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Gallium distribution in gallium-coated aluminum for brazing application

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Abstract. This work deals with the study of a new aluminum brazing process, called Galluminium. This technique, consisting in using gallium as a solder, is advantageous since it enables to braze at ambient air without flux. Indeed if the gallium coating is done mechanically, it descales the alumina layer and acts as a barrier against further reoxidation. Nevertheless, liquid gallium causes a severe aluminum embrittlement since it penetrates into the aluminum grain boundaries. We will show in this paper that this phenomenon has only a little impact on the mechanical resistance of the brazed joints since the amount of deposited gallium is enough low to avoid a severe embrittlement and the heat treatment (from 200°C to 600°C during several minutes) during brazing process dissolves gallium in the bulk.

Introduction

The current aluminium brazing processes (vacuum brazing and Nocolok® brazing) presents several disadvantages: need to work under vacuum or controlled atmosphere, high temperature, use of polluting fluxes... Our project is to study a new technique called « Galluminium » that consists in brazing aluminum at air without any flux by using gallium (a metal which melts at 29.8°C) as a solder.

But aluminum embrittlement by liquid gallium is a famous phenomenon characterized by a very fast intergranular penetration of gallium into aluminum. Thus we take into account this aspect in this study. Firstly we characterize the gallium distribution into coated aluminum samples before brazing by analyzing the coated surface, the bulk distribution and the gallium penetration into the grain boundaries. Then we will be interested in observing the gallium effect on the morphology of aluminum brazed joints.

Experimental techniques

Coating technique. For this study, we use aluminum 1050-O samples polished with 1 µm diamond paste. Then gallium is deposited by “polishing” aluminium samples on a cloth impregnated with liquid gallium. SEM observation of the coated surfaces shows different particles. Fig. 1 indicates the presence of white particles and grey edgings.

Figure 1. Manual coating observation at SEM

Grey edgings are pure gallium especially present at the aluminium grain boundaries. White particles are oxide residues. The zones outside grey edgings and white particles are called “clean zones” and illustrated by the rectangle drawn on Figure 1. EDS analysis operated on these zones show an important decrease of the oxygen rate due to the deposition, averaging to 7.5% before coating and not exceeding 0.5% after, even 80 days after deposition. It reveals that the coating technique descales the alumina layer by a mechanical effect and prevents aluminum sample from further reoxidation.

Brazing process. The gallium-coated specimens are brazed with a lap configuration at air at 500°C for 30 minutes. The contact area was 10x10 mm². A brazing pressure closed to the yield strength of the material was applied using a dedicated tool. Brazed joints are tested with tensile-shear tests. From measured fracture strength, we calculate an equivalent tensile fracture stress, called Von-Mises equivalent stress that we compare to the tensile fracture stress of AA 1050-O: 75Mpa. The average fracture stress in our case is about 43.5 Mpa, which is good for a brazing process.

Analysis techniques. So as to characterize our specimens, we used a “Merlin” SEM from Carl Zeiss company. EDS analysis were performed using an “INCA” SDD spectrometer from Oxford Instruments company. Auger spectroscopy has been also used in collaboration with L’Ecole des Mines de Saint-Etienne.

Measurement of a thin film thickness by EDS analysis. EDS analysis can be used for measuring thin films thickness (from a few nanometers to some hundreds of nanometers). This technique requires making analysis at different accelerating voltages since analyzed volume is function of this voltage. Fig. 2 shows an example of a gallium layer on an aluminum substrate. If the layer is thin enough (less than 2 μm), the proportion of gallium measured with a 5 kV voltage will be higher than with a 20 kV voltage. This is due to the interaction volume of the electron beam on the sample, which is lower at 5 kV; it brings a higher measured percentage of gallium when using a 5 kV voltage.

Figure 2. Representation of the interaction volume of the electron beam on the sample depending on the accelerating voltage. In the case of a thin gallium layer, there is proportionally less gallium which interacts with the beam at 20 kV than at 5 kV.

From the gallium percentages obtained at different voltages (typically 5, 10, 15 and 20 kV), the film thickness is measured using the StrataGEM® software [1] (based on the XPP model [2]) from SAMx company [3].

Measurement of an intergranular layer thickness by EDS analysis. EDS analysis can also be used as a way to measure the thickness of a grain boundary filled with gallium. If we perform an EDS profile through the grain boundary as shown on Fig. 3, we obtain a peak on the gallium concentration profile (see Fig. 4). If the thickness of the gallium film is much smaller than the probe size (which is true at 20 kV in most cases), it can be demonstrated that the peak width corresponds to the probe size and that the peak area is proportional to the thickness of the gallium film. Then, by representing the weight concentration of gallium in function of the beam position, the thickness can be calculated by dividing the peak area by the gallium density. This assessment is true only in the case of a negligible volume of analyzed gallium in comparison with the interaction volume of the beam on the sample (probe size). Thus, at 20 kV, the interaction volume in aluminum is almost a 2.5 μm diameter sphere, while the gallium film at grain boundaries is supposed to be about 100 nm thick.

Figure 3. Configuration of the gallium film thickness measurement at grain boundaries by EDS analysis. The white arrow represents the EDS profile through the grain boundary.

Figure 4. Measurement of the gallium film thickness at grain boundaries from the peak area of the gallium concentration in function of the beam position.

Auger depth profiling. The coated surface has been characterized by Auger spectroscopy using a spectrometer equipped with a FEG electron source and a hemispherical analyzer. The analyses were carried out at 10 kV. Sputtering using Ar ions was used to get the Ga depth concentration profile. Quantification was made using a Ga sensitivity factor previously measured on a homogeneous Al-Ga alloy containing 5% of Ga in solid solution.

