A Review on Corrosion Resistant of Cu-Al Joints

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Abstract

This paper discussed the research profile on corrosion resistance of Cu-Al joints. The review indicated that it was difficult to avoid the corrosion formation in the Cu-Al joint due to the heterogeneous chemical composition and structure. Factors influencing the corrosion resistance of Cu-Al joints could be divided into three categories, the first one is the effect of alloy itself (such as alloy composition, mixed impurities, alloy structure, heat treatment, metal surface condition, stress and strain), the second one is the effect of the surrounding environment (such as corrosion medium, temperature and stress) and the last one is the effect of equipment design and process and anti-corrosion measures (such as spray coating). Hence excellent joints with high-corrosion resistance could be ensured if researchers could take a good use of these factors. Finally, suggestions about the further research orientation on Cu-Al corrosion protection were given.

Keywords: Cu-Al joints; Corrosion resistance; Electronic industries

Introduction

Substitution of aluminum for copper is increasingly used in marine, automotive and electric and electronic industries since their excellent advantages of light weight and low production cost. Hence copper-aluminum connectors were largely introduced in the process of industrial production [1,2]. It is difficult to make a stable and reliable copper-aluminum joint due to these difference between Cu and Al such as large melting point difference, thermal expansion coefficient, electrode potential and mass formation of brittle intermetallic compounds. Besides, the intermetallic compounds formed in the joint are very different with both Cu and Al in these aspects. To solve these problems, many joining technologies were employed [3]. Flash welding was firstly utilized to join copper to aluminum, [4] and then other welding technologies were employed, such as diffusion welding, friction welding, friction stir welding and ultrasonic welding [5-8]. However the problem of Cu-Al joints corrosion is still existing and it deteriorate the properties of Cu-Al joints, which severely shorten the service life of components.

In this paper, some preeminent research on Cu-Al joints corrosion was reviewed. The corrosion forms and mechanism were discussed. Factors influencing the corrosion process were summarized. The efficient methods used to modified the corrosion resistance of the Cu-Al joint were listed.

Corrosion forms in Cu-Al joints

The common corrosion forms occurring in the metallic materials include pitting corrosion, intergranular corrosion, stress corrosion, corrosion fatigue and high temperature corrosion as shown in Figure 1 [9-11]. The chemical composition and structure in metallic materials were not homogeneous, which were responsible for the corrosion potential difference between different phase. The pitting corrosion occurred in the metallic materials when it was immersed in a electrolyte solution [11]. For example, Xue-hui Wang et al investigated the pitting corrosion behavior of 7A60 aluminum alloy in 3.5% NaCl solution. Results showed that pitting corrosion always initiated in the electrochemical active MgZn, region, and followed by Al,MgCu and MgSi [12]. In the process of welding, the introduction of lots of heat input into metallic materials destroyed the chemical and electrochemical balance between grains and grain boundary and increased the tendency of intergranular corrosion [12]. For the stress corrosion, there was still no uniform explanation. But the formation of stress corrosion must meet this two requirements, namely corrosion attack and the existence of stress [13]. Corrosion fatigue and fatigue are different. Corrosion fatigue did not have corrosion fatigue limit compared with fatigue [14]. Metal oxidation is the main corrosion mechanism of high temperature corrosion. High temperature provides enough energy to make metal oxidized, which cannot happen at room temperature [15]. As mentioned above, electrochemical corrosion is the primary problem for Cu-Al joints corrosion. Hence it is important to study electrochemical corrosion mechanism to ensure the enough service life of Cu-Al joints.

