Effect of Cu and Mg on the corrosion behavior of 4004/Al-Mn-Cu-Mg-Si/4004 aluminum alloy brazing sheet

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Abstract. Higher strength and better corrosion resistance are necessary to enable the thickness reduction of the aluminum alloy brazing sheets. In this work, an age-hardenable Al-Mn-Cu-Mg-Si core alloy was developed by the addition of Mg, Si and Cu. The corrosion behavior of 4004/Al-Mn-Cu-Mg-Si/4004 aluminum alloy brazing sheet in sea water acidified accelerated test (SWAAT) was investigated and compared with the traditional 4004/3003/4004 aluminum alloy brazing sheet. The microstructure was characterized by optical microscopy (OM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). After brazing, it was found that the microstructures of two aluminum alloy brazing sheets from outer to the center were precipitate-free zone (PFZ), the band of dense precipitates (BDP) and core material, respectively. In particular, both Cu and Mg concentration gradients were formed in the BDP region of 4004/Al-Mn-Cu-Mg-Si/4004. Moreover, the SWAAT results showed exfoliation corrosion in 4004/Al-Mn-Cu-Mg-Si/4004, while in 4004/3003/4004, severe inter-granular corrosion in core material was observed after corrosion for 584 h. The theoretical electric potential distribution showed that the presence of Cu and Mg concentration gradient promoted the formation of the electric potential trough in the BDP region, which may be the reason for the occurrence of exfoliation corrosion in 4004/Al-Mn-Cu-Mg-Si/4004.

Keywords: 4004/Al-Mn-Cu-Mg-Si/4004, Aluminum alloy brazing sheet, Corrosion, Copper concentration gradient

1 Introduction

Aluminum alloy brazing sheets are commonly used for heat exchangers in the automotive industry, due to their high thermal conductivity, excellent mechanical properties, good corrosion resistance combined with low specific weight [1-3]. Aluminum alloy brazing sheets usually have a multilayered structure – two (or one) AA4xxx clad alloy sheets are assembled to a sandwich with an AA3xxx core alloy in between. The core alloy provides sufficient strength against deformation or collapsed while the clad alloy acts as brazing alloy to achieve a metallic bond between the components. Aiming at the reduction of the thickness, such sheets essentially require improved properties in terms of strength and corrosion resistance [3].

To achieve a higher strength of the sheet on the one hand, some methods have been developed, such as the addition of solid solution strengthening elements [4] and the formation of finely dispersed precipitates [5, 6]. Due to the fact that the brazing process is usually operated at elevated temperatures (~600 °C) for a short time (which is equivalent to the solid solution heat treatment), thus, in principle, it is possible to develop age-hardening AA3xxx core alloy to enhance the strength of aluminum alloy brazing sheets. It has been reported that the

addition of Mg and Si in AA3xxx core alloy followed by the control of cooling rate after brazing, makes it an ideal candidate for this application [7-9].

On the other hand, in order to improve corrosion performance of aluminum alloy brazing sheets, long life alloys with a Cu-containing AA3xxx core alloy, have been developed and used for many years [10-12]. In such sheets, Si atoms diffuse from the cladding into the core during the brazing process, promoting the precipitation of Mn out of solid solution in the core adjacent to the cladding and subsequently the formation of the band of dense precipitates (BDP). Simultaneously, Cu atoms in the core adjacent to the cladding also diffuse into the cladding. Due to the low solution level of Mn and Cu, the electric potential of the BDP region is lower than that of the normal core material, which produces a sacrificial layer on the rest of the core material, and finally the corrosion resistance is remarkably improved.

The aim of this work was to design an age-hardenable aluminum alloy brazing sheet with excellent corrosion resistance. The Al-Mn-Cu-Mg-Si core alloy was prepared by adding Mg, Si and Cu to a traditional 3003 aluminum alloy. The corrosion behavior of 4004/Al-Mn-Cu-Mg-Si/4004 aluminum alloy brazing sheet in sea water acetic acid test (SWAAT) was investigated and compared with the traditional

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4004/3003/4004. Based on the results, we intend to contribute to the understanding of the corrosion mechanism involved.

