Thermodynamic and experimental study of Ti–Ag–Cu alloys

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Abstract

Phase equilibria in the ternary Ti–Ag–Cu system have been studied thermodynamically and experimentally at various temperatures. The thermodynamic analysis was performed by combining the most recent data on the binary Ag–Cu, Ti–Ag and Ti–Cu systems and experimental information obtained by the diffusion couple technique. The eutectic and three non-eutectic binary Ag–Cu alloys were melted and annealed in evacuated Ti ampoules at temperatures of 900, 950 and 1000 °C for various times and subsequently quenched in water. Both the calculations and the experimental results confirm that in the ternary system there is a miscibility gap, which divides the liquid phase into solutions of low and high Ti content. Furthermore, no ternary compounds were found. Several isothermal sections and the activity of titanium as a function of the copper-to-silver ratio and temperature are presented.

Keywords: Ceramic/metal brazing; Active filler alloy; Thermodynamics; Liquid miscibility gap

1. Introduction

The joining of advanced ceramics to metals is of major interest for various industrial applications. Brazing with active filler alloys containing some active element (e.g. Ti), which promotes wetting of ceramic surfaces, is a preferred method of joining. Most of these active filler metals are based on the Ti–Ag–Cu system. However, due to the lack of relevant thermodynamic data on brazing alloys, especially on the activities of titanium in liquid brazes, the reactions between the ceramic and the filler metal are not well understood. Therefore, in order to develop further brazing processes and new filler metals, a consistent thermodynamic description of this basic system is needed.

The isothermal sections of the ternary Ti–Ag–Cu phase diagram often used in active brazing studies are those reported by Eremenko et al. [1]. They studied the Ti–Ag–Cu system experimentally and concluded on the basis of microstructural observations that there exists a liquid miscibility gap. Based on these experimental findings the Ti–Ag–Cu system has been reassessed by Chang et al. [2]. Only some formal changes have been made in this assessment and no new experimental information is given. The modified isothermal sections [2] have been compiled also by Kubaschewski [3]. The miscibility gap divides the liquid braze into solutions of low and high Ti content and this may have a significant effect on the mechanism of active brazing. In order to confirm the existence of the liquid miscibility gap and to predict the stability of the liquids as well as the activity of Ti in the Ti–Ag–Cu system at different temperatures of interest, a thermodynamic analysis of phase equilibria in the Ti–Ag–Cu system has been performed in this study. The liquid miscibility gap and the phase equilibrium were also studied experimentally by melting different Ag–Cu alloys in Ti ampoules in the temperature range 900–1000 °C and quenching them in water. The diffusion couples were examined optically and with the SEM/EDX/EPMA technique.

2. Experimental procedure

Due to the high reactivity of titanium, ternary Ti–Ag–Cu alloys of controlled composition are extremely difficult to produce with the conventional techniques. Titanium reacts with all the known crucible materials during melting and this produces contamination as well as preventing the precise control of the composition. Therefore a solid/liquid diffusion couple technique was employed. Several binary Ag–Cu alloys were melted in the Ti ampoules, shown in Fig. 1. The ampoules were machined from a 99.7% pure C.P. Ti rod (Goodfellow,
The Ti crucibles were filled with the Ag–Cu chips, evacuated and sealed with Ti caps by diffusion bonding in a high-vacuum furnace. The sealed ampoules were then annealed in a laboratory furnace at temperatures between 900 and 1000 °C for 2, 30, 45 and 90 min and subsequently quenched in water. Microstructures of the diffusion couples were examined primarily with a scanning electron microscope (Jeol JXA 840A) equipped with EDS and WDS X-ray spectrometers (Tracor Northern 5500, TN 5600). The quantitative analyses were performed using high-purity titanium, silver and copper as standard materials.

### 3. Thermodynamic modelling

The thermodynamic parameters of the binary Ag–Ti and Cu–Ti systems were optimized using the available thermodynamic and phase diagram data and were subsequently utilized for the calculation of the equilibrium ternary phase diagrams. Some of the data had been assessed previously, some of them were taken from the literature or from the SGTE databank [4] and the rest were assessed in this study. The liquid and solid solutions were regarded as regular or subregular substitutional solutions. All the binary intermetallics were considered as line compounds and therefore only the standard Gibbs energies of formation of the compounds were used. Owing to the isomorphic structures of the Ti$_2$Ag and Ti$_3$Cu compounds the pseudobinary intermetallic compound Ti$_2$(Ag$_{1-x}$Cu$_x$) was considered as a regular-type solid solution with a temperature-dependent interaction parameter. Likewise, since the experimental results revealed significant solubility of Ag in the TiCu, this phase was considered as a subregular solid solution between two line compounds.

