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Study on the Microstructure and Wettability of an Al-Cu-Si Braze Containing Small Amounts of Rare Earth Erbium

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The effect of adding small amounts of rare earth Er on the microstructure of an Al-Cu-Si braze alloy has been investigated. Several Al-20Cu-7Si braze alloys containing various contents of Er were prepared, and their melting temperature, microstructure, hardness, and wettability in contact with 3003 aluminum alloy substrates were determined. The results indicate that the constituents of the microstructure of Al-20Cu-7Si-Er braze alloys are similar to those in the Al-20Cu-7Si alloy, and comprise of solid solutions of aluminum, silicon, and the intermetallic compound $CuAl_2$. When the Er content increases, the size of the Al phase decreases, and the needle-like Si phase is thickened, and transformed to a blocky shape. Moreover, small amounts of Er can improve the wettability and hardness of the Al-20Cu-7Si braze alloy; however, the melting temperature of the Al-20Cu-7Si alloy does not change.

Keywords Al-Si-Cu, braze, erbium, microstructure, rare earth

1. Introduction

Joining technology of aluminum alloys is important in industrial application. Among a variety of technologies, brazing has been considered to be a reliable method for the joining of aluminum components, wherein a eutectic Al-12Si (wt.%) alloy is recognized as the most popular filler metal. The addition of copper depresses the melting point of Al-Si alloys. However, the concentration of copper, which is needed to maintain a narrow melting range, is sufficient to generate a large volume fraction of the hard $CuAl_2$ intermetallic compound (IMC). This makes the alloy brittle, and even unusable as a braze. Recently many efforts have been done for developing new low-melting-point aluminum brazes. For example, small amounts of Ni, Ag, or Sn have been introduced in the Al-Cu-Si system to form quaternary alloys (Ref 1, 2).

It is well known that the rare earth (RE) elements are surface-active and aid refinement of microstructure and metamorphosis of inclusions (Ref 3-7). The effect of RE addition on brazing filler metals has been recently investigated. Wang et al. (Ref 8) found that the strength of vacuum-brazed joints can be increased for the 6061 aluminum alloy, when Al-Si based filler metal was doped with La and Ce. Dong et al. (Ref 9) found that small amount of rare earth Y and Ce additions can refine the grain size of the Al-Cu-Si-Zn brazing filler alloy. At the same time, minute additions of the RE elements can increase the strength and corrosion resistance of the brazed joints. When the CsF-AlF_3 noncorrosive flux was utilized to remove the complex oxide film from the surface of 2024 aluminum alloy, it was found that the RE element La at small percentages was not enriched at the interface, and the RE fluoride enhanced the dissolution of the oxide film (Ref 10). In the present work, the focus is on the effect of the RE element Er on the microstructure of an Al-Cu-Si brazing filler metal.

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2. Experimental

Pure Al and Cu metals with purity of 99.9 wt.% and 99.99 wt.%, respectively, were used as raw materials. Al-11.8Si (wt.%) and Al-6.2Er (wt.%) were used as master alloys. A series of Al-20Cu-7Si (wt.%) alloys with various contents of Er were prepared by melting in alumina crucibles equipped with an air furnace. The Al-Si alloy was melted at 800 °C. Then, Al and Cu were added into the molten aluminum alloy. After melting, Al-Er alloy was added. The melt was mechanically stirred by manual operation for 40 min for homogenization. The stirring operation was intermittently conducted. A eutectic salt of KCl and LiCl (1.3:1 ratio by weight) covered the surface of the liquid braze to protect the melt from oxidation. The melted braze was chill cast into a rod in a steel mold of 15 mm internal diameter. The investigated brazes are listed in Table 1.

The melting temperature was measured from the cooling curves with the help of a NiCr/NiSi thermocouple during solidification with slow cooling. The electromotive force versus time was recorded and pure Al (99.9 wt.%) was used for calibration. The microstructure was observed with an OLYMPUS PMG3 optical microscopy and a FEI QUANTA200 scanning electron microscope (SEM) after metallographic preparation and etching in a mixture of 1 vol.% HF, 1.5 vol.% HCl, 2.5 vol.% HNO_3, and 95 vol.% H_2O at room temperature for 15 s. The phases observed were identified with energy dispersive x-ray analysis.

