Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Surface Science 576 (2005) 175–187

SURFACE SCIENCE

www.elsevier.com/locate/susc

Surface and transport properties of Ag–Cu liquid alloys

R. Novakovic *, E. Ricci, D. Giuranno, A. Passerone

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

Received 7 October 2004; accepted for publication 17 December 2004

Abstract

The applicability of quasi-lattice theory (QLT) to describe surface and transport properties of Ag–Cu liquid alloys is substantiated by surface tension experimental data. The surface tension of molten Ag, Cu and Ag–Cu alloys has been measured by the pinned-sessile drop method over a temperature range. The results obtained are in good agreement with other reported measurements on pure elements and their alloys as well as with calculated surface tension values. The phase diagram of Ag–Cu system shows the existence of a simple eutectic indicating a tendency towards phase separation. The mixing behaviour of Ag–Cu regular alloys has been analysed through the study of surface properties (surface tension and surface composition), dynamic properties (chemical diffusion and viscosity) and microscopic functions (concentration fluctuations in the long-wavelength limit and chemical short-range order parameter) in the frame of quasi-lattice theory combined with a statistical mechanical theory.

Keywords: Equilibrium thermodynamics and statistical mechanics; Surface segregation; Surface tension; Surface thermodynamics (including phase transitions); Copper; Silver; Liquid surfaces

1. Introduction

The interatomic interactions and the related energies of the bonds between *A* and *B* atoms of a binary alloy play a key role in elucidating the mixing behaviour of two metals. From this point of view the condition when heterocoordinated *A*–*B* atom pairs are energetically preferred as nearest neighbours over self-coordinated *A*–*A* or *B*–*B*, or vice versa, leads to classify the binary alloys into either compound forming or segregating systems. In terms of Raoult's law, their thermodynamic properties exhibit negative and positive deviation from this additive rule, respectively. The mixing behaviour of segregating or compound forming alloy systems and their related characteristic phenomena such as phase separation or compound formation cannot be encoded in terms of empirical rules or factors, such as atom size difference, valence and electronegativity differences, solubility

---

* Corresponding author. Tel.: +39 010 6475724; fax: +39 010 6475700.

E-mail address: r.novakovic@ge.ieni.cnr.it (R. Novakovic).

0039-6028/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2004.12.009

Nomenclature

A, B	components of a binary A–B alloys
a_i $(i = A, B)$	activity of component i
a_W	interaction energy parameter
b	size parameter
b_W	interaction energy parameter
C_i $(i = A, B)$	composition of component i
C, $1 - C$	composition of components A and B
C^s, $1 - C^s$	surface composition of components A and B
D_m	inter-diffusion coefficient of any binary alloy
D_{id}	intrinsic diffusion coefficient for an ideal mixture
D_i $(i = A, B)$	self-diffusion coefficient of component i
E	configurational energy of the bulk
E_s	configurational energy of the surface phase
G_M	Gibbs energy of mixing
G_M^{xs}	excess Gibbs energy of mixing
H_M	enthalpy of mixing
k_B	Boltzman's constant
N_A, N_B	number of atoms of components A and B
N_A^s, N_B^s	number of atoms of components A and B in the surface phase
N	total number of atoms
N^s	total number of atoms in the surface phase
N	Avogadro's number
m_i $(i = A, B)$	exponent of viscosity size factor
P	pressure
$q_i^{N_i}(T)$ $(i = A, B)$	atomic partition function of component i for the bulk
$q_{i_s}^{N_i^s}(T)$ $(i = A, B)$	atomic partition function of component i for the surface phase
p, q	surface coordination
R	gas constant
r	size ratio
S	surface area
$S_{cc}(0)$	concentration fluctuations
$S_{cc}(0, \mathrm{id})$	concentration fluctuations for the ideal mixing condition
T	absolute temperature
V_i $(i = A, B)$	atomic volume of the component i
Z	coordination number
W	interaction energy
α	mean surface area of the alloy
α_i $(i = A, B)$	surface area of atomic species i
α_1	short-range order parameter ratio of activity coefficients of A and B components
γ_i $(i = A, B)$	activity coefficient of component i
ϕ_i $(i = A, B)$	parameter of viscosity size factor
η	viscosity
η_i $(i = A, B)$	viscosity of component i
ε_{ij}	energy of i–j bond for regular solution
λ_i $(i = A, B)$	size and shape factor of viscosity of component i
μ, v	stoichiometric coefficients
μ_i $(i = A, B)$	chemical potential of component i
μ_i^s $(i = A, B)$	chemical potential of component i at the surface
σ	surface tension
σ_A	surface tension of pure component A
σ_B	surface tension of pure component B
Ξ^b	grand partition function for the bulk
Ξ^s	grand partition function for the surface phase

parameters and electron concentration [1]. As some of metallic systems do not obey these rules, the factors mentioned above can be only used to indicate a type of mixing and the properties of melts [2,3].

The Ag–Cu system is characterised by a positive interaction energy, indicating the formation of two-phase structures: one phase is Ag-rich and the other is rich in Cu [4,5], as shown by its simple eutectic phase diagram [6]. The constituent elements Ag and Cu have the same fcc-crystal structure [3], the same valence values (=1;2) [3], the same electronegativity value after Pauling (=1.9) [7], but their molar volumes are different. An examination of the Hume–Rothery empirical factors shows the decisive role of the size ratio value