The molar Gibbs energy of an $n$-component substitutional solution phase is given by

$$G_m = \sum_{i=1}^{n} x_i G^0_i + RT \sum_{i=1}^{n} x_i \ln x_i + G^E_m$$

where the $G^0$ parameters represent the Gibbs energies of the pure components and were taken from the SGTE databank [4] and the literature [5]. All the Gibbs energies are relative to the pure element standard state under one bar. The excess Gibbs energy $G^E_m$ is represented by the Redlich–Kister-type polynomial [6] together with a ternary interaction term

$$G^E_m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (L_{ij}^0 + (x_i - x_j)L_{ij}^1 + (x_i - x_j)^2L_{ij}^2)$$

$$+ x_{Ti}x_{Ag}x_{Cu}(L_{Ti, Ag, Cu})$$

where the $L$ parameters describe the interactions between the component atoms.

### 4. Assessment of the binary systems

#### 4.1. The Ag–Cu system

Data for the binary Ag–Cu system were taken from Jönsson and Ågren [7]. Subsequently, the solid solubilities of both Ag and Cu were found to be a little too high in this assessment [8], but since it had only a small effect on the ternary system no corrections on the Ag–Cu system were made in the present work.

#### 4.2. The Ti–Ag system

The Ti–Ag system has been assessed previously [9]. In the literature, there are some conflicting experimental observations of the equilibria involving the silver-rich liquid or solid solution. This is caused by the volatility of silver. Eremenko et al. [10] have reported that the reaction involving (Ag), liquid and TiAg is of the eutectic type and the eutectic composition is about 95 at.% Ag. However, McQuillan [11] reported that the reaction is of the peritectic type, while Adenstedt and Freeman [12] estimated the solubility of Ti in liquid Ag to be <1.1 at.%. Based on the experimental findings of the present study the solubility of Ti in liquid Ag is chosen to be 2.5 at.%. By using the available experimental data [4,13], the re-evaluated lattice stability for titanium [5] and the above-mentioned solubilities of Ti in liquid and solid silver, the Ti–Ag system was reassessed [14].
4.3. The Ti–Cu system

As in the case of the Ti–Ag system, the lattice stabilities were taken from the SGTE databank [4] and from the literature [5], because the lattice stabilities of the compounds used by Murray [13] do not include the heat capacities. The values for the interaction parameters of solid and liquid solutions as well as those for the Gibbs energies of formation of the intermetallics given by Murray [13] and Zeng [15] were optimized together with the experimentally determined phase boundaries [14].

5. Results and discussion

5.1. Experimental results

When the binary eutectic AgCu alloy is annealed in a Ti ampoule at 950 °C, titanium dissolves in the liquid alloy, which rapidly becomes saturated with Ti. After only 2 min reaction the supersaturated AgCuTi alloy is divided into two separate liquids (Fig. 2). The liquid L2 forms between the liquid L1 and solid titanium, and being the lighter component it begins to rise to the surface of the liquid L1 along the brim of the ampoule. The as-quenched L2 liquid is composed of Ti2Cu3, TiCu2, and AgCu eutectic + α-Ag[Cu]. The as-quenched liquid L1 has a near-eutectic composition (AgCu eutectic + α-Ag[Cu]) and there are a lot of spherical L2 particles in it. It seems that these L2 particles are released from the continuous liquid L2 due to the gravity effect.

After 30 min annealing at 950 °C the AgCuTi alloy has clearly been separated into two liquids (Fig. 3). The light-coloured area, being the as-quenched liquid L1, is Ag-rich and locates as a heavier material on the bottom of the ampoule. The dark-coloured area above the L1 is the Ti-rich as-quenched liquid L2.

Fig. 4(a) shows a higher magnification of the interface between the two as-quenched liquids when the eutectic AgCu alloy was annealed in the Ti ampoule at 1000 °C for 30 min. The compositions of the local equilibrium phases were determined from several line scan analyses over the interface between the as-quenched liquids L1 and L2. One of the line scans is shown in Fig. 4(b). Similar analyses were made of the interfaces between L1 and Ti[Cu,Ag] solid solution and L2 and Ti[Cu,Ag]. The Ag-rich phase-region L1 is composed of the solid solution (the average composition being 91.1% Ag, 7.5% Cu, 0.8% Ti) and dark precipitates (61% Ti, 27% Cu, 10.7% Ag), which contain smaller light-coloured Ag particles. The as-quenched liquid L2 is composed of three phases; fine light-coloured Ag particles, light grey TiCu[Ag] phase and the dark-coloured matrix with varying composition (59.8–63.6% Ti). There are also larger (∼2–3 μm) spherical Ag-rich precipitates in the phase region L2 having a composition similar to the as-quenched liquid L1 (90.1% Ag, 8.3% Cu, 1.3% Ti). The spherical L1 and L2 particles in opposite solids are precipitated out from the supersaturated liquids during the early state of quenching.

