Original Article

Effect of Si addition on corrosion behaviors of Cu/Al dissimilar joint brazed with novel Zn-Al-xSi filler metals

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ABSTRACT

Novel Zn-Al-Si filler metals were used to enhance the corrosion resistance of Cu/Al brazed joint. The corrosion behaviors of the joint were investigated by neutral salt spray test. The effect of Si addition on the corrosion behaviors of the joint was discussed, and the corrosion resistance was evaluated for the first time. The results showed that the thickness of the diffusion layer on Al side was remarkably reduced with the addition of Si. Meanwhile, the Zn element aggregation degree was alleviated because the Zn-Al eutectic was divided into narrow strips by scattered fine CuAl phases, especially the Zn-rich Zn-Al eutectic. Thinner diffusion layer suppressed the initiation and propagation of the stress corrosion crack, while the alleviated degree of Zn aggregation significantly slowed down the deepening and expansion rate of the corrosion pit. After 36 h salt spray test, Zn-22Al-1.5Si joints turned out to possess the best corrosion resistance.

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1. Introduction

Copper is commonly used materials for domestic refrigeration pipes and devices due to its excellent electrical conductivity, thermal conductivity and corrosion resistance. However, the density of copper is high, and the price of copper has soared in recent years. Copper pipes and equipment are heavy and costly. Aluminum has much lower density and price than copper, meanwhile, the electrical and thermal conductivity of aluminum are next to that of copper. Therefore, Cu/Al hybrid structure has been one of promising designs to reduce weight and economic cost of refrigeration and electric power devices [1–4]. Brazing is a common method for fabricating these Cu/Al structures, which is Flexible and exercisable [5–7].

Many researches focused on Cu/Al brazing have been carried out. The filler metal, flux and join process of the Cu/Al brazing have been studied systematically [5,6,8–10]. Zn-Al filler metals have lower melting point than Al-Si filler metals, which prevented the melting of aluminum base metal in brazing process. Moreover, The shear strength of the Cu/Al...
joint brazed with Zn-Al filler metals have exceeded 70 MPa as reported [9], Which was much higher than that brazed with Sn-Zn filler metals or Sn-Ag filler metals. The Cu/Al hybrid structures usually act as conductive components in the refrigeration and electric power devices rather than the load-bearing components. Cu/Al joints that possess such strength satisfy practical application. Therefore, Zn-Al filler metal and non-corrosion fluoride flux were demonstrated to be the most appropriate filler metal and flux for the Cu/Al brazing process [5,6,8].

As is well known, Zn and Zn alloy coatings have been used for corrosion protections of metal substrates over a long period of time [11]. The mechanism of the corrosion protection is sacrificial anode and cathodic protection. Zn is the sacrificial anode in the corrosion process [11]. As a result, the joint brazed with Zn base alloy is particularly susceptible to corrosion due to the activity of Zn element. Unfortunately, the devices that contain Cu/Al hybrid structures usually work in a humid environment for a long time, especially the outdoor unit [10]. Therefore, corrosion properties of these Cu/Al hybrid structures are of great importance to the reliability of the refrigeration and electric power devices [12,13]. Although copper and aluminum themselves both have excellent corrosion resistance, the Cu/Al brazed joint is always the weakest part in the hybrid structures, especially for the Cu/Al joint brazed with Zn-Al filler metals. However, few researches have been carried out to investigate the corrosion behavior of the Cu/Al joints brazed with Zn alloys [14]. No effective approach has been proposed to improve the corrosion resistance of these Cu/Al joints. Seeing that the Zn-Al alloys are the most appropriate filler metal for fabricating Cu/Al brazing joints, to explore effective anti-corrosive ways is important and it is also the requirements of economical manufacturing and sustainable development.

