Microstructure and corrosion resistance of in-suit coating on copper alloy using laser shock melt injection of fine-CeO\textsubscript{2} particles

Hongyu Wang \textsuperscript{a}, Xuqiang Zhai and Yongyi Sun

School of Mechanical Engineering Jiangsu University, Zhenjiang City, Jiangsu Province, 212013, People’s Republic of China

\textsuperscript{a} Author to whom any correspondence should be addressed.

E-mail: ujswhytg@163.com

Keywords: laser shock melt injection, synergistic modification, in-suit coating, microstructure, corrosion resistance

Abstract

In order to improve the marine corrosion resistance of the copper alloy, the method of synergistic modification was introduced to prepare the in situ coating on the surface of HSn62-1 by laser shock melt injection of fine-CeO\textsubscript{2} particles. The micrograph and microstructure of the Hsn62-1, in situ coating, and the laser-treated sample were investigated in contrast. Besides, the electrochemical corrosion resistance of the three specimens in 3.5\% NaCl solution was studied. The results demonstrated that the in situ coating had good compactness and no apparent defects. The upper part of the in-suit coating was mainly cellular solidification microstructure, while the microstructure in the middle and lower part was coarse dendrite. Compared with Hsn62-1 copper alloy, the corrosion resistance of the laser-treated sample and the in-suit coating were improved, which proved that the synergistic modification of laser and rare earth could improve the corrosion resistance of the copper alloy. The analysis indicated that the rare earth elements in the in-suit coating would undergo hydrolysis reaction to form the dense rare-earth hydroxide in an ‘island growth’ way, which effectively prevented the invasion of corrosion ions.

1. Introduction

The copper alloy has excellent characteristics such as high strength, good corrosion resistance, and secure processing and forming [1]. It is widely used in the manufacture of essential equipment parts in fields of marine transportation, ocean exploration, and deep-sea mining [2]. However, natural seawater contains extremely corrosive chloride salts, which inevitably harm the service life and safety of copper alloys. Besides, with the deteriorating marine environment, the demand for materials with high corrosion resistance continues to rise, and the seawater corrosion problem of copper alloys has become more prominent. It is of considerable significance to carry out relevant research on the seawater corrosion resistance of copper alloys.

Rare earth is known as ‘industrial gold’, which can significantly improve the alloy’s quality and properties, such as anti-spalling performance, high-temperature oxidation resistance, and corrosion resistance [3–5]. Many studies showed that adding rare earth elements to copper alloys could increase the uniformity and compactness of the passivation film and its film resistance, thereby improving its corrosion resistance [6, 7]. Besides, preparing the protective coating is another effective method to improve the corrosion resistance of copper alloy, which can prevent corrosion medium from invading the copper alloy matrix. At present, the coating preparation technologies include electroplating, thermal spraying, chemical vapor deposition(CVD), and laser surface modification [8–10]. However, compared with the traditional coating preparation technologies, the laser surface modification has unique advantages in optimizing coating structure, coating composition, and thickness control [11–13], which has great application potential in anti-corrosive coatings [14, 15].

In the previous research, we proposed a new method in preparing the in situ coating called fine-particle laser shock melt injection [16]. The method develops the laser to induce binders to form a plasma shock wave, which provides the injection force for particles. Figure 1 presents the schematic diagram of the laser shock injection process. If using the method to introduce the rare earth to the copper alloy, the synergistic strengthening effect of
laser modification, coating protection, and rare earth effect would further improve the copper alloy’s corrosion resistance.

In this study, the method of synergistic modification was introduced to prepare the in situ coating on the surface of HSn62-1 by laser shock melt injection of fine-CeO₂ particles. The micrograph and microstructure of the HSn62-1, in situ coating, and the laser-treated sample were investigated in contrast. The electrochemical corrosion resistance of the three specimens in 3.5% NaCl solution was studied. Besides, the formation mechanism of the passive film on the surface of the in situ coating was discussed.

2. Materials and methods

2.1. Materials
HSn62-1 copper alloy with low temperature annealing (350 °C ~ 370 °C) was used as the substrate. The nominal composition of the substrate was Cu61.4, Zn37.6, Sn0.9, Fe0.04 and Pb0.007. Fine-CeO₂ with a size of 1 μm were used as injected particles. Also, pure analytical ZnCl₂ was used as the binder. Quartz glass was utilized as the confining medium with dimensions of 12 mm length, 2 mm thickness and 11 mm width.

