Ceramic materials can be directly brazed to metals by using the so-called active brazing alloys.\cite{1} In general, these alloys are obtained by modifying conventional brazing fillers by adding an element able to promote wetting of the ceramic surface (typically a group IV element). One of the most common solutions is the addition of Ti to eutectic or quasi-eutectic AgCu or to AgCuIn alloys (In is added to improve the wetting behavior and lower the brazing temperature). The use of AgCuTi and AgCuTiIn for the production of ceramic-metal joints is widely reported in literature, typically for joining Si$_3$N$_4$, but also other ceramics. For instance Incusil™ABA® (Ag$_{59}$Cu$_{27.25}$In$_{12.5}$Ti$_{1.25}$, WESGO®, Erlangen, Germany) is used for various ceramic-metal combinations \cite{2-4}, while a Ag$_{71.5}$Cu$_{19.5}$In$_{5}$Ti$_3$ alloy is utilized to braze AlN to different metals.\cite{5} Given the materials to be joined and the joint geometry, there are two main issues affecting the mechanical performance of a ceramic-metal joint: the bond quality, which depends on the ability of the filler to wet the ceramic surface, and the residual stresses which develop in the assembly after brazing (due to the differences in the mechanical and thermal expansion characteristics of the two joining partners) and primarily depend on the plastic deformation of the filler. The quantity of the active element in the brazing alloy has a two-fold influence on the joint performance: on one hand a large amount ensures better wetting, on the other it would lead to hardening of the filler alloy, detrimental to
residual stress relief. Moreover a low content of active element is generally preferred when brazing ceramics to reactive metals, such as steel, because an excess of active element could promote undesirable reactions (e.g. the formation of brittle intermetallic phases). The optimization of the content of active element in the alloy is crucial for successful brazing of ceramic-steel joints.

In the present work a Ag$_{61.5}$Cu$_{23.5}$In$_{15}$ alloy (Incusil™15, WESGO®, Erlangen, Germany) was modified by adding Ti in different amounts: 0.5, 1.0 and 1.5 wt.%. The considered active element weight fractions are typical of commercial active brazing fillers used in ceramic-steel joints. Bulk specimens of Incusil™15 and Incusil™15-Ti were fabricated and micro-hardness measurements were carried out to study the effect of Ti addition on the plastic properties of the alloy. The microstructure was investigated by optical and electron microscopy and by image analysis techniques. The alloys were used to braze Si$_3$N$_4$/TiN to steel and the joint performance was assessed by four point bend tests. The results of hardness measurements confirm that Ti has a hardening effect on Incusil™15. However, for the considered values of Ti addition (0.5 -1.5 wt.%), experimental results indicate that the extent of the hardening is insignificantly influenced by the amount of Ti introduced in the alloy. This was confirmed by the results of four point bend tests on joints which showed that samples brazed with the three different active brazing exhibited similar bend strengths. This result is of particular importance from the application point of view as the actual Ti content in the alloy after brazing cannot be controlled a priori, both because the actual alloy composition could differ slightly from the producer’s specifications and because contaminants on the joint components could increase Ti consumption.

**Materials and Processing**

Incusil™15 was used in powder form (mesh 325). Ti was supplied in hydried form (TiH powder, mesh 325, Alfa Aesar GmbH & Co KG, Karlsruhe, Germany). The addition of Ti in this form to brazing fillers is widely reported in literature. Both the steel (AISI 3310, Gebrüder Böhler & Co. AG, Wallisellen, Switzerland) and the ceramic composite (FCT-Ingenieurkeramik GmbH, D-96528 Rauenstein, Germany) were cut and machined to obtain samples with dimensions 3x4x25 mm, suitable for the fabrication of
beam-like joints. These materials have potential applications in cutting tool machining industry and have been the subject of previous research by the authors.[4,6]