In our previous research, corrosion resistance of the Cu/Al joint was improved remarkably by adding a small amount of Si in the Zn-Al filler metal [15]. The brief study showed positive effects of the Si addition in the Zn-Al filler metal on the corrosion properties of the Cu/Al brazed joints. In the present paper, the effects of Si contents on the microstructure and corrosion resistance of the joints brazed with Zn-Al-xSi filler metals were investigated. Strength loss ratios, together with corrosion fracture surface and corrosion products analyses, were provided to study the corrosion mechanism and evaluate the corrosion resistance of the joints brazed with Zn-Al-xSi filler metals. Effects of Si elements on corrosion behaviors of Cu/Al dissimilar joint brazed with Zn-Al-Si filler metals were concluded.

The schematic diagram of experimental procedure is shown in Fig. 2. Pure aluminum plates (60 mm × 30 mm × 3 mm) and pure copper plates (60 mm × 20 mm × 2 mm) were employed as the base metals. Before brazing, the surfaces of the plates were polished, degreased, rinsed and coated with non-corrosion AlF₃-CsF flux. Brazing experiments were carried out with lap configuration in a muffle furnace. Brazing clearance between the base metal sheets was maintained 0.3 mm. The tip of the thermocouple was kept on the bonding area to measure the temperature. The brazing temperature was 30° higher than the measured melting points of the filler metals. Holding time of all the experimental groups was 2 min.

After brazing, the microstructure of the joint were investigated by a scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). The salt spray test was performed with a 100% humidity of a 5 wt.% NaCl solution at the temperature of 35° in CK-90 salt spray test chamber. The shear strength of brazed joints and corroded joints were examined by MTS810 universal testing machine. The KEYENCE-2000 stereoscopic microscope (SM) was used to observe the corroded brazing seam. The corrosion products on the surface of the corroded joint were collected, naturally dried and then, analyzed with an X-ray diffractometer. The shear strength of brazed joints and corroded joints were examined by MTS810 universal testing machine.

3. Results and discussion

3.1. Microstructure of brazed joint

The microstructures of the brazed joints were shown in Fig. 3. The pictures in first row exhibit the interface between brazing seam and aluminum base metal. It can be noticed that the most obvious change at the interface is the width of the diffusion layer, as marked by blue dot line. The thickness of the diffusion layer was significantly decreased with the addition of Si in the filler metals. More Si element added in the filler metal, thinner diffusion layer obtained at the Al/brazing seam interface. EDS results in Table 1 indicate that the diffusion layer is the solid solution of Zn and copper in aluminum. The second row of Fig. 3 presents the interface between brazing seam and copper base metal. A wavy intermetallic compounds (IMCs) layer was generated on the interface of all the joints as shown in the pictures. The IMCs layer in all the joints was composed of two phases, which are light gray phase next to the Cu substrate and dark gray phase close to the brazing seam, respectively. EDS results at point C, D, E and F revealed that the atomic ratios of the light gray phase and the dark gray phase were 1 and 2/3, respectively. According to the Al-Cu binary phase diagram, the light gray and dark gray phases were possibly CuAl and CuAl₂. The thickness and morphology of the IMCs layer did not change with the addition of Si in the filler metal. The third row of Fig. 3 presents the microstructure of the brazing seam. There were three kinds of phases in the joint brazed with Zn-22Al filler metal, as shown in Fig. 3(k). According to the EDS results, the dark phase was CuAl₂, the light gray phase was Al-rich Zn-Al eutectic and the bright white phase was Zn-rich Zn-Al eutectic. The brazing seams of the joints

2. Material and methods

Pure Zn, Al and Si with purity of 99.9 wt.% were melted at 750 ± 10° in a salt bath furnace to fabricate Zn-22Al (ZA0), Zn-22Al-0.5Si (ZA0.5), Zn-22Al-1.0Si (ZA1.0), Zn-22Al-1.5Si (ZA1.5) and Zn-22Al-2.0Si (ZA2.0) filler metals. Mechanical stirring was performed every 20 min in 2h melting process. The inherent melting point of the filler metals were tested by differential thermal analysis (DTA), as shown in Fig. 1.
Fig. 1 – DTA results of the filler metals with different Si contents.

Fig. 2 – Schematic diagram of experimental procedure.

