LOW TEMPERATURE BRAZING (680°C) TO Ti-6%Al-4%V TITANIUM ALLOY

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Introduction

Welding titanium and its alloys, Ti-6%Al-4%V (Ti-6-4) in particular, offers relatively little trouble, but important problems remain for brazing. High-temperature brazing (850-1000°C) of these materials has been extensively studied [1-12]. There are a great many filler metals able to braze Ti alloys, but the problem has been at best solved with TICUNI (Ti + 15% Cu + 15% Ni) [12] since the joint rupture takes place in the base metal.

However, high-temperature brazing involves a variety of shortcomings: microstructure adulteration, degradation of the Ti-6-4 mechanical properties induced by an exaggerated grain growth, contamination hazards, deformation of parts etc. This study deals with the design and evaluation of a filler metal apt to Ti-6-4 brazing at temperatures low enough, about 700°C, to prevent these drawbacks.

Research has been orientated towards alloys the composition of which has been derived from the main results of works reported by earlier literature [13-15]. They had finalized a filler metal including 50wt%Ag, 25wt%Cu, 25wt%In, and suitable for brazing Ti-6-4 at 700°C. The mechanical resistance of specimens brazed with this material is 470 MPa in tension and 370 in shear.

However metallographic investigations had revealed the existence of continuous, relatively thick layers of Ti-Cu intermetallic phases at the base metal interfaces. They have a detrimental influence on ductility and mechanical properties of the brazed joints. In order to get free of them, Al has been substituted for In. This new element was expected to retain Cu in the condition of dispersed intermetallic precipitates in the core of the joint. The ternary Ag-Cu-Al diagram denotes the presence of a ternary eutectic suitable for the making of low-temperatures melting alloys.

After selecting a filler metal, we have determined the mechanical properties and the corrosion resistance of brazed assemblies. Of course a companion study of microstructures has also been carried out.

Experimental Techniques

The material to be brazed is Ti-6-4 in the annealed condition. The (α-γ) microstructure is equiaxed. Specimens are designed so that a given gap is imposed between the two parts to be butt-brazed [14-16]. The filler material is generated in an arc furnace to prepare small test ingots and in an induction furnace for larger quantities [16]. Then ingots are crushed.

The result of the operation strongly depends on the quality of the preparation prior to brazing. It is achieved by ultrasonic cleaning at room temperature in a suitable tank and involves:
acetone degreasing (3mn)  
degreasing in an alcohol-ether mixture (3mn)  
1mn chemical etching in the following solution:  
\( \text{HNO}_3 \) (20 wt%), \( \text{HF} \) (2%), \( \text{H}_2\text{O} \) (78%)  
a double rinsing in permuted water  
drying with filtered compressed air.

The pieces of filler metal are placed on a peripheral shoulder of the test specimens prepared in this way. Next they are introduced into a chamber evacuated to a vacuum better than 3.10^{-6} torr. They undergo a brazing thermal cycle similar to that stipulated previously [13-14]. A titanium foil getter etched beforehand is placed around specimens.

Alloys Selection and Characterization of the Selected Filler Metal

A series of 20 Ag-Cu-Al alloys has been arc-furnace generated. Their chemistries have been selected close to the most probable one for the ternary eutectic.

At first, for a brazing operation of 15 mn at 700°C, the selected alloys had to meet the following conditions:
- a wettability angle between 10 to 15° on a Ti-6-4 specimen.
- a resistance to the tension rupture of bonds, higher than what obtained earlier, the initial gap being 50 µm between the 2 parts to join.

Five alloys fulfilled these 2 criterions.

Moreover, industrial applications demand that the bond characteristics be little sensitive to the value of gap and that the filler metal fills the small spaces as well as the large ones, without spreading at the parts surface. This last criterion is easily ascertained by the Blanchet wettability test on variable clearance specimens [11-14].

With the same brazing conditions, the bonds display a maximum rupture resistance for a gap of 50 µm. However, bonds made with the 65 wt% Ag, 30 wt% Al, 5% wt% Cu one present a lower sensitivity to the variation of the initial gap: the tensile strength decreases less than 30% lower than the best value for gaps ranging from 20 to 100 µm. Besides, this alloy fills very well large gaps, up to 0.5mm, without defects or shrinkage [16]. Therefore this alloy has been chosen.

Its micrographic examination shows:
- about 55 vol.% of an Ag-rich primary phase, equivalent to the \( \xi \) intermediate phase of Ag-Al alloys; its crystalline lattice is hexagonal with parameters \( a = 2.88\text{Å} \), \( c = 4.67\text{Å} \) very close to those of the \( \xi \) phase in Ag-Al system.
- about 40 vol.% of a very Al-rich interdendritic FCC phase: its lattice parameter: \( a = 4.04\text{Å} \), is nearly equal to that of pure Al.
- a very Cu-rich phase, one of the constituents of the ternary eutectic. Its crystalline lattice has not been identified because of its too small amount.