Keywords: Cu-Al joints; Corrosion resistance; Electronic industries

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Corrosion Mechanism in Cu-Al joints

As mentioned above, the main cause of electrochemical corrosion is the heterogeneous chemical composition and microstructure in the Cu-Al joint, which in turn constitute the cathode and anode of electrochemical corrosion. From the Cu-Al phase diagram, IMCs CuAl2, CuAl, Cu3Al2, Cu4Al3, and Cu9Al4 are likely to be formed in the Cu-Al joint [2]. Li et al. investigated the corrosion behavior of CuAl, CuAl, CuAl2, CuAl3, Cu, and Al in an acidic chlorine solution, and results indicated that CuAl2 was most susceptible to corrosion compared with CuAl and CuAl3. Besides, the impedance of these phases followed the descending order of Al, CuAl, CuAl2, CuAl3, and Cu. And the corrosion current of these phases followed the order Cu < Cu9Al4 < CuAl < CuAl2 < Cu. It meant that Cu had the least electrode potential and excellent corrosion resistance. Al was contrary, which was in agreement with Moghadam et al. results [16,17]. Shi et al. found that Al always be an anode and involved the Al dissolution, conforming the eqn. (1), and the other phases played a role of the cathode, which conforming the eqn. (2) [18]

\[
\text{Al} - 3e^-=\text{Al}^3+ \quad (1)
\]

\[
\text{O}_2+2\text{H}_2\text{O}+4e^-=4\text{OH}^- \quad (2)
\]

For the Cu-Al IMCs corrosion resistance, Adeline Lim et al. thought that the number of Al atoms in the empirical formula was the main reason. Hence CuAl had the highest corrosion susceptibility, followed by CuAl2 and CuAl3. For the stress corrosion mechanism, there were several main views. We only introduced one of them in detail, that was the theory of film rupture, suggested by Logan. The crack initiation occurred when the surface layer of Cu-Al joints was damaged by electrochemical effect or mechanical effect. Because the surface damage could generate electrochemical corrosion, which led to localized anodic dissolution. And then the crack propagated along the grain boundary. The stress resulted from dislocation pile-up generated on the grain boundary resulted in the dissolution of passivation layer, which in turn promoted the formation of the stress through the generation, propagation, and movement of dislocation. The film rupture theory suggested a repeating, cycling process of film rupture, underlying alloy dissolution and passivation [19]. Besides, Edeleanu and Forty raised the theory of fracture-induced cleavage [20]. Jones suggested the theory of localized surface plasticity, Galvele et al. suggested the theory of Atomic surface mobility [21].

From this section, Cu-Al IMCs promoted the corrosion process of joints due to the heterogeneous chemical composition and microstructure. Stress corrosion cracks formed when the stress and corrosion attack was interacting.

Factors Influencing Corrosion Process

Numerous research on Cu-Al joints corrosion had been done to investigate the factors impacting corrosion. The investigation results showed that these factors could be divided into three categories. The first one was the effect of alloy itself, such as alloy composition, mixed impurities, alloy structure, heat treatment, metal surface condition, stress and strain. For instance, Ye et al. examined the corrosion behavior of Cu-Al joints brazed with Zn-Al-Si and Zn-Al filler metals respectively. The results they obtained indicated that the shear strength of the joints brazed with Zn-Al-Si filler metal maintained 34 MPa after salt spray for 42 days, but that brazed with Zn-22Al fractured after 15 days. Besides, Si element addition could inhibit the propagation of corrosion cracks because the formation of the Al-Si eutectic made the diffusion layer thinner and refined the microstructure in the joint [9]. Both Wu et al. and Lim et al. studied the effect of Pd element on the corrosion behavior of Cu-Al joints [17,22]. Wu et al. research implied that Pd element addition could enhance the corrosion resistance of Cu-Pd phase in the Cu-Al joint when NaCl concentration was given [22]. And corrosion resistance was increased with the increasing Pd content because the enrichment of Pd element on the corrosion surface restrained the anode dissolution. For Pd-bearing Cu9Al4 IMC in the Cu-Al joint, Pd addition reduced the extent of Al passivation, which in turn increased corrosion current density. Hence the corrosion resistance could be slightly improved. Osorio et al. investigated the effect of tool profile on the corrosion behavior of Cu-Al joints and results showed that grain coarsening was beneficial to improvement of corrosion resistance due to the reduction of the galvanic coupling [23]. Osorio et al. researched the effect of Cu-based IMC on the corrosion behavior of Cu-Al alloy [23]. They found that the corrosion resistance of Cu-Al joints was improved when anode/cathode area ratio transformed from 9:1 to 3:1. Because a proper ratio could enhance the enveloping effect, which in turn modified the corrosion resistance of Cu-Al joints. Besides, they thought that enveloping effect was the main reason of the improvement of corrosion resistance from grain coarsening. Another research from Rao et al. indicated that heat input could promote the dissolution of strengthening precipitates and thereby improve the corrosion resistance of Cu-Al joints [24]. Rao et al. found that heat input could enhance the corrosion resistance of Cu-Al joints due to the improvement of the homogeneity of chemical composition and structure [14].