2.2. Sample preparation
The three copper alloy specimens with dimensions of 10 mm × 10 mm × 5 mm were obtained using wire-electrode cutting, and one of the specimen surfaces was ground by using 400 grit sandpaper, followed by cleaning with absolute ethanol. Subsequently, 50 ml absolute ethanol, 50 ml deionized water, 20 g CeO₂ powder and 5 g ZnCl₂ were mixed to prepare the fine-CeO₂ slurry, and the ultrasonic dispersion was carried out for
15 min. Afterwards, the surface of the specimens was brushed with the slurry for 3–5 times and dried using the electrical heating device, as shown in figure 2. Finally, the surface of the specimens was covered with quartz glass.

2.3. Laser shock melt injection

The single-channel laser shock injection test was carried out using ZKSX-3008 fiber-optic coupled all-solid-state laser processing systems. High purity argon was used as the shielding gas with a flow rate of 10 l·min⁻¹, as shown in figure 3. Based on the orthogonal experiment, the laser power is 1200 W, the scanning speed is 950 mm·min⁻¹, and the spot diameter is 3 mm. Besides, in the test, the three specimens are treated in different processing conditions as shown in table 1.

2.4. Testing and analysis

1. Microscopic characterization

   The metallographic specimens were prepared from the same samples at three different positions perpendicular to the laser scanning direction. The specimens were chemically etched in a solution containing FeCl₃, HCl and H₂O in a volume ratio of 1:2:5 for approximately 20 s. The morphology,
microstructure and composition of coatings were observed by using the EDS spectrometer equipped with Zeiss Merlin compact scanning electron microscope.

(2) Electrochemical characterization

The electrochemical test was carried out on the PRA2273 electrochemical workstation. The three-electrode system was used. The experimental sample was a working electrode. The saturated calomel electrode and plugin capillary with a salt bridge were used as a reference electrode. The platinum electrode was used as an auxiliary electrode. The corrosion solution was 3.5% NaCl solution. The polarization curve’s scanning range was ± 800 mV, and the scanning rate was 0.8 mv s⁻¹.

3. Results and analysis

3.1. Morphology of the in-suit coating

Figure 4 shows the morphology of the in-suit coating after laser shock melt injection of fine-CeO₂ particles. The whole coating is crescent-shaped, and its upper surface is concave with local pits. Besides, the content of Ce in the molten pool is as high as 1.15%. It was believed that due to the difference in thermal properties between coating material and substrate, the standard preset laser modification technology inevitably causes defects such as holes and cracks [17, 18]. However, it can be seen from figure 4 that there are almost no such defects. The analysis shows that when the laser energy acted on the preset layer, the inorganic binder was gasified, which did not introduce impurities, therefore, this method can hardly produce porosity defects. Meanwhile, in the experiment, the considerable laser power value (1200 W) and the small scanning speed (950 mm · min⁻¹) can reduce the temperature gradient of the coating, thus avoiding the trend to form cracks [11].

3.2. The microstructure

Figure 5 shows the microstructure of the three samples. Figure 5(a) is HSn62-1; figure 5(b) is the laser-treated sample without fine-CeO₂ particles; figure 5(c) the upper part of the in-suit coating, and figure 5(d) is the middle and lower parts of the in-suit coating.
The microstructure of the HSn62-1 is mainly composed of $\alpha + \beta$ phase \cite{19}. It can be seen from figure 4 that the $\beta$ phase is a black strip or block, and the $\alpha$ phase exists as a white block. After the laser treatment without fine-CeO$_2$ particles, the $\alpha$ phase is in the shape of an ordered long strip, while the $\beta$ phase changed to ordered fibrous and finely granular. The analysis shows that laser modification is a process of high temperature and rapid cooling \cite{20}. The directional solidification and 'high temperature and rapid cooling' lead to the microstructure's growth in a particular direction. After adding the Ce, the upper part of the in-suit coating is mainly cellular solidification microstructure with a small amount of white granular compounds dispersing at the grain boundary (figure 5(c)). The EDS analysis shows that it is composed of Cu, Zn, and a small amount of Ce, while the microstructure in the middle and lower part of the in-suit coating is coarse dendrite with the white granular compounds mainly distributing on the surface of the tissue (figure 5(d)). The reason for the changes in the microstructure at different parts of the in-suit is that, on the one hand, cerium-containing compounds are distributed at the grain boundaries, which act as nucleating particles during the solidification of the molten pool and quickly interrupt the orderly growth of the tissue, thereby refining the microstructure of the coating \cite{21}. The plasma shock wave induced by the laser may interrupt the growth of the near-surface microstructure of the coating.