Notwithstanding its low hardness: Hv30 = 180, this alloy is brittle. Accordingly it can be laid only in a ground condition. Its industrial utilization would entail the use of a binding material.

Ingots generated in an induction furnace during the following of this study have always appeared as homogeneous.
1. Influence of brazing parameters

Until this stage of investigation, the brazing parameters were arbitrarily fixed. Being concerned by the optimization of the mechanical resistance of bonds, we have carried out tensile tests on bonds made:
- either at different temperatures, for a constant duration of 15 min
- or at a constant temperature of 700°C, for various durations.

The influence of the value of gap having been investigated at the earlier stage of alloy selection, it has been set to a best value of 50 µm.

The results appear on table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>670</th>
<th>680</th>
<th>700</th>
<th>720</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td>890±130</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 min</td>
<td>755±63</td>
<td>880±104</td>
<td>780±110</td>
<td>450±230</td>
</tr>
<tr>
<td>30 min</td>
<td>460±270</td>
<td></td>
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</table>

This shows the existence of 2 temperature-time couples enabling to achieve an optimal resistance for a 50 µm gap, namely 5 min at 700°C and 15 min at 680°C.

2. Micrographic appearance of the bond

A micrograph of the brazing performed with the selected alloy, a 50 µm gap, and for 15 min at 680°C appears on Fig.1. It is very similar to that supplied by 5 min at 700°C.

Figure 1. Cross section of a brazed joint
(Initial gap: 50 µm, 15 min at 680°C)
The brazing core is made of large precipitates with rectilinear outlines, and smaller ones with less delineated outlines and dispersed in the matrix. Their size decreases and their geometrical appearance fades rapidly off, when nearing to the parent metal. Their density becomes very important at the interface, but they do not appear to build up a continuous layer.

Microprobe analysis indicate that large precipitates include about 50 wt% Al + 25% Ti, + Ag and Cu in equal ratios.

The matrix contains essentially Ag and 10 to 12% Al; its nature is likely the same as that of the $\xi$ diagram.

A more general study of the bonds microstructure evolution carried out with other alloys, demonstrates that the best resistance to rupture is consistently achieved with such a kind of structure [16].

3. Main mechanical characteristics of the brazed bond

Brazing for 15 min at 680°C is the brazing which has been selected at this investigation progress. Holding for 15 min is indeed more favorable to a good thermal homogeneity and approximates more to industrial conditions.

Microhardness filiations with 20 g as a load and made perpendicularly to the brazed joint do not evidence very significant differences in each zone of the brazing. In the core, hardness undergoes a minimum (220 - 250 Hv) which can be explained by the lower precipitates density. Measurements at the interface sometimes achieve values above 400 Hv.

Table 2 gives values of tensile and shear strength just as the rupture load in a 3 points bending test where 40 mm separate bearings

<table>
<thead>
<tr>
<th>UTS (MPa)</th>
<th>Shear strength (MPa)</th>
<th>Rupture load in bending (daN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>883±104</td>
<td>430±26</td>
<td>1350±243</td>
</tr>
</tbody>
</table>

Before the rupture of about 20% of the specimen tested in tension, a very weak plastic strain takes place and comes out as a small curvature of the stress-strain curve whereas the bending angle is almost nil. These illustrate the brazing lack of ductility. UTS values are very close by the base metal yield strength, and sometimes even higher. This seems to demonstrate that the bonds resistance is limited by the plastic strain of the base metal. In fact, as soon as the yield strength is exceeded, a stress triaxiality and concentration build up at the interface which lead to bond rupture. This is confirmed by tensile tests carried out on T 40, commercial unalloyed grade of titanium with a nominal UTS of 40 MPa: rupture takes place at an average stress of 350 MPa.

Finally fatigue tests show that brazed joints have a repeated fatigue limit of about 200 MPa, which presents a stress approximately 25% of the rupture stress during a slow tensile test.

4. Rupture appearances
The light microscopy examination of ruptured specimens shows that rupture always takes place in the vicinity of the base metal while the joint structure does not seem to have been plastically strained (Fig. 2).

Figure 2. Cross section perpendicular to the brazed joint, after its rupture in tension

For the high strength levels, rupture is attended with the ejection of an alloy film which seems to flake off simultaneously from each face of the base of the parent metal. For the low strength levels, the film keeps adhering to one face, or splits in two parts each adhering to a different face.

Scanning Electron Microscopy (SEM) shows little ductility and a decohesive rupture regardless of the stressing mode whether tension, bending or shear.

Semi-quantitative chemical analysis performed with an energy dispersion analyzer shows the existence of rupture surfaces with 2 differing compositions for the layers brought to evidence after rupture. On the base metal side there would be essentially 2/3 wt Ti and 1/3 Al and on the brazing side one would find approximately inversed ratios plus some Ag. Thus it would appear that rupture occurs at the boundary between 2 layers with different compositions, likely intermetallic compounds, thin enough to escape on the micrographic cross section of the joint.

This study of the rupture appearance confirms the brittle character of rupture.