Incusil™15 and TiH were manually mixed to ensure a homogeneous dispersion of the TiH powder. To fabricate bulk specimens the powders were poured in molybdenum crucibles and molten at 750°C (dwell time 20 min) in high vacuum conditions (pressure lower than 10⁻⁵ mbar). Note that an intermediate step at constant temperature (510°C) was introduced in the thermal cycle to re-establish high vacuum conditions after TiH dehydrogenation. [9] The procedure for the fabrication of Incusil™15-Ti pills for the brazing of joints was more complex than that for the bulk specimens. A binder (octyl acetate – 0.4 wt.% cellulose nitrate) was added to the powders and the slurry was cast on teflon plates and dried (24 hours at room temperature, atmospheric pressure) to obtain a green sheet with a thickness of about 0.3 mm. The sheet was cut into rectangular pills (about 4x5 mm) stiff enough to be handled during the joint assembly. The ceramic and steel samples were degreased using wet chemical methods and degassed at 1100°C and 850°C, respectively. The joints were assembled on a customized jig and brazed at 750°C (dwell time 10 min) and again an intermediate step to allow for TiH dehydrogenation was introduced. All the processing was carried out using a GERO F-VS 100-200/13 vacuum furnace (GERO Hochtemperaturöfen GmbH & Co. KG, Neuhausen, Germany). After brazing the joints were visually inspected to check their quality and those which presented misalignments or visible defects were discarded.

**Microstructural Analysis**

Samples for optical and scanning electron microscopy (SEM) energy dispersive X-ray analyses (EDX) were extracted from the bulk specimens. Then coarse grinding and fine grinding were performed by using SiC paper, down to a grit size of 1200. The last stage of the polishing was carried out by using diamond suspensions with a grain size of 1 μm. Optical microscopy images were taken using a Reichert Jung MeF3 microscope (Reichert Inc., Depew, NY, US) equipped with a Leica DC500 camera (Leica Microsystems GmbH, Wetzlar, Germany) while SEM-EDX analyses were carried out using a Philips XL30 SEM (Philips, Eindhoven, the Netherlands).
Figure 1 summarizes the results of optical microscopy analyses while phase compositions (determined by EDX) are reported in table 1. In Incusil™15 three phases are identifiable: a Cu-rich solid solution phase (orange, labeled Cu), a second solid solution phase, mainly consisting of AgIn (white, labeled AgIn), in which fine precipitates of the Cu phase can be found, and finally finer bluish AgCuIn precipitates (labeled AgCuIn). Incusil™15-Ti alloys present the same three phases as Incusil™15 with the addition of two Ti-containing intermetallic phases (both grey, hardly distinguishable in optical microscopy) with compositions Cu₄Ti and Cu₂InTi, respectively. Figure 1 shows clearly that two general trends are observable in the evolution of the microstructure of the alloy with the increase of the Ti-content: on one hand the volume fraction of the Ti-containing phases increases, on the other hand that of the AgCuIn precipitates decreases to the point that they have almost disappeared in the Incusil™15-Ti 1.5 wt.% alloy. The weight compositions of the two main phases (Cu, AgIn) and of the Ti-containing intermetallics in the four alloys were assessed by averaging at least 5 EDX point measurements for each phase. Table 1 shows that the AgIn phase has the same composition in all the four alloys and the same can be said for the Cu₄Ti and Cu₂InTi intermetallics in the three Ti-containing alloys. On the contrary, the composition of the Cu phase changes slightly as in Incusil™15-Ti alloys it contains about 1 wt.% Ti. This variation of the composition is due to the solid solubility of Ti in Cu[10], whereas Ti solubility in In and Ag is lower.[11] The obtained phase compositions are in agreement with those reported in the literature for Incusil™15 and for Incusil™ABA®.[12,13] Note that the assessment of the composition of the AgCuIn precipitates was not performed as it would require a more sophisticated analysis which is beyond the purposes of the present work.