Table 1 – EDS analysis results of marked points (at.%).

<table>
<thead>
<tr>
<th>Position</th>
<th>Al</th>
<th>Cu</th>
<th>Zn</th>
<th>Si</th>
<th>Possible phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>88.17</td>
<td>06.78</td>
<td>05.05</td>
<td>–</td>
<td>α-Al</td>
</tr>
<tr>
<td>B</td>
<td>89.31</td>
<td>04.31</td>
<td>05.68</td>
<td>00.70</td>
<td>α-Al</td>
</tr>
<tr>
<td>C</td>
<td>43.85</td>
<td>43.32</td>
<td>12.83</td>
<td>–</td>
<td>CuAl</td>
</tr>
<tr>
<td>D</td>
<td>55.00</td>
<td>35.96</td>
<td>09.03</td>
<td>–</td>
<td>Cu₂Al₃</td>
</tr>
<tr>
<td>E</td>
<td>42.82</td>
<td>45.73</td>
<td>10.60</td>
<td>00.85</td>
<td>CuAl</td>
</tr>
<tr>
<td>F</td>
<td>54.25</td>
<td>36.33</td>
<td>09.08</td>
<td>00.34</td>
<td>Cu₂Al₃</td>
</tr>
<tr>
<td>G</td>
<td>34.37</td>
<td>09.68</td>
<td>55.95</td>
<td>–</td>
<td>α-Al + Zn-Al eutectic</td>
</tr>
<tr>
<td>H</td>
<td>68.34</td>
<td>28.26</td>
<td>03.40</td>
<td>–</td>
<td>CuAl₂</td>
</tr>
<tr>
<td>I</td>
<td>58.92</td>
<td>07.02</td>
<td>34.06</td>
<td>–</td>
<td>α-Al + Zn-Al eutectic</td>
</tr>
<tr>
<td>J</td>
<td>65.15</td>
<td>27.99</td>
<td>06.39</td>
<td>00.48</td>
<td>CuAl₂</td>
</tr>
<tr>
<td>K</td>
<td>33.85</td>
<td>09.47</td>
<td>56.46</td>
<td>00.22</td>
<td>α-Al + Zn-Al eutectic</td>
</tr>
<tr>
<td>L</td>
<td>63.24</td>
<td>09.29</td>
<td>27.23</td>
<td>00.25</td>
<td>α-Al + Zn-Al eutectic</td>
</tr>
</tbody>
</table>
brazed with Zn-Al-Si filler metals were composed of three kinds of phases as well. However, within the Si addition range of 0.5–1.5 wt.%, the morphology of the CuAl2 phase changed significantly, as shown in Fig. 3(l), (m), (n). In the brazed seam of Zn-Al-Si joints, the CuAl2 phase smaller and more dispersed. The Zn-Al eutectic was divided into many narrow strips, especially the Zn-rich Zn-Al eutectic. With the increase of the Si addition, the effect of microstructure refinement is weakened. Excessive addition of silicon (exceeded 1.5 wt.%) resulted in the harmful growth of CuAl2 phase, as shown in Fig. 3(o).

