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Interfacial reactions in alumina/CuAgTi braze/CuNi system

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Abstract

The objective of this study is to investigate experimentally the reactions occurring at the solid/liquid interfaces of alumina/molten CuAgTi/CuNi system in high vacuum and the effect of temperature on these reactions.

Keywords: Brazing; Adhesion; Reactivity; Alumina; CuNi alloy

1. Introduction

The standard industrial process to braze alumina to itself or to metallic solids involves Mo–Mn metallization and subsequent Ni plating of alumina surfaces prior to brazing. As this technique is complex and expensive, attempts are being made to eliminate the metallization step by using brazes containing "active" alloying elements, such as Ti. These elements react with the surfaces of alumina, and of many other ceramics, to produce wettable products [1–4]. The main factor which controls the interfacial chemistry in a MTi/alumina system at a given temperature is the thermodynamic activity a_{Ti} of Ti in the metallic matrix M. a_{Ti} is proportional to the molar fraction x_{Ti} in the molten alloy and also depends on the strength of M–Ti interactions in the melt. For instance, additions of Fe and Cr in Ni–Ti alloys in contact with alumina increase a_{Ti} because the Fe–Ti and Cr–Ti interactions are much weaker than the Ni–Ti interactions. This modifies the type of interfacial reactions and results in improved wetting and adhesion [5].

The most frequently used reactive brazes are nearly eutectic composition CuAg alloys containing a few per cent of Ti. Many studies on reactive brazing of alumina have focused on braze–alumina interfacial chemistry (see for instance [6–8]). However, when alumina is brazed to metallic solids, the braze–alumina reactivity can be affected by interactions between elements contained in the metallic solid and the active alloying element of the braze. Indeed, for a typical brazing time of 10^3 s and a diffusion coefficient in the molten braze $D \approx 10^{-9}$ m^2/s, the diffusion distance in the molten alloy $(Dt)^{1/2}$ is in the order of 1 mm, which is much greater than the thickness of the braze foils (tens of microns). As a result, rapid dissolution of the metallic solid into the molten braze is expected to occur, thus modifying the braze composition and Ti activity. This agrees with the conclusions of calculations performed by Arróyave and Eagar [9] for the interactions between solid Ni and a liquid CuTi layer at temperatures higher than the melting point of Cu, showing that rapid dissolution of Ni into the liquid leads to a strong decrease in the thermodynamic activity of Ti due to the strong Ni–Ti interactions. According to these calculations, this

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effect becomes more pronounced when the temperature increases from 1100 °C to 1300 °C. Arróyave and Eagar did not verify their calculations experimentally but reported experimental results obtained by Stephens et al. [10] on Kovar/AgCuTi/alumina brazed joints which appear to confirm their findings. They found that strong interactions developed between the Ni contained in Kovar and the Ti of the braze led to a discontinuous reaction layer of Ti_xO formed at the braze/alumina interface, resulting in poor hermeticity of the joint.

The objective of this work is to investigate experimentally the physicochemical interactions that occur during brazing in a system consisting of a metallic solid (a commercial CuNi alloy), a CuAgTi braze and alumina and to study the role of temperature on these interactions. For this purpose, isothermal brazing experiments were performed with the CuNi/AgCuTi/alumina system and also with the alumina/CuAgTi, and CuNi/CuAgTi systems taken separately.

2. Experimental procedure and materials

The brazing experiments were performed under a vacuum of 10^{-4} Pa in a metallic furnace consisting essentially of molybdenum resistors located in a water-cooled stainless steel chamber. The experiments were done in the "sandwich" configuration, by placing a 100-μm thick foil of the brazing alloy between the two substrates to braze. The α-alumina substrates used were $20 \times 20 \times 6\,mm^3$ polycrystalline platelets of 99.5% purity with an average roughness Ra value of 0.6 μm. The metallic substrates were $20 \times 20 \times 1\,mm^3$ platelets of commercial CuNi alloy containing 51.5 at.% of Cu, 46.9 at.% of Ni, 0.9 at.% Mn. The alloy also contains several other elements (C, Zn, P, Mg, Sn, Co) with a total content of 0.7 at.%. Point experiments were performed using a $20 \times 20 \times 2\,mm^3$ Cu (purity higher than 99.99%) substrate. The average roughness Ra of CuNi and Cu platelets is in the range of 0.1–0.2 μm. Most of the experiments were performed using the commercial brazing alloy Cusil ABA, with a nominal composition of Ag–48.1Cu–3.1Ti (at.%). SEM analysis showed that the microstructure of this alloy is composed of a eutectic AgCu matrix containing particles with a composition close to that of Cu_4Ti intermetallic present in the Cu–Ti phase diagram [11]. A few experiments were carried out using another commercial brazing alloy, Incusil ABA, whose nominal composition is 49.2 at.% Ag, 38.6 at.% Cu, 2.4 at.% Ti and 9.8 at.% In. The addition of In enables the solidus and liquidus temperatures of the braze to be lowered from 780 °C and 815 °C respectively for Cusil ABA to 605 °C and 715 °C for Incusil ABA. Both these brazes are supplied by Wesgo Metals.

Before joining, the alumina substrates were cleaned in acetone and in ethanol, and then dried with nitrogen. The metallic samples were subjected to the following preparation: degreasing with soda, rinsing with demineralised water, cleaning with hydrochloric acid 50%, rinsing with demineralised water and drying with nitrogen. A stainless steel weight, creating an applied pressure of 3.2 kPa, was used in order to ensure contact between the brazing alloy and the substrates.

The brazing cycle involves heating at an initial rate of 20 °C/min up to a temperature situated just below the solidus of the brazing alloy (750 °C for Cusil ABA and 560 °C for Incusil ABA), at which point it was held constant for 40 min. The temperature was then increased at 5 °C/min for the experiments performed at 900 °C and at 20 °C/min for the others, up to the brazing temperature, and then kept steady for 15 min. The temperature was then lowered back to room temperature at a rate of 15 °C/min.

Two sessile drop experiments were performed at 900 °C under a static atmosphere of pure He. Note that results presented elsewhere [12] showed that wetting and interfacial reactions are the same when experiments are performed in high vacuum or in pure He. The change in the drop profile was monitored by means of an optical system and a video camera connected to a computer enabling automatic image analysis. In the first experiment, the droplet was made of the CuAg eutectic alloy. This droplet was first prepared by melting Cu (99.999 wt.%) with Ag (99.999 wt.%) on an alumina substrate in a high vacuum. In the second experiment, a CuAg–3.1 at.% Ti droplet was used. This alloy was processed in situ during the sessile drop experiment by directly melting a piece of Ti over the CuAg on the substrate. Therefore, there was no contact between Ti and the substrate before melting the alloy. For both experiments, the substrate used was CuNi alloy with a Ra value of 5 nm.

The joint chemistry and morphology were studied using a scanning electron microscope (SEM) equipped with an EDX spectrometer and microprobe analysis.

The coefficient of thermal expansion of alumina ($8.2 \times 10^{-6}\,°C^{-1}$) is half that of CuNi ($16 \times 10^{-6}\,°C^{-1}$). During cooling from the brazing temperature, this difference generated internal stress which may lead to failure. The type of failure observed at the end of the brazing cycle or during cutting is used to characterize qualitatively the mechanical strength of the alumina–brazing alloy bond. Two types of failure were observed in this study: cohesive failure, which takes place in the alumina substrate and leads to the conclusions that the interface is stronger than the alumina itself, and adhesive failure, which occurs at the brazing alloy–alumina interface indicating that the interface is mechanically weak.