Image analysis was carried out on optical microscopy images to assess the volume fraction of the Ti-containing intermetallic phases. Ti-containing phases were manually outlined using the software Corel DRAW (Corel Corporation, Ottawa, Canada) and then the volume fraction was computed by using the software IMAQ Vision Builder (National Instruments, Austin, TX, US). Ten images were analyzed for each alloy. The results are summarized in figure 2. It can be seen how the volume fraction of Ti-containing phases evolves linearly with the Ti wt.% and the regression line intercepts the abscissa at a
point corresponding to 0.4 Ti wt.%, which approximately corresponds to the amount of Ti dissolved in the Cu phase (which in Incusil™15-Ti alloys, as reported in table 1, contains about 1-2 wt.% Ti, in agreement with the Ti-Cu binary phase diagram \cite{10}).

**Mechanical Tests**

Micro-hardness tests were performed with a Zwick Universal Hardness Tester HU2.5 (Zwick Roell AG, Ulm, Germany). Vickers hardness (HV) was measured with two different applied loads: 0.01 kg (HV 0.01) to measure the hardness of individual phases and 0.3 kg (HV 0.3) to assess the global hardness of the alloy. The hardness value was assessed by averaging the results of at least seven independent measurements. The results are summarized in figure 3. The obtained HV 0.01 values for the AgIn and the Cu phase in Incusil™15 (104 and 119, respectively) are in agreement with HV 0.05 measurements reported in the literature \cite{14} (111 and 112, respectively). The results show that Ti induces an increase in the global hardness of the alloy, with the hardness of Incusil™15-Ti alloys being about 20% higher than that of Incusil™15. This increase in the global hardness is due to two factors: not only the Ti-containing phases are much harder than the other phases (HV 0.01 about 340) but there is also a considerable increase the hardness of the Cu phase (about 25%, as HV 0.01 increases from 120 to 160) deriving from the presence of Ti in solid solution.

The mechanical strength of the joints was assessed by 4-point bend tests. The tests were performed following the same specifications adopted by the authors in previous work\cite{4}: a lower load span \(l_1\) of 40 mm and an upper load span \(l_2\) of 20 mm and a cross-head speed of 0.015 mm/s. The tests were performed on a Zwick Z005 testing machine (Zwick Roell AG, Ulm, Germany). The applied moment \(M\) and the maximum nominal applied stress \(\sigma_{\text{max}}\) were calculated according to beam theory:

\[
M = \frac{P}{4} (l_1 - l_2),
\]

\[
\sigma = \frac{6M}{bh^2},
\]
where $P$ is the total applied load while $b$ and $h$ are the section width and height (4 mm and 3 mm, respectively). It is important to highlight that $\sigma_{\text{max}}$ is a nominal stress, calculated as if the specimen were a homogeneous beam. At least six specimens were tested for each brazing alloy. All the specimens broke in the ceramic joining partner close to the interface (typically at a distance of 100-400 microns). The nominal bend strengths were calculated from the rupture load according to (2). After the bend tests it was also possible to measure the actual brazing gap: the filler in excess was ground away and the broken sample polished, then the gap was measured by optical microscopy. An average brazing gap of about 150 \( \mu \text{m} \) was measured. The results of bend tests for joints brazed with the three Incusil™15-Ti alloys are reported in figure 4. No appreciable difference can be observed between the obtained joint nominal strengths (346, 322 and 324 MPa for the alloys with 0.5, 1.0 and 1.5 Ti wt.% respectively) and the results are close to those obtained for Incusil™ABA®.[6] The scatter of the results (standard deviation) is compatible with that of the ceramic joining partner which has a nominal bend strength of 785 ±51.2 MPa.[15] These results are in agreement with those of the HV 0.3 measurements: since the three Incusil™15-Ti alloys exhibit very similar hardness values, there should be no significant difference in their plastic behavior, and as a consequence in the magnitude of residual stresses and in the joint nominal strengths.