3.2. Corrosion behaviors of Al/Cu joints

The investigation on the corrosion behaviors of Al/Cu joints was started with two aspects, i.e. exposed surface and interior of the joint. Fig. 4 shows the stereoscopic images of the brazed joints after 24 h standard salt spray test. The hypsometric topographies indicate that the addition of Si element limited the depth and size of the corrosion pit on the exposed brazing seam. The proportion of the seriously corroded area (navy blue region) in the joint brazed by Zn-22Al filler metal was obviously greater than those in the Zn-22Al-Si joint, as shown in Fig. 4(a), (b), (c), (d) and (e). The maximum corrosion pit depth in the Zn-22Al joint was 118.1 µm, about two times the maximum depth of the corrosion pit in the joints brazed with Zn-22Al-Si filler metals. The joint brazed with Zn-22Al-1.0Si filler metal presented the best pitting corrosion resistance, only a 27.1 µm deep corrosion pit was detected, as shown in Fig. 4(e). Additionally, the corrosion products were checked by X-ray diffraction (XRD) analyses. The XRD results shown in Fig. 5 indicated that the corrosion products mainly contained Zn5(OH)8Cl2H2O and Zn(OH)2. Therefore, it can be deduced that the initial position of the pit corrosion was the Zn-rich area according to the XRD results. According to the analysis of the previous section, the Zn-rich Zn-Al eutectic in the brazing seam was significantly dispersed with the addition of Si. In the Zn-22Al joint, the large amount of zinc rich phases suffered serious corrosion during the salt spray test. Corrosion products detached from the brazing seam rapidly. This resulted in the swift deepening and expansion of corrosion pits. While in the joints brazed with Zn-22Al-Si filler metals, the Zn element was in the finely broken Zn-Al eutectics that distributed at the gaps among CuAl2 phases. The Zn reaction of the corrosion was suppressed, and the depth increasing rate of the corrosion pit was reduced. Thus, the joints brazed with Zn-22Al-Si filler metals exhibited better pit corrosion resistance.

The corrosion inside the joint referred to the corrosion crack. The corrosion crack was observed at the brazing corner near Al side. Fig. 6(a–e) shows the optical microscope images of the corrosion crack after 24 h salt spray test in the brazed joints. The crack in the Zn-22Al joint was the widest, as illustrated in Fig. 6(a). It had already extended from the brazing corner to the interior of the brazing seam. Corrosion crack extending was suppressed when Si was added into the filler metals. When the mass fraction of Si in the filler metal reached 1.0%, the crack extending was remarkably slowed down, as shown in Fig. 6(c), (d) and (e). With the microstructure analysis of the corrosion crack by SEM shown in Fig. 6(f) and (g), it is not difficult to find out that the propagation of the crack was closely related with the diffusion layer on Al side. The corrosion crack initiated from the brazing corner and propagated inside the diffusion layer. Combining the SEM images Fig. 3(a–e) with the optical microscope images Fig. 6(a–e), it can be concluded that thicker diffusion layer facilitated the faster propagation of the corrosion crack. It was due to the thicker diffusion layer provided greater expansion space for the cracks [15]. At the same time, the wider cracks provided more unimpeded transport channels for corrosive media. The two aspects were complementary to each other. According to the EDS results listed in Table 1, the diffusion layer contained a small amount of Zn and Cu elements. The reason why the
corrosion crack initiated and propagated in the diffusion layer was illustrated in Fig. 6(h). Due to the huge linear expansion coefficient of the filler metal and Al substrate, the brazing seam and Al substrate shrunk drastically after brazing. The diffusion layer located between the brazing seam and Al substrate. Therefore, the diffusion layer subjected to tensile stress on both sides. Under the impact of corrosive medium, stress corrosion was generated inside the diffusion layer.

3.3. Corrosion kinetics of pit corrosion in Al/Cu joints

The corrosion kinetics the Al/Cu joints was studied with the maximum corrosion pit depth and the loss of joint strength. The maximum depth of the corrosion pit reflected the degree of the pit corrosion directly. The deepening process of the corrosion pit in the joints brazed by Zn-22Al and Zn-22Al-1.5Si were analyzed for comparison. The stereoscopic images of the Zn-22Al and Zn-22Al-Si brazed joints after standard salt spray test with different duration were shown in Figs. 7 and 8, respectively. After 72 h standard salt spray test, the maximum pit depth in the Zn-22Al brazed joint exceeded 190 μm, while that in the Zn-22Al-1.5Si brazed joint was 106 μm. The detailed maximum depth data after different period salt spray test was recorded in Fig. 9(a). The data points were fitted by the allometric growth model [16]:

$$y = a \ast t^b$$ (1)

where y was the maximum depth of the corrosion pit, t was the corrosion time, a and b were the fitting parameters. The

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**Fig. 4** – Stereoscopic images of the brazed joints after 24 h standard salt spray test: (a) Zn-22Al, (b) Zn-22Al-0.5Si, (c) Zn-22Al-1.0Si, (d) Zn-22Al-1.5Si and (e) Zn-22Al-2.0Si.

