



## Thermodynamics and surface properties of liquid Cu–B alloys

A. Passerone, M.L. Muolo, F. Valenza, R. Novakovic\*

National Research Council (CNR) – Institute for Energetics and Interphases, Via De Marini, 6-16149 Genoa, Italy

### ARTICLE INFO

#### Article history:

Received 13 April 2009

Accepted for publication 9 July 2009

Available online 14 July 2009

#### Keywords:

Equilibrium thermodynamics and statistical mechanics

Surface tension

Surface segregation

Surface thermodynamics

Liquid surfaces

Copper

Boron

Adsorption

### ABSTRACT

The study of the thermodynamic and the surface properties of liquid Cu–B alloys can help better understanding of a complex interfacial chemistry related to liquid Cu–brazes in contact with boride substrates. Despite a simplicity of the Cu–B phase diagram, only a few thermodynamic data are available in the literature, while in the case of the surface properties a complete lack of data is evident. The quasi-chemical approximation (QCA) for the regular solution has been applied to describe the mixing behaviour of liquid Cu–B alloys in terms of their thermodynamic and surface properties as well as the microscopic functions. In view of joining processes related to liquid Cu–brazes/solid boride systems a particular attention is paid to the surface properties of the Cu-rich part of the system and the calculated values are substantiated by the new surface tension experimental data of liquid Cu and Cu–10 at.% B alloy. The tests have been performed by the sessile-drop method under the same experimental conditions. Considering the experimental uncertainties, the effect of oxygen on the surface tension of liquid Cu and Cu–10 at.% B alloy has been analysed by simple model that combines the physical property data included in Butler's equation with the oxygen solubility data and it gives the same results as Belton's adsorption equation.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

The properties of interfaces between dissimilar materials are of fundamental importance in defining the processing, controlling the performance and dictating the functionality of a majority of advanced materials. Indeed, as more stringent requirements and exotic properties are demanded for material components, the use of monolithic single-phase materials is rapidly decreased in favour of multiphase, interface dominated material combinations. Among these, metal–ceramic systems have drawn the highest degree of attention since these systems have proven to possess such unique and versatile material combinations that are deemed to be indispensable for applications ranging from structural to electronic, biomedical, thermal and chemical [1]. In order to exploit the specific characteristics of these materials it is often necessary to join the ceramic parts one to the other or to special metallic alloys. Thus, the knowledge of the interfacial energetics, i.e., the interfacial tensions, interfacial reactions and wettability is mandatory to understand what happens at the liquid metal–ceramic interface during the joining processes [2,3].

Cu-based brazing alloys are widely used and their thermophysical properties are well known. However, in the joining processes, interactions occur between the filler alloy and the substrate which imply an exchange of components and, as a consequence, a modification of the alloy composition. In particular, when dealing with

ultra high temperature ceramics (UHTC) such as transition metal borides, some dissolution of boron has been observed, and a possible variation in the liquid alloy surface tension hypothesized [4,5]. Accordingly, the study of the thermodynamics and the surface properties of liquid Cu–B alloys can help better understanding of a complex interfacial chemistry related to molten Cu–brazes in contact with boride substrates. On the other side, as concerns the applications of the Cu–B system, it is important to mention that, due to the experimental difficulties, only the alloys containing up to 13 at.% of boron have been investigated [6,7]. The high melting point of boron and its strong affinity for oxygen in the liquid phase either make impossible the alloy preparation or put in question the reproducibility of their composition, and thus, the reliability of measured property data [8]. Boron is often used to deoxidize copper and copper alloy melts preventing  $\text{Cu}_2\text{O}$  formation, which exists within the melt as a liquid phase, that, after solidification, results in porous casting artefacts [6]. For the same reason 0.005–0.1 wt.% boron is added to certain gold casting alloys, in which it also acts as a grain refiner [9]. The recent research on copper for microelectronic device interconnections showed that the addition of 2 at.% B may drastically reduce the electrical resistivity, suggesting possible applications for silicon devices. Moreover, when boron is incorporated in copper, improved resistance to oxidation and thus, corrosion has been shown [10]. Another important application of Cu–B alloys concerns the fabrication of Cu/ZrB<sub>2</sub> electrical discharge machining (EDM) electrodes. Namely, the addition of boron to copper significantly improves the wetting characteristics and enables wetting and infiltration [11]. The improved wet-

\* Corresponding author. Tel.: +39 010 6475724; fax: +39 010 6475700.  
E-mail address: [r.novakovic@ge.ieni.cnr.it](mailto:r.novakovic@ge.ieni.cnr.it) (R. Novakovic).