2 Experimental

2.1 Material preparation

The investigated sheets with the size of approximately 100 mm×60 mm were cut from a rolled sheet consisting of an Al-Mn-Cu-Mg-Si core alloy (~2 mm thick) and two AA4004 clad alloy (~0.25 mm thick). The comparative material includes slightly thinner sheets, i.e. ~1.7 mm for AA3003 core alloy and ~0.15 mm for AA4004 clad alloy. The chemical compositions were shown in Table 1. The brazing experiment was conducted at 610 °C for 15 min in a vacuum brazing furnace, furnace cooled to 400 °C and then air cooled to room temperature.

2.2 Corrosion test

The corrosion properties of two aluminum alloy brazing sheets were evaluated by the sea water acidified accelerated test (SWAAT). The SWAAT was conducted in a cyclic corrosion test chamber (Ascott, CC450ip) according to the ASTM G85 A3 standard. The electrolyte was synthetic seawater (ASTM D1141), acidified at 49 °C to a pH of 2.8 using acetic acid. The corrosion tests took 64~584 h, depending on the experiments.

2.3 Characterization analysis

After brazing, the cross-sectional microstructures of two aluminum alloy brazing sheets were analysed using optical microscopy (OM) and scanning electron microscopy (SEM) with backscatter electron (BSE) imaging. Element line analysis on the cross-sections has also been performed by means of electron probe microanalysis (EPMA) on a Shimadzu EPMA-1720 system. After SWAAT, the surface and the cross-sectional corrosion morphologies of the sheets were investigated by OM.

3 Results and Discussion

3.1 Microstructure

The cross-sectional microstructures after brazing are shown in Fig. 1. It is found that large precipitation-free α -Al grains, i.e. precipitate-free zone (PFZ), are formed on the surface of two aluminum alloy brazing sheets due to the liquid film migration [11, 12]. The average thicknesses of PFZs in 4004/Al-Mn-Cu-Mg-Si/4004 and 4004/3003/4004 aluminum alloy brazing sheets are ~139 and ~51 μ m, respectively. These α -Al grain boundaries, however, provide fast-diffusion paths for the solutes during the brazing process, leading to the formation of needle-like Si phases along the boundaries, as shown in the inset of Fig. 1. Besides, no BDP region can be observed beneath the PFZ region, as shown in Fig. 1.

Fig. 2 shows the microstructure of core material adjacent to and away from the PFZ region, respectively. It is obvious that large numbers of finely dispersed precipitates are present in the core material of two aluminum alloy brazing sheets. The statistical data shows that, for 4004/Al-Mn-Cu-Mg-Si/4004, the number densities of finely dispersed precipitates in core material adjacent to and away from the PFZ region are $\sim 1.92 \times 10^6$ and $\sim 1.67 \times 10^6$ mm⁻², respectively; while for 4004/3003/4004, they are $\sim 1.20 \times 10^6$ and $\sim 0.55 \times 10^6$ mm⁻², respectively. Hence, the number density of finely dispersed precipitates is higher in core material adjacent to the PFZ region than that away from the PFZ region in both cases. This phenomenon is due to the in-diffusion of Si from the cladding to the core material and the subsequent precipitation of densely-distributed dispersoids. BDP region can hardly be observed in Fig. 1, but BSE images provide more evidences, see the BDP region beneath the PFZ region as shown in Fig. 2. In addition, due to the higher Si content, more precipitates are observed in the core material of 4004/Al-Mn-Cu-Mg-Si/4004 than 4004/3003/4004 – in accordance with H. Ahmed et.al [10].

Based on the above, it can be found that the microstructures of two aluminum alloy brazing sheets from outer to the center after brazing are both precipitate-free zone (PFZ), the band of dense precipitates (BDP) and core material, respectively.