**Fig. 5** – Typical XRD results of corrosion products.
Fig. 6 – Optical microscope images of corrosion crack after 24 h salt spray test: (a) Zn-22Al, (b) Zn-22Al-0.5Si, (c) Zn-22Al-1.0Si, (d) Zn-22Al-1.5Si and (e) Zn-22Al-2.0Si and (f) Typical scanning electron microscope images of the corrosion crack after 24 h salt spray test, (g) enlarged images of the corrosion crack and (h) diagrammatic sketch of stress corrosion cracking.

Fig. 7 – Stereoscopic images of the Zn-22Al brazed joints after standard salt spray test with different duration: (a) 12 h, (b) 24 h, (c) 36 h, (d) 48 h, (e) 60 h and (f) 72 h.

Fig. 8 – Stereoscopic images of the Zn-22Al-1.5Si brazed joints after standard salt spray test with different duration: (a) 12 h, (b) 24 h, (c) 36 h, (d) 48 h, (e) 60 h and (f) 72 h.
value of the parameters was listed in Table 2. According to the results, the fitting curve equation of the Zn-22Al joint was

\[ y_1 = 30.96 t^{0.42} \]

while the fitting curve equation of the Zn-22Al-1.5Si joint was

\[ y_2 = 9.33 t^{0.57} \]

Differentiating the pit depth with respect to time:

\[ y_1' = 13 t^{-0.58} \]

\[ y_2' = 5.32 t^{-0.43} \]

Combining the stereoscopic images Fig. 7 with Fig. 8, it can be seen that the pitting area presented a sharp increase in the Zn-22Al joint. After 72 h salt spray test, the corrosion pit, which was marked by dark blue, expanded on almost half of the field.

![Fig. 9 – Maximum depth of corrosion pit in Zn-22Al and Zn-22Al-1.5Si brazed joints.](image)

Table 2 – Parameters of fitting curve for the maximum corrosion pit depth.

<table>
<thead>
<tr>
<th>Subject</th>
<th>Parameter</th>
<th>Value</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion pit depth of Al/Zn-22Al-1.5Si/Cu joint</td>
<td>a</td>
<td>9.33383</td>
<td>1.05788</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.56895</td>
<td>0.04123</td>
</tr>
<tr>
<td>Corrosion pit depth of Al/Zn-22Al/Cu joint</td>
<td>a</td>
<td>30.96133</td>
<td>9.26539</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.41563</td>
<td>0.07752</td>
</tr>
</tbody>
</table>

Table 3 – Tensile strength of joint after a certain period salt spray test.

<table>
<thead>
<tr>
<th>Corrosion period / h</th>
<th>Zn-22Al</th>
<th>Zn-22Al-0.5Si</th>
<th>Zn-22Al-1.0Si</th>
<th>Zn-22Al-1.5Si</th>
<th>Zn-22Al-2.0Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>39.63</td>
<td>39.66</td>
<td>39.92</td>
<td>41.10</td>
<td>41.16</td>
</tr>
<tr>
<td>12</td>
<td>30.47</td>
<td>30.85</td>
<td>32.53</td>
<td>35.98</td>
<td>36.42</td>
</tr>
<tr>
<td>24</td>
<td>25.08</td>
<td>26.59</td>
<td>28.04</td>
<td>30.91</td>
<td>30.55</td>
</tr>
<tr>
<td>36</td>
<td>21.21</td>
<td>23.97</td>
<td>24.38</td>
<td>27.57</td>
<td>26.27</td>
</tr>
</tbody>
</table>

While in Zn-22Al-1.5Si joint, there were some scattered small pits. It can be assumed that the joint is considered to be failed if the corrosion depth exceeds 200 \( \mu \)m. Then the Zn-22Al and Zn-22Al-1.5Si joint failed after 84.94 h and 216.45 h salt spray test, respectively. Thus, it can be determined that the Zn-22Al-1.5Si joint possessed better pit corrosion resistance than Zn-22Al joint in the early stage of surface corrosion.