3.3. Electrochemical corrosion

Figure 6 shows the electrochemical polarization curve. Figure 6(a) is HSn62-1 copper alloy; figure 6(b) is the laser-treated sample without fine-CeO$_2$ particles; figure 6(c) is the in-suit coating prepared by laser shock melt injection of fine-CeO$_2$ particles.

The polarization curve gradually moves to the lower right from (a) to (c), which indicates that the self-corrosion potential positively shifted. Compared with sample (a), the self-corrosion potential of the sample (c) positively shifted by 385.94 mV; however, the self-corrosion potential of sample (b) positively shifted by 220.24 mV. Based on the self-corrosion potential, the degree of corrosion difficulty is (c) > (b) > (a).

Table 2 shows the relevant results of the self-corrosion current density and polarization resistance of electrochemical corrosion. The fitting results are calculated based on the Stern formula \cite{17}:

$$R_p = \frac{b_a \cdot b_c}{2.303(b_a + b_c)} \cdot \frac{1}{i_{corr}}$$

Table 2. The relevant results.

| Samples | $E_{corr}$ (mV) | $I_{corr}$ (A - cm$^{-2}$) | $-b_a$ (mV) | $b_c$ (mV) | $R_p$ (Ω - cm$^2$) |
|---------|----------------|---------------------------|-------------|-------------|-------------------|
| a       | -495.92        | $2.573 \times 10^{-3}$    | 43.36       | 58.13       | $4.19 \times 10^2$ |
| b       | -275.68        | $2.767 \times 10^{-3}$    | 52.64       | 61.35       | $2.45 \times 10^4$ |
| c       | -109.98        | $3.001 \times 10^{-4}$    | 38.63       | 59.19       | $3.38 \times 10^5$ |
$R_p$ is the polarization resistance; $b_r$ and $b_s$ are the reciprocal of the slope of the two epitaxial lines of the polarization curve; $I_{self}$ is the self-etching current density.

The self-corrosion current densities of sample (a), (b) and (c) are respectively $2.573 \times 10^{-5}$ A · cm$^{-2}$, $2.767 \times 10^{-7}$ A · cm$^{-2}$, and $3.001 \times 10^{-8}$ A · cm$^{-2}$. The self-corrosion current density reflects the degree of corrosion that the smaller the value, the slower the corrosion rate of the sample in the corrosive medium \cite{22}. The sample (c) presents a lower corrosion rate and the best corrosion resistance.

Figure 7 shows the XRD analysis of the samples after electrochemical corrosion. The surface corrosion products of samples (a) and (b) mainly include Cu$_2$O, CuO, and Cu$_2$(OH)$_3$Cl. However, besides CuO, Cu$_2$O, and Cu$_2$(OH)$_3$Cl, the corrosion surface of sample (c) also contains Ce(OH)$_4$.

Figure 8 shows the surface morphology of samples before and after electrochemical corrosion. Figure 8(a) is HSsn62-1 before corrosion; figure 8(b) is HSsn62-1 after corrosion; figure 8(c) is the laser-treated sample without CeO$_2$ before corrosion; figure 8(d) is the laser-treated sample without CeO$_2$ after corrosion; figure 8(e) is the in situ coating before corrosion; figure 8(f) is the in situ coating after corrosion.

The surface of the laser-treated sample without CeO$_2$ and the in situ coating show good compactness. After electrochemical corrosion, the protective passivation film on the surface of HSsn62-1 seriously exfoliates, and there were local corrosion pits, which is mainly caused by the damage of Cl$^-$. In the process of forming a passivation film on copper alloy, it is impossible to keep the uniformity of passivation film, which result in different adsorption of Cl$^-$ on the passive film and local corrosion spots. Although the laser-treated sample’s passive film partially detached after corrosion, no noticeable corrosion pits exist, as shown in figure 8(d). The analysis shows that the laser treatment can effectively control and optimize the original matrix structure, which is conducive to improve the structure density and the uniformity of the structure composition, thus forming a dense and uniform passivation film. From figure 8(f), there are no pitting pits on the surface of the in situ coating after corrosion. However, many 'island-like' corrosion products appeared on the surface, which tended to be interconnected. Studies showed that during the corrosion process, the rare earth cations tended to form dense rare-earth hydroxide on the alloy surface in the way of ‘island growth,’ which gradually formed a thin film covering the surface of the alloy through a mutual connection \cite{23,24}. According to figure 7, it can be inferred that those mentioned above rare earth-containing island compound is Ce(OH)$_4$, which isolates the corrosive medium from contacting the Cu$_2$O and CuO passivation film and plays a role in protecting the passivation film.