5. Influence of aging treatments on the mechanical and microstructural characteristics of the brazed joints

Ti-6-4 is commonly used at temperatures up to 350°C. Therefore, it is interesting to know the behavior of brazed bonds after holding at temperatures between 20 and 350°C.

Micrographic examinations of brazed specimens aged for 24 hrs at 250 or 350°C do not reveal noticeable structural modifications and the hardness filiations indicate no hardening. Accordingly, the mechanical properties, with the possible exception of bending ones, are not affected and table 3 even denotes a reduced experimental scatter, which can be ascribed to relaxation of the internal stresses of the joint.
Table 3. Mechanical characteristics of aged brazed bonds

<table>
<thead>
<tr>
<th>Aging treatment</th>
<th>UTS (MPa)</th>
<th>Flexion rupture load (daN)</th>
<th>Shear rupture stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hr at 250°C</td>
<td>930 ± 36</td>
<td>913 ± 320</td>
<td>447 ± 35</td>
</tr>
<tr>
<td>— 350°C</td>
<td>920 ± 46</td>
<td>913 ± 380</td>
<td>420 ± 35</td>
</tr>
</tbody>
</table>

More severe aging treatments, 4 days at 450 to 510°C evidence a rapid decrease of the tensile strength beyond 480°C: UTS = 375 ± 63 MPa after aging at 510°C. On such 2 specimens, micrography shows the presence of a 3 to 4 μm thick continuous layer, not yet detected on the 480°C aged material. This thick layer, certainly made of intermetallic compounds can explain why the joint mechanical properties noticeably decrease.

6. Behavior of brazed bonds during tensile tests at elevated temperatures

Still in the prospect of a possible use of brazings above RT, tensile tests have been carried out, in the 150 - 470°C range, on as-brazed and machined specimens. Fig. 3 indicates that the bond resistance decreases slightly faster than the tensile strength of Ti-6-4 between 200 and 470°C.

The same tests run on aged specimens confirm that aging, not above 470°C, has no influence on the joint mechanical characteristics and reduces experimental scatter.

Figure 3. Influence of temperature on the brazings
UTS and the Ti-6-4 yield strength

Corrosion Resistance of Brazed Joints Exposed to Chloride Ions

The susceptibility to Cl⁻ induced corrosion is well known for Ag-base filler metals used for brazing Ti and its alloys this has been evaluated in case of our brazings.

1. Salt spray *

* Salt content = 5±0.5 wt% - Relative humidity = 85-90% at 35°C at a pressure of 1±0.2 atm.
Six brazed tensile specimens are salt fog exposed; every 30 hrs 2 of them are sampled out and slowly tensile tested. Results appear on table 4.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>30</th>
<th>60</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTS (MPa)</td>
<td>800 - 740</td>
<td>200 - 230</td>
<td>180 - 150</td>
</tr>
</tbody>
</table>

A microscopic examination of cross sections shows that:
- for exposure times of about 60 hrs
  - the brazing Ag-rich, single phase is partly dissolved
  - precipitates rich areas are not corrosion affected
- for longer exposure times up to 160 hrs this corrosion cracking increasingly becomes the most detrimental effect and appears to be mainly responsible for the sudden degradation of the mechanical properties of the bond.

2. Open air contamination by hot sodium chloride

This kind of contamination is often met in some aircraft engine components and accordingly it is interesting to evaluate its effect on brazed joints. The UTS of specimens contaminated for 4 hrs at 400°C is strongly affected: its mean value is 400 MPa.

Scanning electron microscopy on such a specimen brings to evidence a deep contamination penetration of the joint and its bulk dissolution which comes out by a spongy appearance; again corrosion cracking takes place at the interface with the base metal.

Contamination by hot NaCl is very pronounced. The bond degradation belongs to the same type so that observed in a wet chloride environment, but the joint is more severely affected in its depth; the precipitates and the matrix phase are not spared.

NaCl at 400°C is likely more detrimental to the joint, especially due to the higher temperature and the possible formation of TiCl₄.

The sharp shape of the crack, its orientation perpendicular to tensile stresses, the lack of ductility of the zone where corrosion cracking takes place, explain the spectacular decrease of the tensile behavior of contaminated bonds.

Conclusions

This investigation has made it possible to design and evaluate a filler metal Ag-Al-Cu (65%-30%-5%) which supplies Ti-6-4 butt-brazed assemblies markedly more resistant than those obtained with the other known "low-temperature" brazings.

With an initial play of 50 µm, after brazing at 680°C for 15 mm, UTS can achieve 800-1000 MPa, that is 100% better than previous results. Mean
resistance to shear is 470 MPa. The fatigue limit after $10^7$ cycles repeated fatigue averages 200 MPa. But rupture angles less than 2° during bend tests emphasize the bonds lack of ductility. Obtained brazings do not seem aging-sensitive at temperatures where Ti-6-4 is usable.

In a general way, this filler metal which fulfils the usually required operating conditions, should enable the making of assemblies where the lack of ductility is not a rejection criterion and when a salt environment is not to be feared.

A patent has been taken out for this work.

References