## Nomenclature

$A, B$	components of a binary $A$ – $B$ alloys	$n$	cluster size parameter
$A_{Me}$ ( $A_{MeO}$ )	surface area of metal (metal oxide)	$p, q$	surface coordination fractions
$a_i$ ( $i = A, B$ )	activity of component $i$	$R$	gas constant
$a$	interaction energy parameter	$S$	surface area of alloy
$b$	interaction energy parameter	$S_{cc}(0)$	concentration fluctuations
$C_i$ ( $i = A, B$ )	composition of component $i$	$S_{cc}(0, id)$	concentration fluctuations for the ideal mixing condition
$C, 1 - C$	composition of components $A$ and $B$	$T$	absolute temperature
$C^s, 1 - C^s$	surface composition of components $A$ and $B$	$V_i$ ( $i = A, B$ )	atomic volume of the component $i$
$C_i^j$ ( $i = Me, MeO; j = b, s$ )	composition of components metal and metal oxide	$Z$	coordination number
$E$	configurational energy of the bulk	$\alpha_1$	short-range order parameter
$E_S$	configurational energy of the surface phase	$\alpha_0$	area per adsorbed oxygen atom
$G_{ID}$	ideal Gibbs energy of mixing	$\beta$	reduced coordination factor
$G_M$	Gibbs energy of mixing	$\beta$	auxiliary variable for the bulk phase description
$G_M^{XS}$	excess Gibbs energy of mixing	$\beta^s$	auxiliary variable for the surface phase description
$\bar{G}_i^{Ex,j}$	partial Gibbs excess energy of component $i$ in the phase $j$	$\gamma$	ratio of activity coefficients of $A$ and $B$ components
$H_M$	enthalpy of mixing	$\gamma_i$ ( $i = A, B$ )	activity coefficient of component $i$
$k_B$	Boltzmann constant	$\gamma_{MeO}^{b,0}$	activity coefficient of MeO at infinite dilution
$L$	structural factor	$\Gamma_0$	maximum value of oxygen adsorption at liquid/vapour interface
$N_A, N_B$	number of atoms of components $A$ and $B$	$\varepsilon_{ij}$	energy of $i$ – $j$ bond for regular solution
$N_A^s, N_B^s$	number of atoms of components $A$ and $B$ in the surface phase	$\mu_i$ ( $i = A, B$ )	chemical potential of component $i$
$N$	total number of atoms	$\mu_i^s$ ( $i = A, B$ )	chemical potential of component $i$ at the surface
$N^s$	total number of atoms in the surface phase	$\omega$	interaction energy of alloy
$N_0$	Avogadro's number	$\sigma$	surface tension
$P$	pressure	$\sigma_A$	surface tension of pure component $A$
$q_i^{N_i}(T)$ ( $i = A, B$ )	atomic partition function of component $i$ for the bulk	$\sigma_B$	surface tension of pure component $B$
$q_{i_s}^{N_i^s}(T)$ ( $i = A, B$ )	atomic partition function of component $i$ for the surface phase	$\Xi^b$	grand partition function for the bulk
		$\Xi^s$	grand partition function for the surface phase
		$W_{Me-MeO}$	interaction energy metal–metal oxide

ting of  $ZrB_2$  by Cu–B alloys is related also to the tensioactivity of boron in Cu–B melts, as shown by the thermodynamic calculations reported in [4].

The Cu–B system is characterised by a positive interaction energy, indicating the formation of different two-phase structures due to several polymorphic modifications of boron, as shown by its simple eutectic phase diagram. There is some uncertainty in the reported values. The last Cu–B phase diagram assessment [12] is still incomplete and the evaluated liquidus line should be reassessed. Due to the paucity of the thermodynamic data, there is some uncertainty in the reported values for the eutectic temperature and composition. In order to reoptimise the Cu–B phase diagram, it is necessary to perform experimental measurements to obtain the thermodynamic data over the whole composition range. Moreover, a complete lack of the experimental data on the thermophysical properties of liquid Cu–B alloys was observed. However, some information can be deduced by combining the existing thermodynamic data and theoretical modelling [13,14].

Preliminary investigation of the Hume–Rothery empirical factors such as valence differences ( $=0; 1; 2$ ) [15,16], electronegativity difference ( $=-0.14$ ) [17] and size ratio ( $=1.77$ ) [18,19] for the Cu–B system, with exception of a size ratio, indicate values that are characteristic for segregating alloys [16] confirming a limited solubility in the solid state, and hence the presence of an eutectic reaction [15]. On the other hand, the size ratio,  $V_{Cu}/V_B \approx 1.77$ , has a value that is typical for phase separating alloys, such the Bi–Ga or Ga–Tl monotectic systems. The activity [6,20] and the enthalpy of mixing [21,22] of molten Cu–B alloys deviate positively from the ideal values, confirming a tendency of this system towards segregation.

The concentration dependence of thermodynamic and surface properties as well as the microscopic functions of liquid Cu–B

has been investigated by the quasi-chemical approximation (QCA) for regular solution. For segregating alloys the size effects have an appreciable influence on their surface properties. The magnitude of these effects increases together with a tendency of a system to phase separation [16].

The surface tension literature data on Cu reported in Keene's review [23] together with such data published in the last 10 years and recently collected by Mills and Su [24], including our present experimental results, exhibit a significant scatter. The surface tension of copper measured at its melting point varies between 1257 and 1400 mN/m, while its temperature coefficient takes values from  $-0.38$  to  $-0.10$ . As in previous wetting experiments on borides [4,25] the equilibrated Cu-based alloys have always shown boron contents not higher than  $10 \div 15$  at.%. Accordingly, the Cu–10 at.% B alloy has been chosen for surface tension measurements. The tests have been performed by the sessile-drop method under the same experimental conditions as those of Cu.

The effects of surface-active species on the surface tension of liquid metals and alloys are important in numerous industrial applications as well as for understanding the wetting behaviour of solid substrates by melts. A clear picture of wetting phenomena in such systems allows the predictions of the interface reactions when a liquid is put into contact with a solid phase [26]. The new experimental results have been analysed by using Tanaka's model [27] aiming at establishing the effect of oxygen on the surface tension of Cu and Cu–10 at.% B melts. This model combines Gibbs's and Butler's equations having as input data the Gibbs free energy data, surface tension reference data of pure components, oxygen solubility data, structural data (coordination number, molar volume) and temperature data and it gives the same results as Belton's adsorption equation [28].

Download English Version:

<https://daneshyari.com/en/article/5424054>

Download Persian Version:

<https://daneshyari.com/article/5424054>

[Daneshyari.com](https://daneshyari.com)