Results

Coating characterization. In this part, we analyze the coated surface (only the “clean” zones, see Fig. 1) by 2 techniques:

- EDS analysis at different beam accelerating voltages;
- Auger depth profiling.

EDS analysis. Most of the analyses were performed at 20 kV, which led to gallium apparent weight concentration from 1 to 3%. Such dispersion can be explained by the fact that we deposit gallium by a manual way, which cannot be reproducible. Some samples were also analyzed at other voltages: 5, 10, 15 and 20 kV. Average values are represented on Figure 6. The StrataGEM® software [1] was used to calculate the variation of the Ga apparent concentration over the accelerating voltage, taking

the sample geometry into account (Al substrate + Ga coating). The Ga coating thickness was adjusted in the model so as to get the best fit with the experimental data (dashed line in Fig. 5). The best fit was obtained using a 30 nm thick gallium layer.

Figure 5. Gallium weight percentages in function of the beam accelerating voltage. Points with error bars are experimental data obtained at 5, 10, 15 and 20 kV. The dashed line is the fitting coming from the XPP model on StrataGEM®.

Auger depth profiling. Auger depth profiling was carried out on a “clean” zone (Fig. 1). Fig. 6 shows the gallium weight percentage in function of the sputtering time. The sputtering rate was not accurately measured here but, based on previous experience on similar materials, it can roughly be estimated to 0.05 nm/s.

Figure 6. Gallium weight percentages measured by Auger spectroscopy in function of the ionic sputtering time and the supposed sputtering depth (top axis)

We observe that the coating is made of almost pure gallium in the very first monolayers (< 5 nm). For depth higher than 5 nm, the gallium amount is decreasing from almost 100% to less than 10% after 70 nm in the depth. We can think this is due to the diffusion of aluminum atoms in liquid gallium during the deposition more than the gallium diffusion into aluminum grains which is a much slower phenomenon.

“In-grain” analysis. A cross-section of a coated sample was prepared by ion cutting using the “Cross-Polisher” system from Jeol company. EDS analysis performed inside a grain on the cross-section shows a small amount of gallium. One could think that the gallium detected by EDS inside the grains could be the result of bulk diffusion from the surface and / or from the grain boundaries.

But it can be observed that the result of the EDS analysis varies over accelerating voltage. For example, Fig. 7b shows the gallium weight percentages measured by EDS 5 and 20 kV inside a grain represented in Fig. 7a.

Figure 7. (a) Cross-section of a gallium-coated sample and (b) EDS profile lines performed at 5 kV and 20 kV along the arrow in Fig. 7a.

Even if gallium diffuses into aluminum grains (which would be surprising since solid state diffusion is expected to be very slow at room temperature), measured concentrations should be the same at 5 kV and 20 kV. In our case, $\%Ga_{5kV} > \%Ga_{20kV}$, which means we have a thin gallium layer covering the surface of the cross-section. The only way to explain that phenomenon is that gallium would propagate very quickly from grain boundaries to external surfaces of the sample during and after cross-section preparation. This has been recently confirmed by Auger depth profiling measurements that will not be detailed in this paper.

Intergranular penetration. Liquid gallium penetrates into aluminum grain boundaries very fast at room temperature (a few $\mu\text{m/s}$). But the deposited gallium amount is so low that we wonder if it really embrittles the whole aluminum sample. So as to study this aspect, we measured the thickness of the gallium layer at grain boundaries using EDS analysis (concentration profile technique described in Figs 3 and 4). Fig. 8 shows the variation of the Ga grain boundary thickness over the distance from coated surface.

Figure 8. (a) SEM observation of grain boundaries in a sample cross-section and (b) thickness of the gallium layer at grain boundaries, marked by the arrows in Fig. 8a, in function of the depth of the grain boundary from the coated surface.

We notice that the first grain boundaries are filled with gallium films of several tens of nanometers thick. There can be a great variation of Ga thickness from one grain boundary to another, which means that the sensitivity to Ga penetration is not the same for all the grain boundaries. Beyond 200 μm in depth, Ga grain boundary thickness is decreasing to small values hardly detectable by EDS.

From these EDS measurements, it is expected that only the first 200 or 300 μm of aluminium beneath the coated surface will be strongly embrittled. This has been confirmed by mechanical tests that will not be detailed here.

Brazed joints characterization. Brazed joints were mechanically characterized with tensile/shear tests. The average fracture stress is 43.5 MPa while the theoretical tensile fracture stress of AA 1050-O is 75 MPa. Fig. 9 represents the cross-section of a brazed joint at a x400 magnification.

Figure 9. SEM observation with chemical contrast of a brazed joint cross-section (x400)

We can notice two main phenomena on this cross-section:

- There are several porosities at the brazed joint certainly due to the first grain boundaries embrittlement by liquid gallium. These porosities can explain the lower breaking stress observed compared to the one of AA 1050-O.
- Grain boundaries are not filled with liquid gallium anymore. We clearly observe that the gallium grain boundary film has dissolved into the bulk by diffusion (white diffuse areas).

Thus heat treatment during brazing process dissolves the Ga grain boundary film. Gallium does not represent anymore an embrittlement risk for aluminum. Only some grain boundaries were embrittled at the beginning of the process certainly because of the brazing pressure.

References

- [1] J.L. Pouchou and F. Pichoir: *Scanning* 12 (1990) 212.
- [2] J.L. Pouchou and F. Pichoir: *Electron Probe Quantitation* (Plenum Press, New York, 1991), p. 31.
- [3] <<http://www.samx.com>>.