4. The formation mechanism of passivation film

The corrosion behavior of copper alloy in seawater is the same as the pitting corrosion mechanism of passivated metal in Cl$^-$ solution. The local damage of corrosion-resistant passivation film on the surface of copper alloy...
caused by Cl−, which results in stress corrosion, pitting corrosion, crevice corrosion, and hydrogen embrittlement. Therefore, the passive film’s stability is the critical factor in determining the copper alloy’s corrosion resistance. The formation of a passivation film on in-suit coating prepared by laser shock melt injection of fine-CeO2 particles in NaCl solution consists of four parts.

Firstly, Cu reacts with Cl− in corrosive medium to form cuprous dichloride complex in anode region [25], as shown in figure 9(a).

\[ Cu + 2Cl^- \rightarrow CuCl_2^- + e^- \]

Secondly, the partially dissolved O2 in the corrosion medium reacts with water to form a small amount of strong oxidizing H2O2, which oxidizes Cu+ to Cu2+ [26], as shown in figure 9(b)

\[ O_2 + H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \]

\[ Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- \]

Then, Cu+ and Cu2+ are hydrolyzed to form dense CuO + Cu2O composite passive film [27], as shown in figure 9(c).
In the process of forming a stable passive film, Cl\(^-\) in the corrosion medium will continue to erode the defects or loose parts of the passive film. At this time, the rare earth elements in the in-suit coating will also undergo hydrolysis reaction to form the dense rare-earth hydroxide, which grows in a 'island growth' way, and gradually covers the surface of the passive film, which can effectively prevent the invasion of corrosion ions, as shown in figure 9(d). The explanation of precipitation mechanism of rare earth oxides and hydroxides is based on the hydrolysis reaction of rare earth cations proposed by Baes and Mesmer [28]:

\[ xM^{2+} + yH_2O \rightarrow M_x(OH)_{x+y}^- + yH^+ \]

Therefore, the hydrolysis reaction of Ce\(^{4+}\) in corrosive medium can be written as:

\[ Ce^{4+} + H_2O \rightarrow Ce(OH)_4 + 4H^+ \]

The corrosion resistance of the in-suit coating and the laser-treated sample is higher than that of the original copper alloy. The main reasons for the increased corrosion resistance are the improvement of the matrix tissue by laser modification and the dense rare-earth hydroxide protective film, proving that the synergistic modification of laser and rare earth can improve the corrosion resistance of the copper alloy.

5. Conclusion

In this study, the method of synergistic modification was introduced to prepare the in situ coating on the surface of HSn62-1 by laser shock melt injection of fine-CeO\(_2\) particles. The micrograph and microstructure of the HSn62-1, in situ coating, and the laser-treated sample were investigated in contrast. The electrochemical corrosion resistance of the three specimens in 3.5% NaCl solution was studied. Besides, the formation mechanism of the passive film on the surface of the in situ coating was discussed. The results of the study were summarized as follows:

1. The in-suit coating prepared by laser shock melt injection of fine-CeO\(_2\) particles had good compactness and no apparent defects. Its upper part was mainly cellular solidification microstructure, but its middle and lower parts are mostly coarse dendritic microstructure.

2. Compared with the original copper alloy, both the in-suit coating and the laser-treated specimen showed excellent corrosion resistance. The in-suit coating had high self-corrosion potential, low self-corrosion current density, and significant electrochemical capacitance resistance, which proved that the synergistic modification of laser and rare earth could improve the corrosion resistance of the copper alloy.

3. The rare earth cations tended to form dense rare-earth hydroxide on the copper alloy surface, which isolated the corrosive medium from contacting the Cu\(_2\)O and CuO passivation film and played a role protecting the passivation film.
Acknowledgments

This work was supported by the Colleges and Universities Graduate Innovation Practice Program of Jiangsu Province [Grant number SJLX16_0439], and the National Natural Science Foundation of China [Grant number 51372216].