Conclusions

In the present study AgCuInTi active brazing alloys were obtained from the conventional AgCuIn brazing filler Incusil™15 by adding 0.5, 1.0 and 1.5 wt.% Ti (in hydride form). Procedures for the production of both bulk alloy specimens and ceramic-metal joints were successfully applied. Microstructural analyses show that Ti forms two intermetallic phases (Cu$_4$Ti and Cu$_2$InTi) with the alloy constituents and that a non negligible amount of Ti is present in the Cu-rich solid solution phase. Microhardness results indicate that the addition of Ti leads to a hardening of the alloy, due to both the presence of the hard intermetallics and the hardening of the Cu phase. No significant difference could be observed between the hardness
values for the three Incusi™15-Ti alloys, this leading to the conclusion that the three alloys have very similar plastic behaviors. This hypothesis was indirectly confirmed by the results of the four point bend test on joints as joints brazed with the different alloys exhibited very similar strength values. These findings suggest that for the range of compositions considered herein the amount of Ti contained in AgCuInTi alloys has a negligible influence on the mechanical strength of joints.


Figure 1. Optical microscopy images of the microstructures of the alloys: a) Incusil™15, b) Incusil™15-Ti 0.5 wt.%, c) Incusil™15-Ti 1.0 wt.%, d) Incusil™15-Ti 1.5 wt.%. 
Figure 2. Evolution of the volume fraction of Ti-containing phases in Ti-doped Incusil™15 against the alloy Ti-content, obtained by image analysis. Experimental points and error bars represent average values and standard deviations, respectively. The linear interpolation of the data leads to conclude that about 0.4 wt.% is the maximum amount of Ti that can dissolve in alloy (mainly in the Cu phase, see text for details), without forming intermetallics.
Figure 3: Results of micro-hardness tests. Color bars stand for average values and error bars represent standard deviation. Incusil15-Ti alloys exhibit a higher overall hardness (HV 0.3) due to presence of hard Ti-containing phases and to the hardening of Cu-phase (green). Refer to text for details.
Figure 4. Comparison of the obtained average nominal bend strengths of Si₃N₄/TiN-steel joints brazed by Incusil™15-Ti alloys with joints brazed by Incusil™ABA®[^6]. Error bars represent standard deviation. The difference in the obtained strengths is negligible and the scatter in the results is compatible to that of the ceramic joining partner.
Table 1. Weight composition of the phases in the brazing alloys determined by EDX.

<table>
<thead>
<tr>
<th>Material</th>
<th>Phase</th>
<th>Ag (wt.%)</th>
<th>Cu (wt.%)</th>
<th>In (wt.%)</th>
<th>Ti (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incusil™15</td>
<td>AgIn</td>
<td>81</td>
<td>5</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>4</td>
<td>93</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Incusil™15-Ti 0.5 wt.%</td>
<td>AgIn</td>
<td>78</td>
<td>6</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>4</td>
<td>89</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Cu₂Ti</td>
<td>2</td>
<td>81</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Cu₂InTi</td>
<td>2</td>
<td>56</td>
<td>26</td>
<td>16</td>
</tr>
<tr>
<td>Incusil™15-Ti 1.0 wt.%</td>
<td>AgIn</td>
<td>80</td>
<td>6</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>5</td>
<td>89</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Cu₂Ti</td>
<td>2</td>
<td>81</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Cu₂InTi</td>
<td>2</td>
<td>56</td>
<td>26</td>
<td>16</td>
</tr>
<tr>
<td>Incusil™15-Ti 1.5 wt.%</td>
<td>AgIn</td>
<td>81</td>
<td>5</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>4</td>
<td>91</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Cu₂Ti</td>
<td>2</td>
<td>80</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Cu₂InTi</td>
<td>2</td>
<td>53</td>
<td>29</td>
<td>16</td>
</tr>
</tbody>
</table>