Fig. 5(a) shows a cross-section of the interface between the two liquids formed after annealing the binary Ag25Cu75 alloy at 950 °C for 30 min. Owing to the high Cu content, the amount of Ag-rich liquid L1 is essentially smaller than that of the Ti-rich liquid L2 at 950 °C. A line scan across the interface between L1 and L2 is presented in Fig. 5(b). The as-quenched Ag-rich liquid L1 consists mainly of α-Ag[Cu,Ti] solid solution (90.2% Ag, 8.8% Cu, 1% Ti) and eutectic-type phase mixture (65.2% Ag, 33.8% Cu, 1% Ti). The
small volume fraction of L1 leads to a high Ti content of the L2. Accordingly, L2 is composed of large Ti$_2$(Cu$_{0.8}$Ag$_{0.2}$) grains and small Ag[Cu] precipitates in the TiCu$_2$[Ag] matrix, with 13 at.% Ag. It is very likely that the Ti$_2$Cu$_b$ intermetallics are solid at the annealing temperature; thus most of the liquid L2 has been consumed in the reaction with solid Ti, as is shown below.

The as-quenched structures of Ag50Cu50 and Ag75Cu25 alloys after annealing at 950 °C do not differ markedly from the above. The relative amounts of the two liquids are dependent on the nominal composition of the alloy.

After annealing the eutectic AgCu alloy at 900 °C for 45 min, a large amount of liquid L1 is formed (A in Fig. 6). The as-quenched liquid is composed of Ag[Cu] solid solution grains (86.3% Ag, 13.6% Cu), AgCu eutectic (53.7% Ag, 45.1% Cu, 1.2 Ti) and dark TiCu$_2$[Ag] precipitates (66.3% Cu, 28.5% Ti, 5.2% Ag). At this temperature the amount of liquid L2 remains small and it is gathered in the upper corners of the sample (B in Fig. 6), next to the solid titanium. The complex structure of this phase region, consisting of several Ti$_x$Cu$_y$ intermetallics and Ag-rich phase indicates that the L2 has been solidified partly at the annealing temperature. Large Ti$_3$Cu$_4$(2.8% Ag) grains form the matrix and between the Ti$_3$Cu$_4$ needles TiCu$_2$, TiCu$_4$, eutectic AgCu + $\alpha$-Ag[Cu] structure and small TiCu precipitates are found. In order to clarify whether the Ti-rich liquid is solidified already at the annealing temperature an additional experiment was performed. After the first 60 min annealing, the Ti ampoule was turned upside down in the furnace and annealed in this position for another 30 min. The as-quenched liquid has a structure similar to the area A in Fig. 6, while the Ti-rich shell was found in the upper part of the ampoule where the liquid L1 is initially located. From
this it can be concluded that the Ti-rich liquid had solidified mainly during annealing.

5.2. Thermodynamic calculation

The isothermal sections of the Ti–Ag–Cu system calculated at 1000 °C and 950 °C are shown in Figs. 7 and 8. The solubilities of Ag in the Ti₅Cu₆ intermetallics, except Ti₃(Cu,Ag) and TiCu, are not included in the present assessment, since they are not essential for explaining the experimental results. When the isothermal section was calculated using only binary data concerning the liquid and the b.c.c. phase, compositions of the solutions L₁, L₂ and b.c.c. differed from those values determined experimentally. Consistency could not be obtained without taking the ternary parameter into account. The ternary parameter for the solid solutions was disregarded, because it had such a minor effect on the phase equilibria. By optimizing the parameters for the liquid the results shown in Fig. 7 were obtained. The agreement between the calculations and the experimental results is quite satisfactory. Because of the limitations of the technique used, a better fit was not attempted. These limitations are due to the fact that some decomposition of liquids takes place on quenching. Although the water quenching is rapid, the temperature falls roughly about 50–100 °C while moving the ampoule from the furnace into the water.

The calculated diagram at 950 °C (Fig. 8) shows that the equilibrium compositions of phases L₁, Ti₅Cu₆[Ag] and Ti₃(Cu,Ag) correspond well to those measured experimentally. This may be expected on the basis of the fact that L₂ has already largely transformed into solid constituents during annealing, i.e. decomposition of the phases is not as extensive as at 1000 °C. The Ag-rich liquid L₁ decomposes to Ag[Cu] and AgCu eutectic, but the amount of AgCu eutectic is small. Thus, the measured composition is very close to the real composition of the liquid L₁.

The apparently fast diffusion of titanium into the liquid L₂ also indicates a strong attractive interaction between titanium and copper in the system. This can also be seen in Fig. 9, which shows the activity of titanium as a function of the Cuₐ/(Ag + Cu) ratio assessed in this work. By calculating the activity of Ti as a function of composition and temperature we can determine the possible diffusion paths at the beginning of contact. In a liquid/solid diffusion couple, where the other end of the diffusion couple, here Ti, is dissolving and diffusing rapidly in the other member (in this case
the liquid), the diffusion path is moving from its initial position (shown as a dotted line with \( t_1 \sim 0 \)) towards higher Ti contents. Local equilibrium conditions are, however, maintained at the interfaces—so far as the phase layers can be clearly resolved. The possible diffusion paths at 950 °C are shown in Fig. 8 by dotted lines. Hence, the activity considerations are, in addition to the existence of the liquid miscibility gap, of great importance when predicting the brazing mechanism in actively brazed ceramic-metal joints.

References