In spreading test, the substrate was a Chinese LF 21 aluminum alloy (3003 Al alloy in the US) sheet with dimension of 40 mm × 40 mm × 1.5 mm. The solidus and liquidus temperature of the 3003 Al alloy is 643 and 654 °C, respectively. Brazing temperature is usually 30-40 °C lower than the solidus temperature of the brazed alloy at least, thus the spreading test was carried out in a SK-4-10 tube resistance furnace at 575 °C for 7 min. It is well known that spreading area increases with brazing temperature. At higher temperature, the spreading will obviously be quite high. In this test, the brazing temperature was 68 °C below the solidus temperature of 3003 Al alloy substrate. In the test, a small braze ball (0.15 g weight) was used. An activated flux QJ201 was adopted, which consisted of 32 wt.% LiCl, 50 wt.% KCl, 10 wt.% NaF, and 8 wt.% $ZnCl_2$. After testing, the specimen was cleaned with acetone to remove the residue. The specimen was scanned into a computer along with a reference sample of known area. The spreading area of the braze was calculated through the function of "inquire" in AUTOCAD software. All the test results were an average of three specimens. The Vickers hardness measurement was taken under a 1000 g load for 15 s using a HXD 1000 hardness tester.

Table 1 Series of investigated brazing alloys

Braze series	1	2	3	4	5	6
Er (wt.%)	0	0.025	0.05	0.1	0.25	0.5
Initial alloy	Al-20Cu-7Si*					

*The percentage of Al, Cu, and Si is calculated by 73:20:7 after adding RE

3. Results and Discussion

Microstructure is observed on cross section of specimens for the spreading test. The microstructure is mainly comprised of solid solutions of aluminum, silicon, and the intermetallic compound $CuAl_2$. Figure 1 shows the microstructure of Al-20Cu-7Si brazed alloys with different amounts of Er.

It can be seen that the constituents of the microstructure of Al-20Cu-7Si-Er braze alloys are similar to those in the Al-20Cu-7Si alloy. However, small additions of Er seem to modify the microstructure of the alloys. With the increase in Er addition, the needle-like Si phase is thickened and transformed to a blocky shape. At the same time, the size of the Al phase is decreased with the increase in Er addition. Er may affect the structure in two ways: (1) formation of the IMC Al_3Er may offer preferred sites for nucleation, and refinement of grains; and (2) Er can refine the grain size and change the shape of Si phase due to the decrease of surface tension.

In this investigation the RE compound phase begins to appear in the microstructure of the Al-20Cu-7Si braze alloy at 0.5 wt.% Er (Fig. 2). The RE phase mainly consists of complex RE compounds, such as Al_3Er. Although the RE containing phase appears very locally in this investigation, the excessive addition of RE element in aluminum alloy is recognized to be harmful. Because the RE phases are hard and distribute nonuniformly, the excessive addition of RE may deteriorate the ductility of aluminum alloys. Similar result was found in a Sn-based alloy experiment (Ref 11).

The RE addition may affect wetting behavior of the brazing alloy in addition to modifying the alloy microstructure. Wettability is important for successful brazing. The wettability test results are shown in Fig. 3. In the tests, the spreading area

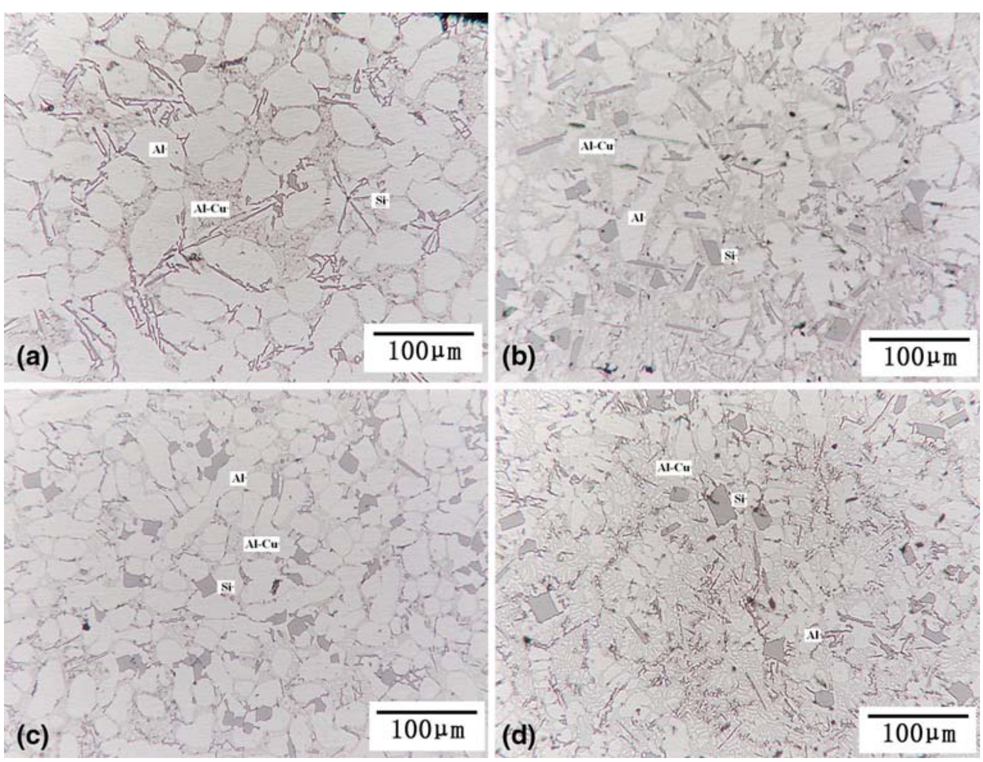

Fig. 1 Microstructure of Al-20Cu-7Si braze alloys with different amounts of Er (a) 0.025 wt.% Er; (b) 0.05 wt.% Er; (c) 0.1 wt.% Er; (d) 0.5 wt.% Er