The second one was the effect of environment, such as corrosion medium, temperature and stress. Rao et al. study showed that the value of NaCl concentration had an obvious effect on the corrosion resistance of Cu-Al joints. The higher the NaCl concentration was, the lower corrosion resistance become as shown in Figure 2 [22]. Warner et al. examined the effect of the addition of molybdate into NaCl and HCl solution on corrosion fatigue cracks. Results indicated that molybdate addition could availably restrain the expansion of corrosion fatigue cracks since molybdate can stabilize the passive film at the crack tip, which in turn reduced H generation and absorption [25].

The last one was the effect of equipment design and process and anti-corrosion measures. For instance, Rao et al. examined the effect of tool profile on the corrosion behavior of Cu-Al welded nugget joined by using friction stir welding. They found that the pitting corrosion

![Figure 2: Effect on NaCl concentration corrosion resistance of Cu-Al joints.](image-url)
potential value of stir area processed changed with using different tools as shown in Figure 3 and Table 1 [24]

![Figure 3: Effect of tool profile on the corrosion resistance of Cu-Al joints.](Image)

![Table 1: Values of Pitting corrosion potential with different tool profiles.](Table)

<table>
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<tr>
<th>Tools</th>
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This section showed that factors impacting the corrosion resistance could be divided into three categories, that is the alloy itself (such as alloy composition, mixed impurities, alloy structure, heat treatment, metal surface condition, stress and strain), the environment (such as corrosion medium, temperature, stress and equipment design) and the process and anti-corrosion measures.

**Methods Improving the Corrosion Resistance of Cu-Al Joints**

After discussed the corrosion mechanism and the factors impacting the corrosion resistance of Cu-Al joints, in this section, we discuss how to make a good use of these factors to protect Cu-Al joints from corrosion. As abovementioned, the formation of corrosion attack was mainly resulted from heterogeneous chemical composition and microstructure of Cu-Al joints, resulting in electrochemical corrosion. Hence methods decreasing heterogeneity could enhance corrosion resistance, such as the addition of the third element or compound, heat treatment, mechanical processing and weld tools design. For instance, Rao et al. successfully enhanced the corrosion resistance of Cu-Al joints by using friction stir processing, which could carry out heat treatment and change grain size. Their study aimed at a kind of condition, where friction stir welding was not suitable such as thick plate welding and inaccessible locations. Besides it could enhance the fatigue property and refine the microstructure of Cu-Al joints [14], Wang et al. successfully decreased the corrosion cracks of aluminum joints by using laser shock penning (LSP). LSP changed the residual stress, refined the microstructure and enhanced the toughness and tensile properties, which in turn decrease the susceptibility of Cu-Al joints to stress corrosion cracks [13].

**Conclusion**

In this review, we summarized the main recent research on the corrosion resistance of Cu-Al joints, which included these aspects as followed: Researchers studied the corrosion behavior of Cu-Al joints through simulating a variety of practical corrosion environments, and then observed the evolution of the structural morphology and tested the performance changes. The relationship between the evolution of the structural morphology in the Cu-Al joint, the corrosion environment and corrosion mechanism was established. Factors impacting corrosion were explored. However, in these experiments, corrosion process was accelerated in the laboratory, which is not in agreement with the complex practical corrosion situation. In addition, most of research aimed at understanding the corrosion performance of Cu-Al joints welded by using friction stir welding, ignoring other welding methods especially the brazing and laser welding, which have been used widely in Cu-Al joining. In order to obtain a good welded joint, all kind of actual corrosion parameters should be collected as much as possible to establish a Cu-Al corrosion database, and software simulation based on the actual corrosion parameters should be carried out for the purpose of saving materials and time.

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