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First conductive atomic force microscopy investigation on the oxide-film removal mechanism by chloride fluxes in aluminum brazing

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ABSTRACT

In the paper, conductive atomic force microscopy (CAFM) technique was used, for the first time, to obtain direct evidence of oxide-film removal during fluxing, *via* measuring the electrical conductivity of aluminum sample surfaces. The CAFM results show that the F^- ions from the flux loosened the film, forming micro cracks on the oxide film. Subsequently, the Zn^{2+} ions permeated into the film through the cracks and chemically reacted with the aluminum substrate, destroying the bonding between the oxide layer and the aluminum substrate. These important findings pave the way for developing Cl-free environment-friendly fluxes for industrial applications.

Aluminum (Al) and its alloys have been widely used in automotive, aerospace and construction industries, because of their low density and high strength-to-weight ratio [1]. Brazing has been an efficient and inexpensive joining method for Al alloys, providing strong and consistent joints. Moreover, brazing can be also used to join dissimilar materials (including metals to ceramics), which cannot be joined by traditional fusion welding processes due to metallurgical incompatibilities between many materials [2].

Under normal atmosphere, any exposed surface of an Al alloy is always covered by a continuous and dense oxide film, which is chemically stable and liable to reproduce if any fresh surface is exposed in air. In order to make a strong bond with such an Al alloy, one needs to keep its surface free of oxide [3]. When an Al alloy is brazed, fluxes are used to remove the oxide film, which cannot only prevent reoxidation by coating the surface, but also assists the wetting between the base metal and the molten filler metal [4]. Thus, fluxing is an essential step in Al brazing.

Chloride fluxes have been widely used in Al-alloy brazing owing to their low melting points and easy application to varieties of Al alloys. Terrill et al. reported that the oxide film was not dissolved in molten chloride flux in brazing [5], while other reports maintained that the oxide film is electrochemically dissolved during brazing [6]. Zhang et

al. [7–10] investigated the role of each constituent compound in chloride fluxes on pure aluminum surfaces during brazing. They proposed that the surface alumina film caused cracks during the heating process, due to the differences of thermal expansion coefficients between the Al and its oxide film. Then, the molten flux permeated the film through the cracks and chemically reacted with the Al substrate, destroying the bond between the oxide film and Al substrate. Finally, the molten filler metal pushed in and removed the film. Xiao et al. [4,11] found that the addition of activator in chloride flux, such as $ZnCl_2$ or ZrF_4, into $CsF-AlF_3$ flux can remove the oxide film on the surface of 5000-series Al alloys effectively. However, the film-removal mechanism of chloride fluxes has not been very clear, since it is difficult to detect whether the oxide films (typically about 5 nm [12]) have been removed during brazing due to the instrumental limitations.

Additionally, commercial chloride-based fluxes contain many constituents, such as molten salt mixture and alkali metal fluorides. The role of each constituent plays during fluxing is not very clear to this date, and some of them need to be removed/substituted due to toxicity and corrosion concerns. Therefore, there is a pressing need to clearly understand the role of each constituent in oxide-film mechanism during fluxing, to develop more effective and more environment-friendly fluxes for brazing and bimetallic casting [3] applications.

Conductive atomic force microscopy (CAFM) is a powerful tool, firstly developed in 1993, to study the local tunneling currents through 12 nm thick SiO_2 films [13]. This research was aimed to reveal the oxide-film removal mechanism during chloride flux, using *in-situ* CAFM technique, for the first time. The electrical conductivity of the

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aluminum samples treated with chloride fluxes was measured by *in-situ* CAFM, to detect the oxide-film during fluxing. Because the electrical resistivity of Al substrates is relatively low (27.8 nΩ m at 20 °C) and that of Al_2O_3 layer ($>10^{12}$ Ω m) is far higher than the substrate [12], the surface oxide-film thickness and distribution can be determined from the current maps obtained by CAFM. In short, the CAFM results can provide new insights into the oxide-film removal mechanism.

Molten salt mixture of KCl-LiCl eutectic flux matrix, and alkali metal fluoride LiF and surfactant $ZnCl_2$, were selected in this investigation. Commercial aluminum fluxes generally contain more types of surfactant (such as $CdCl_2$ and TlCl) to meet the complex production requirements [15]. The matrix acts as the carrier of chloride flux, and provides appropriate melting point for the flux. According to the KCl-LiCl binary phase diagram [14], the LiCl-KCl eutectic molten salt is composed of 59.2 mol% LiCl and 40.8 mol% KCl. Chloride fluxes were prepared by melting method and the solidified products were ground in a planetary ball mill.

The base metal used in this work was commercial 1060 Al alloy. Test specimens of 15 mm × 15 mm × 3 mm were machined and mechanically ground flat on 200 to 800 abrasive papers and polished using a suspension of 0.05 μm Al_2O_3 in water. Specimens were then ultrasonically cleaned in acetone. Then the polished specimens were electropolished in perchloric acid/ethanol (1:9). After electropolishing, the specimens were cleaned in ethanol and dried in air. Finally, the cleaned samples were heated in an electric resistance furnace for 3 h at 300 °C in for oxide analysis.

It is reported [6] that the role of alkali metal fluoride in the flux was disrupting the oxide film, while the surfactant is used to remove the film and improve the wettability between the filler metals and the Al surface during brazing. However, no direct evidence of oxide removal has been reported to this date. To understand the precise mechanism of oxide-film removal in 1060 Al alloy, we probed into the effects of heating, flux matrix LiCl-KCl, F^- ions, heavy metal Zn^{2+} ions on the oxide film during brazing, respectively. The experiments were carried out as follows.