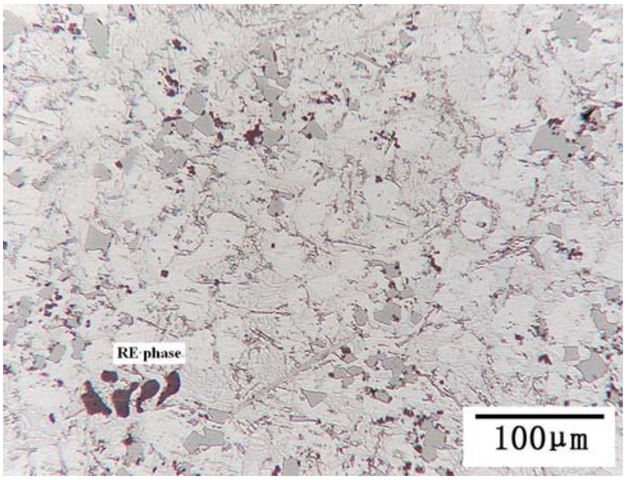

Fig. 2 RE phase in the Al-20Cu-7Si-0.5Er brazed alloy

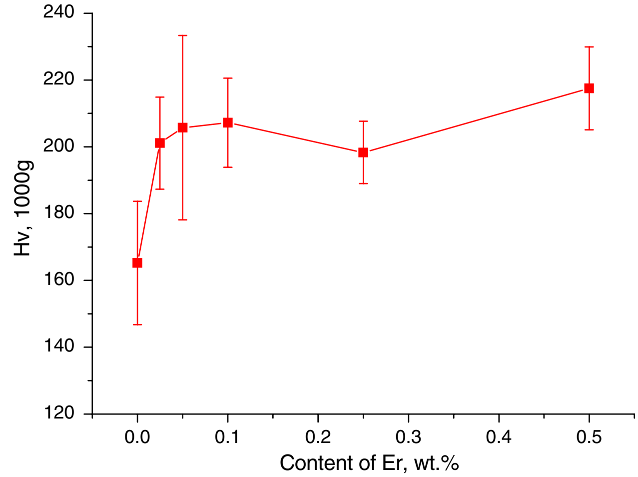

Fig. 4 Effect of Er addition on hardness of the Al-20Cu-7Si braze alloy

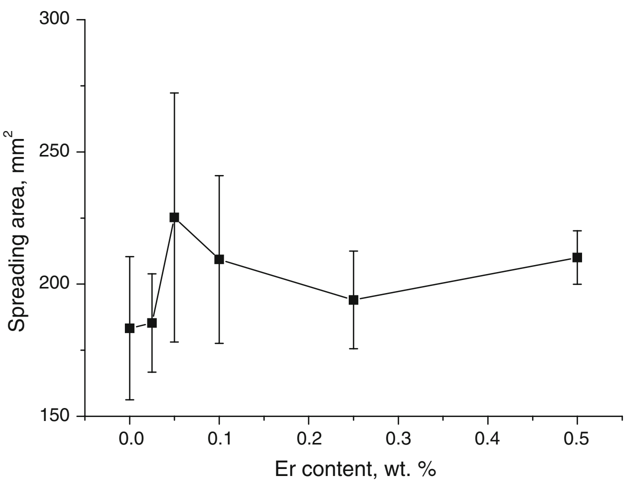

Fig. 3 Effect of Er content on spreading area

of the Al-20Cu-7Si-0.05Er brazing alloy is 225.2 ± 18.6 mm^2, which is 23% larger than that of Al-20Cu-7Si brazing alloy (area: 183.3 ± 27.2 mm^2). This improvement in wettability is due to the lowering of surface tension of liquid braze by Er. Moreover, spreading of braze may be enhanced, if it possesses a highly refined grain size (Ref 1, 12). Similar results indicated that a pre-crystallined NiCrBSi braze with rather fine grain size increased the fluidity compared to the conventional NiCrBSi braze, because the melting of the pre-crystallined braze was more homogeneous (Ref 13). The fine grain structure helps promote uniform and rapid melting as the temperature of the braze is raised because the discrete phases are finely divided and the alloy tends toward homogeneity. However, RE elements are prone to oxidation, which may lessen the wetting. Thus, with further increase in RE content, the disadvantage of the oxide residue may exceed the favorable effect of the RE. Actually, it is suggested from the test results that the appropriate addition of rare earth Er should not be larger than 0.1 wt.%.

The test results indicate that the liquidus and solidus temperatures are 537 and 525 °C, respectively, for the Al-20Cu-7Si alloy. If 0.05 wt.% Er is added in the Al-20Cu-7Si alloy, the liquidus temperature and solidus temperature drop to 536 and 524 °C, respectively. If excessive additions of RE element are made in the Al-20Cu-7Si alloy, the liquidus and solidus temperatures will rise up to 539 and 528 °C, respectively. It should be mentioned that the error of temperature measurement is less than ± 1 °C. Thus, it is expected that the small amount of Er addition will not increase the melting temperature of the Al-20Cu-7Si brazing alloy. The change of solidus temperature of Al-20Cu-7Si braze alloy is < 3 °C for < 0.5 wt.% of Er. The melting temperature will be unchanged at about 0.1 wt.% Er.

The effect of Er addition on hardness of the Al-20Cu-7Si brazing alloy is shown in Fig. 4. It is clear that a small amount of Er addition remarkably increases the hardness of the braze alloy. The hardness curve shows a typical trend of initial rise up to 0.1 wt.% RE, then slight drop for 0.25 wt.% RE and then rise again. The excessive addition of RE element leads to the formation of a complex RE phase. Thus, it is unnecessary to go beyond 0.5 wt.% RE for the test aluminum alloys. Previous research indicated that the metastable solid solubility of Er in aluminum can reach 7.5 at.% under rapid solidification (Ref 14). However, the cooling rate is slow under the condition of brazing in furnace. The Al-Er binary phase diagram (Ref 15) shows that the solid solution of Er in aluminum matrix is limited at ambient temperature, although the atomic radius of Er (0.1757 nm) is smaller than that of most of RE elements, and is 23% larger than that of Al (0.1432 nm). In addition, the electronegativity of Er and Al are 1.2, and 1.5, respectively, and their electronegativity difference is small. Thus, the rare earth Er makes almost no solid solution strengthening contribution to the Al-20Cu-7Si brazing alloy. The increase in hardness is mainly caused by the refinement of the microstructure and the strengthening of dispersed Al_3Er particles, when Er is added.

4. Conclusions

In present work, the effect of RE addition on microstructure of Al-20Cu-7Si braze alloy is investigated and the results are summarized as follows:

- The constituents of the microstructure of Al-20Cu-7Si-Er braze alloy are similar to those in the Al-20Cu-7Si alloy, which is mainly comprised of solid solutions of aluminum, silicon, and the intermetallic compound $CuAl_2$.
- Minute amounts of Er addition obviously modify the size and shape of the phase constituents. When the Er content increases, the size of Al phases is decreased, and the needle-like Si phase is thickened and transformed to a blocky shape.
- Adding a small amount of Er can improve the wettability and hardness of the Al-20Cu-7Si brazing alloy. However, the melting temperature of the Al-20Cu-7Si alloy is not changed, when trace amount of Er is added.

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