3.4. Corrosion fracture failure of Al/Cu joint

The shear strength of the joints before and after salt spray tests was given in Fig. 10. It can be seen that there was not much difference between the shear strengths of the joints before salt spray test. After 36 h salt spray test, the residual shearing strength of the joints showed a distinct difference. The Zn-22Al-1.5Si joint maintained the highest residual strength (27.57 MPa), which exhibited a strength loss rate of 33% (from 41.10 MPa to 27.57 MPa), as listed in Table 3. While the strength loss rate of the Zn-22Al joint exceeded 45% (from 39.63 MPa
to 21.21 MPa. The final fracture occurred at the interface between Al substrate and the diffusion layer. The stress corrosion cracking illustrated in Fig. 6(h) was the main inducement of the fracture failure. The tip of the stress corrosion crack in the diffusion layer became the stress concentration point in the process of shearing test. The joint that possessed better stress corrosion cracking resistance exhibited higher shearing strength.

The fracture surface of the shearing test specimen was observed by SEM and presented in Fig. 11. There were some bright white area on the fracture surface of Zn-22Al joint and Zn-22Al-0.5Si joint, as shown in Fig. 11(a). Enlarged image of such area revealed that there were numerous particulate crystals on the surface. EDS results on M and O areas listed in Table 4 indicated that the particulate crystals mainly contained Zn, Cl and a large amount of O elements. Meanwhile, debris that contained Al, Zn, Cl and O elements were detected on the fracture surface of Zn-22Al joint. The content of O element exceeded 50%. Therefore, it can be known that the corrosive medium had already penetrated into the fracture surface of Zn-22Al and Zn-22Al-0.5Si joints in the corrosion process before the shearing test. While no particulate crystal was observed on the fracture surface of Zn-22Al-1.0Si, Zn-22Al-1.5Si and Zn-22Al-2.0Si joints, as shown in Fig. 11(c), (d).
and (e). The contents of Cl and O elements were much lower than that of the Zn-22Al and Zn-22Al-0.5Si joints. Thus, it can be reached that more than 1.0% additive contents of Si element in the filler metal improved the corrosion resistance of the Al/Cu brazed joint remarkably.

4. Conclusions

The addition of Si element in the novel Zn-Al-Si filler metals significantly improved the corrosion resistance from two aspects: reducing the growth rate of pit depth and slowing down the stress corrosion cracks propagation.

With the appropriate addition of Si (0.5–1.5 wt.%), the morphologies of the CuAl2 phase and Zn-Al eutectics were changed. The Zn-Al eutectics were broken and dispersed, and the reaction of Zn was suppressed. The pitting corrosion resistance of the Zn-Al-Si joints was therefore greatly improved. However, excessive addition of silicon (exceeded 1.5 wt.%) resulted in the growth of CuAl2 phase. The kinetics study indicated that the increasing rates of corrosion pit area and depth in the Zn-22Al joint were both higher than that in the Zn-22Al-Si joints.

The stress corrosion crack initiated in the diffusion layer beside Al substrate. More than 1.0% addition of Si in the filler metal decreased the thickness of the diffusion layer significantly, which suppressed the propagation of the corrosion crack. Zn-22Al-1.5Si and Zn-22Al-2.0Si joints exhibited the highest residual strength (27.57 MPa) after 36 h neutral salt spray test. No corrosion products and massive corrosive medium were detected on the fracture surface of the shearing specimen.

Integrating two aspects of corrosion behavior, the Cu/Al joint brazed with Zn-22Al-1.5Si filler metal was evaluated as the most corrosion resistant joint. In the actual production and application, the novel Zn-Al-Si filler metals are more suitable for fabricating corrosion resistant Cu/Al joints than the traditional Zn-Al filler metal. The Si content in brazing filler metals is the key for achieving satisfactory joint.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES