-Al-8: (b) 0 h, (c) 1 h, (d) 5 h, (e) 9 h, (f) MAB-LSM, 8 h[61].

Therefore, with ceramic-reinforced coatings, the interface bonding between metal and ceramic is poor. The interface is an easily attacked part in cavitation corrosion. If the selected ceramic can react with the metal, it can increase the bonding between them and increase the strength of the coating. In addition, the cavitation corrosion resistance of the coating has a great relationship with the hardness. The higher the hardness, the better the cavitation corrosion resistance of the coating.

4.4 Conductivity coatings

Usually, to improve the hardness and wear resistance of copper alloys, it is often premised on sacrificing conductivity. Surface modification of copper often leads to a sharp decline in conductivity, which cannot meet the application of certain copper parts in special environments, such as an electromagnetic gun giveaway. The parts not only require high hardness and strength at high

temperature, but also good conductivity. To improve the strength and conductivity of copper at the same time, Li et al.[32] prepared a Ni-based coating on the copper surface. When the laser energy is 2.2kW and the scanning speed is 4mm/s, a crack-free, fine and uniform coating can be obtained. The resistivity data and IACS conductivity of the coating are listed in Table 3. The conductivity of IACS decreased slightly. This value is consistent with the change of the dilution rate, as shown in Table 4. The decrease in resistivity of the coating is due to the low copper content in the coating. Therefore, due to the higher dilution rate between Cu and Ni, the conductivity drops less.

Table 3. Electrical conductivity of the specimens[32].

Samples	$\rho(10^{-8}\Omega m)$	%IACS
Copper substrate	1.780	96.9
Modified at 2mm/s	2.019	85.4
Modified at 3mm/s	2.218	81.0
Modified at 4mm/s	1.928	89.4
Modified at 5mm/s	1.856	92.9
Cu-Ni-Si-Fe	4.3	40.1
Cu-Ni-Si-Zn	-	60
Cu-Cr-Zr-Fe	-	82
Cu-Cr-Zr-Mg-RE	-	82
Cu-TiC-Al_2O_3	-	77
GlidCop ®Al-60	2.21	78
GlidCop ®Al-15	1.86	92

Table 4. Dilution rate of the modified layer at different scanning speed[32].

V(mm/s)	H(mm)	h(mm)	η(%)
2	0.94	0.28	23.0
3	1.01	0.29	22.3
4	0.82	0.30	26.8
5	0.77	0.29	27.4

At present, most of the research on laser cladding on the surface of copper alloy is to improve the wear resistance and corrosion resistance, and there is little research on the conductivity of copper itself. Therefore, how to prepare highly conductive, wear-resistant and corrosion-resistant composite coatings on the surface of copper alloys is a future research direction.

5. PROSPECTS

Laser cladding has the characteristics of rapid heating and cooling, small heat-affected zone of the workpiece, the metallurgical combination of the coating and the substrate, and optional zone cladding. It is widely used in the remanufacturing of copper alloys. Although laser cladding has made

some achievements in copper surface modification, the wavelengths of commonly used lasers (such as CO_2 lasers, YAG lasers and fiber lasers) are quite different from those of copper. Therefore, laser cladding of copper surface is still very difficult, and there are many problems to be solved.

(1) Due to the low absorption of copper to infrared and near-infrared lasers, and the high thermal conductivity of copper, it is necessary to comprehensively consider the difference in melting point, coefficient of linear expansion and mutual solubility between the cladding materials and the cladding material and the matrix. It is a future direction to coat the materials which are different from the matrix.

(2) In the preparation process of the cladding layer, how to prepare a metallurgical bonded, non-porous and crack-free coating without the introduction of the binder and additional technology is a research direction in the future.

(3) In terms of the performance of the cladding layer, the flow model of the molten pool and the thermal action model of the laser can be established to play a role in the technological parameters and the quality of the cladding layer on the copper.

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