3.2 Corrosion behavior

Fig. 3 shows the macroscopic surface morphologies of two aluminum alloy brazing sheets after SWAAT for 64, 288 and 584 h, respectively. As shown in Figs. 3a, b, at the initial stage of corrosion (64 h), more corrosion pits are found on the 4004/Al-Mn-Cu-Mg-Si/4004, compared with 4004/3003/4004. When corrosion proceeds (288 h),

Table 1. Chemical compositions (wt.%) of the alloys investigated

Alloy	Mn	Si	Fe	Mg	Cu	Ti	Al
Al-Mn-Cu-Mg-Si	1.1-1.5	0.3-0.8	0.1-0.6	0.3-0.8	0.3-0.8	0.01-0.05	balance
AA4004	-	8-10	0.1-0.3	1.0-1.6	-	0.010	balance
AA3003	1.116	0.060	0.503	0.002	0.070	0.024	balance

Fig. 1. Cross-sectional morphologies of (a) 4004/Al-Mn-Cu-Mg-Si/4004 and (b) 4004/3003/4004 aluminum alloy brazing sheets after brazing

Fig. 2. BSE images of core material (a, b) adjacent to and (c, d) away from PFZ region: (a, c) 4004/Al-Mn-Cu-Mg-Si/4004 and (b, d) 4004/3003/4004 aluminum alloy brazing sheets

local exfoliation is observed on the surface of 4004/Al-Mn-Cu-Mg-Si/4004, while crater-like corrosion pits are present on the surface of 4004/3003/4004, see in Figs. 3c, d. As the corrosion time further increases to 584 h, the area of exfoliation increases significantly on the surface of 4004/Al-Mn-Cu-Mg-Si/4004, Fig. 3e. Meanwhile, the area of crater-like corrosion pits also increases on the surface of 4004/3003/4004, Fig. 3f.

Fig. 4 displays the cross-sectional morphologies of 4004/Al-Mn-Cu-Mg-Si/4004 and 4004/3003/4004 aluminum alloy brazing sheets after corrosion. At the initial stage of corrosion (64 h), the corrosion quickly goes along primary α -Al grain boundaries and reaches the core material of two aluminum alloy brazing sheets, as shown in Figs. 4a, d. After 288 h of corrosion, the PFZ region is gradually peeled away from the core material of 4004/Al-Mn-Cu-Mg-Si/4004, see in Fig. 4b, while for 4004/3003/4004, the corrosion directly spreads into the core material and the corrosion depth reaches ~ 800 μm , as shown in Fig. 4e. After 584 h of corrosion, the PFZ region continues to be peeled away, and the corrosion in depth direction (the sheet thickness direction) is still not found in 4004/Al-Mn-Cu-Mg-

Si/4004, as shown in Fig. 4c. In contrast, the corrosion depth further increases in 4004/3003/4004 and the maximum depth reaches ~ 1150 μm , as shown in Fig. 4f. High magnification OM image in Fig. 4f also reveals that the corrosion of core material in 4004/3003/4004 is in the form of inter-granular corrosion (IGC). Therefore, 4004/Al-Mn-Cu-Mg-Si/4004 aluminum alloy brazing sheet developed in this work presents a different form of corrosion in comparison with 4004/3003/4004.

3.3 The corrosion mechanism

The above SWAAT results show that the corrosion behaviors of 4004/Al-Mn-Cu-Mg-Si/4004 and 4004/3003/4004 aluminum alloy brazing sheets are entirely different – the former demonstrates typical exfoliation corrosion while the latter rather shows IGC. The corrosion behavior usually depends on various factors, such as the distribution of alloying elements, grain size, the nature and morphology of precipitates. In this work, we focus on the effect of alloying element distribution on corrosion behavior.

During the brazing process, the diffusion of solutes

Fig. 3. Macroscopic surface morphologies of (a, c, e) 4004/Al-Mn-Cu-Mg-Si/4004 and (b, d, f) 4004/3003/4004 aluminum alloy brazing sheets after corrosion for (a, b) 64, (c, d) 288 and (e, f) 584 h

