A Review on Corrosion Resistant of Cu-Al Joints

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Abstract. This paper discussed the profile of research 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 of Cu-Al corrosion protection was given.

1. 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] It is difficult to make a stable and reliable copper-aluminum joint due to these differences 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 joining problems, many joining technologies were employed. Flash welding was firstly utilized to join copper to aluminum, [2] and then other welding technologies was employed, such as diffusion welding, friction welding, friction stir welding, laser beam welding and ultrasonic welding.[3-5] However the problem of Cu-Al joints corrosion still exists and it deteriorates 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 modify the corrosion resistance of the Cu-Al joint was listed.

2. 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.[6, 7] 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 an electrolyte solution.[7] 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 MgZn2 region, and followed by Al3MgCu and Mg2Si.[8] In the process of welding, lots of heat input destroyed the chemical and electrochemical balance between grains and grain boundary and increased the tendency of intergranular corrosion.[9] For the stress corrosion, there was still no uniform explanation. But the formation of stress corrosion must meet these two requirements, namely corrosion attack and the existence of stress.[10] Corrosion fatigue and fatigue is different. Corrosion fatigue did not have corrosion fatigue limit compared with fatigue.[11] 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.[12] As mentioned above, electrochemical corrosion is the primary problem for Cu-Al joints corrosion. Hence it is important to study electrochemical corrosion mechanisms to ensure the enough service life of Cu-Al joints.

3. 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, Cu3Al, CuAl3, CuAl4 and Cu9Al4 are likely to be formed in the Cu-Al joint. Adeline B.Y. Lim et al investigated the corrosion behavior of CuAl2, CuAl, Cu9Al4, Cu and Al in an acidic chlorine solution, and the results indicated that Cu9Al4 was most susceptible to corrosion compared with CuAl and CuAl2. Besides, the impedance of these phases followed the descending order by Al, CuAl, CuAl2, Cu9Al4 and Cu. And the corrosion current of these phases followed the order Cu < Cu9Al4 < CuAl2 < CuAl < Al. It meant that Cu had the lowest electrode potential and excellent corrosion resistance while Al was contrary. [13] Xue-hui WANG et al found that Al always be an anode and involved the Al dissolution, conforming the Eq(1), and the other phases played a role of the cathode, which conformed the Eq (2) [14]

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\begin{align*}
\text{Al} - 3e = \text{Al}^{3+} \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^-
\end{align*}
\]

For the Cu-Al IMCs corrosion resistance, Adeline B.Y. Lim et al thought that the number of Al atoms in the empirical formula was the main reason. Hence Cu9Al4 had the highest corrosion susceptibility, followed by CuAl and CuAl2.

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 H.L. 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 the dislocation pile-up generated at 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, undermining alloy dissolution and passivation.[15] Other views had also been suggested such as the theory of fracture-induced cleavage, the theory of localized surface plasticity, the theory of Atomic surface mobility.

4. Factors influencing corrosion process
Numerous researches on Cu-Al joints corrosion had been done to investigate the factors impacting corrosion. 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, and stress and strain. For instance, Zheng Ye et al examined the corrosion behavior of Cu-Al joints brazed with Zn-Al-Si and Zn-Al filler metals respectively. The results 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, the 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.[6] Both Yuelin Wu et al and Adeline B.Y. Lim et al studied the effect of Pd element on the corrosion behavior of Cu-Al joints.[16, 17] Yuelin Wu et al’s 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. And corrosion resistance was increased with the increasing Pd content because the enrichment of Pd element on the corroded surface restrained the anode dissolution. For Pd-bearing Cu_{9}Al_{4} IMC in the Cu-Al joint, the addition of Pd reduced the extent of Al passivation, which in turn increased corrosion current density. Hence the corrosion resistance could be slightly improved.[16] Ch VENKATA 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 the improvement of corrosion resistance due to the reduction of the galvanic coupling.[18] Wislei R et al researched the effect of Cu-based IMC on the corrosion behavior of Cu-Al alloy. 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 Ch VENKATA et al indicated that heat input could promote the dissolution of strengthening precipitates and thereby improve the corrosion resistance of Cu-Al joints.[19]

The second one was the effect of the environment, such as corrosion medium, temperature and stress. Ch VENKATA et al’s 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.[16] Jenifer S. Warner et al examined the effect of the addition of molybdate into NaCl and HCl solution for 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.[20]

The last one was the effect of equipment design and process and anti-corrosion measures. For instance, Ch. VENKATA 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 potential value of stir area processed changed by using different tools as shown in Table 1.[19]

| tools   | conical | triangle | square | pentagon | Hexagon | Base |
|---------|---------|----------|--------|----------|---------|------|
| $E_{pit}$ | -528    | -576     | -565   | -551     | -534    | -642 |

5. Methods improving the corrosion resistance of Cu-Al joints

In this section, we discussed how making a good use of these factors to protect Cu-Al joints from corrosion. As above mentioned, the formation of corrosion attack was mainly resulted from heterogeneous chemical composition and microstructure. Hence, methods, decreasing heterogeneity could enhance corrosion resistance, such as the addition of the third element or compound, heat treatment, mechanical processing and weld tool design. For instance, K. Prasad 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. In such cases, it may avail for friction stir processing the fusion welds by using a portable equipment.[11] 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, which in turn decrease the susceptibility of Cu-Al joints to stress corrosion cracks.[10]
6. 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 observed the evolution of the structural morphology and tested the performance changes. The relationship between the evolution of the structural morphology, the corrosion environment and corrosion mechanism was established. Factors impacting corrosion was 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 kinds 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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