1) To determine the effects of heating and flux matrix on the alumina film during brazing, the KCl-LiCl eutectic flux matrix was melted in a porcelain crucible at 600 °C, then the Al specimens were immersed in the matrix for 180 s. After the immersion, the samples were rinsed in deionized water and ethanol successively and, finally, dried in air.

2) 5 wt% and 10 wt% LiF was added to the flux matrix, respectively, to identify the effects of alkali metal fluoride on the alumina film. Then the Al specimens were immersed in the flux for 10–120 s at 600 °C, followed by rinsing in deionized water and ethanol and drying in air.

3) $ZnCl_2$-containing fluxes were prepared by adding 10 wt% and 20 wt% $ZnCl_2$ to the KCl-LiCl matrix to determine the effect of heavy metal ions. Then the specimens were immersed in the fluxes for 10–120 s at 600 °C. The specimens were subsequently cleaned and dried.

4) The effects of chloride flux containing both alkali metal fluoride and heavy metal ions on the aluminum oxide film were also investigated. The flux containing 5 wt% LiF and 10 wt% $ZnCl_2$ was used in immersion experiments of similar procedures as above.

The surface microstructure of the 1060 Al-alloy specimens after electropolishing and flux treatment was observed using a MR2000 optical microscope (OM), a SIRION200 scanning electron microscope (SEM) and a JXA-8230 electron probe micro-analysis (EPMA) equipped with an energy dispersive spectroscope (EDS). For *in-situ* investigation of the surface morphology and electrical conductivity of the specimens, a Bruker Dimension Icon atomic force microscopy (AFM) equipped with a conductive module (CAFM) was used. The CAFM measurements were performed in a contact mode under ambient conditions, employing Cr/Pt coated Si probes on both sides. The bias applied to the tip was 10 V in all CAFM current-map measurements. Based on

the observations and test results, the oxide-film removal mechanism by chloride flux is discussed as follows.

The natural alumina layer is continuous and dense on the Al alloy specimens. Even if the oxide layer is removed by any mechanical or chemical method, it is liable to regenerate in air in presence of oxygen. But the thickness of the film is different between the fresh film and the initial one. Because of the huge differences in electrical resistivity between Al and Al_2O_3, the current maps, reflecting surface oxide-film thickness and distribution, can vary as the scanning tips contacting with certain area of the samples during CAFM measurements. The regions where the oxide film has been removed by chloride flux will exhibit higher electrical conductivity and *vice versa*.

As seen in the Fig. 1(a), the surface of initial 1060 Al-alloy sample exhibited no electrical conductivity in CAFM current map due to the dense and thick initial oxide film. In Fig. 1(b), the surface morphology and CAFM current map showed no apparent changes after the heating and immersion in KCl-LiCl solution at 600 °C for 180 s, suggesting that the heating and the immersion in matrix had no obvious effect on alumina film.

As seen in the Figs. 2(a) and (b), some dark gray and light gray areas are present on the Al surfaces after treatments with chloride flux containing 5 wt% LiF for 30 s and 120 s, respectively. The grain boundaries were clearly visible. Since chloride is easily soluble in water, the chloride flux residues on the Al specimens were removed after washing in deionized water. Because Li^+ in LiCl-KCl matrix did not react with the oxide film (Fig. 1), the variation of the surface morphologies can be attributed to F^- ions. Figs. 2(c) and (d) show the CAFM measurements on samples after the flux treatment for different times, with the red reticles marked as the regions of CAFM measurements. Compared to Fig. 1(b), some high conductive spots (displayed as white) were present in the current maps, suggesting that the F^- ions locally has destroyed the oxide film. The conductivities in the current maps with different flux immersion times had no apparent differences. This is consistent with the literature [8]. The alumina film is not dissolved into the chloride flux by the action of alkali metal fluorides during brazing.

The X-ray diffraction (XRD) analysis was used to study the function of F^- in detail. It is reported [10,16] that the oxide film on aluminum surface is crystalline γ-Al_2O_3 at higher temperatures (933 K> T > 573 K). Thus, γ-Al_2O_3 powder was used in the XRD analysis. Fig. 2(e) shows XRD patterns of γ-Al_2O_3, and after immersion in LiCl-KCl flux matrix, and LiCl-KCl matrix containing 10 wt% LiF, respectively. The immersion products were rinsed in deionized water and dried before XRD analysis. Compared to patterns ① and ②, the XRD pattern of γ-Al_2O_3 powder after LiCl-KCl matrix treatment had no apparent change from the initial state. Since all constituent compounds in chloride flux were in ion state at 600 °C, suggesting that the Li^+, K^+ and Cl^- could not change the γ-Al_2O_3 structure. Compared to patterns ② and ③, the XRD pattern of γ-Al_2O_3 powder was changed after the addition of F^- to the flux matrix, and the degree of crystallinity of γ-Al_2O_3 was increased. More importantly, the diffraction peak of γ-Al_2O_3 (440) crystal face has shifted to a low-angle region by about 0.3°, indicating distortions of the γ-Al_2O_3 lattice. The F^- ions from the flux can be absorbed into the interstitial sites of alumina film crystal lattice during brazing, because of the relatively small radius of F^- ions, resulting into some lattice distortions in the adjacent lattice sites. Finally, these lattice distortions can loosen the film and cause local cracks in some stress concentration areas on the oxide-film surface.

Figs. 3(a) and (b) show the surface morphology of 1060 Al alloy after 60 s reactions with chloride fluxes containing 10 wt% and 20 wt% $ZnCl_2$, respectively. According to literature [8], when aluminum specimens were immersed in a chloride flux, molten $ZnCl_2$ would gradually permeate into the oxide film through the grain boundary and expend toward the interior of grains. Then $ZnCl_2$ would react with the Al substrate