ORCID iDs

Hongyu Wang  https://orcid.org/0000-0002-9038-6239

References

[1] Miao Cao A et al 2020 Microstructural evolution and deformation behavior of copper alloy during rheoforging process Journal of Materials ence & Technology, 42 17–27
[2] Tillmann W, Lehmert B et al 2020 Investigation of wetting behaviour of hardenable copper-based alloys for brazing applications Science & Technology of Welding & Joining 25 1362–768
[3] Huiming J, Congrade F and Haryara A 2006 Rare earth effect of yttrium on formation and property of Cr2O3 oxide film formed on Co–Cr binary alloy Advances in Natural Science. 16 72–7
[4] Wang H, Wang H, Zhao Q et al 2018 Investigation on hot corrosion behaviour of Aluminum Rare Earth coating in mixed sulphate at 1050 °C Corrosion Science 135 99–106
[5] Zain M Z M et al 2012 Improvement of corrosion resistance of rare earth element (REE)-based anodic oxidation coating on AZ91D magnesium alloy Applied Mechanics and Materials, 187 210–4
[6] Chen J J et al 2012 Corrosion behavior of novel imitation-gold copper alloy with rare earth in 3.5% NaCl solution Mater. Des. 34 618–23
[7] Gaoyong L et al 2011 Influence of rare earth elements on corrosion behavior of AI-brass in marine water J. Rare Earths 29 638–44
[8] Luo C et al 2009 Mass loss of copper alloy electrode during TiB 2 coating by electrospray deposition Surface & Coatings Technology. 203 3333–7
[9] Fanghong S et al 2012 Research progress of surface coating preparation on pure copper Ordnance Material ence and Engineering. 35 82–6
[10] Hollingsworth J A, Hepp A F and Buhro W E 2015 Spray CVD of copper indium sulfide films: control of microstructure and crystallographic orientation Chem. Vap. Deposition 5 105–8
[11] Wang H Y et al 2017 Micromechanism characteristics of modified Al–Si coating by melt injection CeO2 nanoparticles Surface & Coating Technology. 219C 88–94
[12] Vora H D et al 2013 Design and optimization of microstructure for improved corrosion resistance in surface alloyed aluminum with molybdenum International Journal of Precision Engineering & Manufacturing 14 1421–32
[13] Verezub O, Kálazi Z, Buza G, Verezub N V and Kaptay G 2009 In-situ synthesis of a carbide reinforced steel matrix surface nanocomposite by laser melt injection technology and subsequent heat treatment Surface & Coatings Technology. 203 3049–57
[14] Wang S L, Zhang Z Y, Gong Y B et al 2017 Microstructures and corrosion resistance of Fe-based amorphous/nanocrystalline coating fabricated by laser cladding Journal of Alloys and Compounds 728 1116–23
[15] Ma C et al 2018 Laser surface modification of Mg–Gd–Ca alloy for corrosion resistance and biocompatibility enhancement Appl. Surf. Sci. (https://doi.org/10.1016/j.apsusc.2018.03.174)
[16] Wang H Y, Yuan X, Zhou J et al 2016 Coating method of high-dispersion strong-adhesion light-permeable fine particle preset layer for laser melt injection CN105603419
[17] Li X, Jin G, Kang L et al 2018 Study of Corrosion Behavior of HSn62-1 in Acid, Alkali and Salt Solution Cailiao Daobao/Materials Review 32 228–33
[18] Gao P, Huang W and Yang H 2020 Crack behavior and control of 3-solidifying Ti–40Al–9V–0.5Y alloy produced by selective laser melting Journal of Materials Science and Technology 39 144–54
[19] Zhou S et al 2008 Analysis of crack behavior for Ni-based WC composite coatings by laser cladding and crack-free realization Appl. Surf. Sci. 255 1646–53
[20] Forbes A et al 2010 Studies of the microstructure of polymer-modified bitumen emulsions using confocal laser scanning microscopy J. Microsc. 204 252–7
[21] Duan H et al 2006 Electrochemical corrosion behavior of composite coatings of sealed MAO film on magnesium alloy AZ91D Electrochim. Acta 51 2898–908
[22] Davi B and Damborenea J J D 2004 Use of rare earth salts as electrochemical corrosion inhibitors for an Al–Li–Cu (8090) alloy in 3.56% NaCl Electrochim. Acta 49 1937–45
[23] Guanjie S, Xiujuan Q and Haiyan W 2003 Influence of RE element on Ni-P coelectrodeposition process Materials Chemistry and Physics 80 334–8
[24] Zhang J J, Sang Y X et al 2014 Influence of Substrate Pretreatments on Anticorrosion Properties of Rare Earth Conversion Coatings Journal of Materials Engineering 35 46–52
[25] Kear G et al 2004 Electrochemical corrosion behaviour of 99.5 Cu–Ni alloy in chloride-based electrolytes J. Appl. Electrochem. 34 659–69
[26] Vazquez M V et al 1994 The electrochemical reduction of hydrogen peroxide on polycrystalline copper in borax buffer J. Electroanal. Chem. 374 179–87
[27] Zhao P et al 2019 Effect of passive film on the galvanic corrosion of titanium alloy Ti60 coupled to copper alloy H62 Mater. Corros. 70 10
[28] Baes F C and Mesmer R 1976 The hydrolysis of cation Interciences 40 6