Fig. 4. Cross-sectional morphologies of (a-c) 4004/Al-Mn-Cu-Mg-Si/4004 and (d-f) 4004/3003/4004 aluminum alloy brazing sheets after corrosion for (a, d) 68, (b, e) 288 and (c, f) 584 h

determines the distribution of the alloying elements in the aluminum alloy brazing sheet. The electric potential of such an alloy, however, mainly depends on the type and the concentration of the alloying element in the solid solution. For AA3xxx, the electric potential can be theoretically estimated as follows [12-14]:

$$E(mV) = -755 + 54 \times [Mn] + 48 \times [Cu] + 20 \times [Si] - 12 \times [Mg] \quad (1)$$

where $[M]$ is the alloying element concentration in solid solution. According to Eq. (1), and except for Mg, a higher Mn, Cu and Si content leads to a higher E . Hence, the diffusion of alloying elements during brazing may cause the formation of electric potential difference

between different regions. It has been reported that when the electric potential of the BDP region is lower than that of the core material, the exfoliation corrosion will set in [4].

To demonstrate the effect of alloying element concentration on the corrosion properties, the EPMA line analysis of Mn, Si, Cu and Mg in the cross-sections of 4004/Al-Mn-Cu-Mg-Si/4004 and 4004/3003/4004 aluminum alloy brazing sheets after brazing is given in Fig. 5. As shown in Figs. 5a, b, the Mn concentration profiles of two aluminum alloy brazing sheets show that the Mn content in the core material and BDP region is almost the same. There is no obvious difference in the Mn concentration profile between two sheets. In Figs.

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5c, d, the Si concentration profile is very similar between

Fig. 5. EPMA line analysis of Mn, Si, Cu and Mg in (a, c, e, g) 4004/Al-Mn-Cu-Mg-Si/4004 and (b, d, f, h) 4004/3003/4004 aluminum alloy brazing sheets after brazing

two sheets, and the enrichment of Si is both observed in the BDP and PFZ regions. Due to the out-diffusion, both Cu and Mg concentration gradients are formed in the BDP region of 4004/Al-Mn-Cu-Mg-Si/4004 (Figs. 5e, g). In contrast, neither Cu nor Mg concentration gradient can be observed in 4004/3003/4004, due to the low Cu and Mg in the core material (Fig. 5f, h).

In Fig. 6, the theoretical electric potential distribution in the cross section of two aluminum alloy brazing sheets is calculated based on the EPMA measurement of the alloying element concentration in solid solution and Eq. (1). It is shown that a distinct potential trough is formed in the BDP region of 4004/Al-Mn-Cu-Mg-Si/4004, as indicated by the arrow in Fig. 6. Usually, the

corrosion preferentially happens in the adjacent zone with lower electric potential. Therefore, when the corrosion reaches this potential trough, the corrosion in depth direction is likely to be retarded, and finally the exfoliation corrosion occurs, as shown in Figs. 4a-c. Such a trough, however, cannot be found in the case of 4004/3003/4004, and Fig. 4f shows only IGC regions in the core material. Moreover, it appears that the Mn and Si concentration profiles are almost same in two aluminum brazing sheets, as shown in Figs. 5a-d. Hence, the electric potential distribution difference probably correlates with the distribution of Cu and Mg.

Fig. 6. Theoretical electric potential distribution in the cross section of 4004/Al-Mn-Cu-Mg-Si/4004 and 4004/3003/4004 aluminum alloy brazing sheets

4 Conclusions

(1) After brazing, the microstructures of 4004/Al-Mn-Cu-Mg-Si/4004 and 4004/3003/4004 aluminum alloy brazing sheets from outer to the center were both primary α -Al (PFZ), the band of dense precipitates (BDP) and core material, respectively. Meanwhile, both Cu and Mg concentration gradients were formed in the BDP regions of 4004/Al-Mn-Cu-Mg-Si/4004.

(2) The SWAAT results showed that 4004/Al-Mn-Cu-Mg-Si/4004 presented a different form of corrosion in comparison with 4004/3003/4004. The former showed typical exfoliation corrosion, while the latter showed rather IGC in the core material.

(3) The theoretical electric potential distribution showed that the presence of Cu and Mg concentration gradient promoted the formation of the electric potential trough in the BDP region, which may be the reason for the occurrence of exfoliation corrosion in 4004/Al-Mn-Cu-Mg-Si/4004.

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