Thermodynamic Assessment of the Ag-Cu-Ti System

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Abstract

The $Ag-Cu-Ti$ ternary system is critically assessed and the thermodynamic model is refined so the available experimental data are represented as accurately as possible. The phases $CuTi_2$ and $AgTi_2$ phases are modelled using a single model and assuming that these phases form a continuous solid solution. The $CuTi$ and $AgTi$ phases are also modelled using a single model and their penetration into the ternary compositional triangle is correctly predicted. Ternary interactions for the liquid phase were incorporated. Experimental and calculated results are compared and the reliability of the model is confirmed.

Introduction

The $Ag-Cu-Ti$ system is widely used in ceramic/metal joining applications. The alloys based on the $Ag-Cu$ eutectic with Ti additions allow wetting of stable ceramic surfaces through the reaction of the chemically active Ti in solution in the $Ag-Cu$ melts with the ceramic. The low temperature of the $Ag-Cu$ system allows brazing at reasonable temperatures, while the presence of Ag increases the activity of Ti rather noticeably [1], promoting interfacial reactions with even the most stable technically relevant ceramics. The understanding of the chemical behavior of the $Ag-Cu-Ti$ system is of importance when trying to understand the mechanisms of reactive wetting [6]. Although the $Ag-Cu-Ti$ system has been modelled before [7], no thermodynamic description has been made available. In this work, a model for the ternary $Ag-Cu-Ti$ system will be proposed and phase diagram and thermochemical calculations will be compared with the experimental evidence.

Experimental Data

In order to perform the assessment, phase diagram equilibria data on the $Ag-Cu-Ti$ system [2] were used. Solubility data on the ternary miscibility gap in the liquid phase, ternary invariant reactions involving this phase, as well as maximum solubilities for the intermetallic compounds were incorporated in the thermodynamic optimization.In addition to these phase equilibria experiments, diffusion couple experiments [7] as well as thermochemical experiments [6] were also used in the present assessment. A detailed analysis of the reliability and implications of the experimental information available is given in [1].

Thermodynamic Modelling

In thermodynamic modelling of phase diagrams, the accuracy of the thermodynamic description of higher-order systems depends heavily on the reliability of the thermodynamic descriptions for the lower-order sub-systems, provided there are no ternary compounds involved. The reason for this is the low probability that ternary chemical interaction energies play an important role in the stability of ternary phases. In the case of the $Cu-Ag-Ti$, reliable descriptions for the $Cu-Ti$ [3] and $Ag-Cu$ [4] systems are available in the literature. In the case of the $Ag-Ti$ system, a simple description is given by [5]. For this work, we will consider the binary thermodynamic descriptions by [3], [4] and [1], and implement ternary contributions in the liquid phase so the proper phase equilibria and stability ranges are obtained.

The assessment was performed using the often-called Calphad method. The models were based on the sublattice formalism proposed by [8]. A detailed mathematical description of the models used for all the phases present in the $Ag-Cu-Ti$ system cannot be presented here. However, a model describing one of the phases is presented as an example (for a more detailed description, refer to [1]):

Model for solution phases

The liquid can be described using the single-sublattice model, having a Gibbs free energy of:

$$G_m^\phi = \sum_i x_i^{\phi 0} G_i^\phi + RT \sum_i x_i^\phi \ln \left(x_i^\phi \right) +^{ex} G_m^\phi$$
$$^{ex}G_m^\phi = \sum_{i}^{n-1} \sum_{j=i+1}^{n} x_i^\phi x_j^\phi L_{i,j}^\phi \tag{1}$$

where elements Ag, Cu and Ti are identified as 1,2,3; n is equal to 3; x_i^ϕ is the molar fraction of element ; $^0G_i^\phi$ corresponds to the Gibbs energy of the pure element in the state ϕ; $^{ex}G_m^\phi$ is the excess Gibbs energy of the liquid phase; and $L_{i,j}^\phi$ is the binary interaction parameter between elements i and j.

Using the Redlich-Kister formalism, the binary interaction parameter $L_{i,j}^\phi$ can be further expanded:

$$L_{i,j}^\phi = \sum_k {}^k L_{i,j}^\phi \left(x_i^\phi - x_j^\phi \right)^k$$
$$^k L_{i,j}^\phi =^k a +^k bT \tag{2}$$

As noted above, a ternary interaction parameter was incorporated in to the description of the excess Gibbs energy of the liquid phase:

$$^{ex}G_m^\phi = \sum_{i}^{n-1} \sum_{j=i+1}^{n} x_i^\phi x_j^\phi L_{i,j}^\phi + x_i^\phi x_{j\neq i\neq k}^\phi x_{k\neq i\neq j}^\phi L_{i,j,k}^\phi \tag{3}$$

Except for the ternary interaction parameter, Eqs. (1) and (2) describe the solid solution phases $BCC - Ti$ (βTi), $HCP - Ti$ (αTi), $FCC - Cu$ and $FCC - Ag$.

Comparison between Model and Experimental Data

As noted above, in order to obtain a reliable description of a ternary system, the degree of accuracy of the description of the binary sub-systems plays a determinant role. In the case of the $Ag - Cu$ and $Cu - Ti$ binary sub-systems, thermodynamic assessments available in literature show excellent agreement with published experimental data [3], [4]. Despite the fact that the models used for describing the $Ag - Ti$ system do not seem to be as reliable as the models for the other sub-systems, the experiments and assessment for the ternary $Ag - Cu - Ti$ system may shed light on the validity of the models for the $Ag - Ti$ system.

Fig. (1) shows the calculated and experimental $Ag - Cu - Ti$ phase diagram at 700^0C. As can bee seen, in most of the compositional triangle the agreement is excellent and the single, two- and three-phase fields have the adequate compositional ranges and all the important features of the experimental diagram are reproduced.
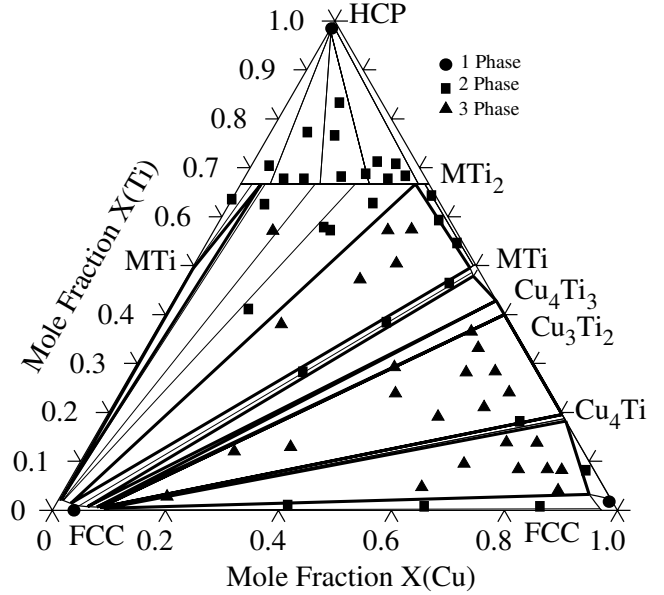

Figure 1: Calculated and experimental data for the $Ag - Cu - Ti$ system at 700^0C.

A detailed comparison of experimental vs. calculated data, as well as the values for the parameters used in the thermodynamic description is available in [1].

References

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