FEB 29 1996

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FREE ENERGY CALCULATIONS OF Cu-Sn INTERFACES

R. Ravelo*, M. Baskes**

*Department of Physics and Material Research Institute, University of Texas, El Paso, TX 79968

**Materials Reliability Department, Sandia National Laboratories, Livermore, CA94551-0969

ABSTRACT

Excess free energies of solid Cu - Solid Sn and Solid Cu - liquid Sn have been calculated employing an adiabatic switching formalism in a Molecular Dynamics (MD) framework. The atomic interactions are described by modified embedded atom method (MEAM) potentials which includes the angular dependence of the electron density to describe bond bending forces necessary to model covalent materials.

INTRODUCTION

The excess energy present in the surface or the interface boundary is an important parameter which controls various thermodynamic and metallurgical processes such as sintering, grain growth, nucleation, cold welding, crack nucleation and growth, adhesion, friction and wear among others. It is thus a pivotal quantity in the understanding of material processes and properties, yet there have been few direct measurements of "interphase" interfacial free energies except in the cases of interfaces separating a solid with its saturated liquid or vapor. Excess surface free energies of interfaces separating two phases of different chemistry, crystallography or in different state (i.e. solid-liquid) are difficult to measure and lacking in the literature. The difficulties, both theoretical and experimental have been summarized by Duga [1]. For instance, calorimetry measurements based on the Åstrom technique [2] assume some value for the associated entropy at the interface and therefore there is a high degree of uncertainty in these type of measurements. Homogeneous nucleation experiments of solid-liquid interfacial free energies also show large variations, with values found in the literature differing by as much as a factor of 2 [3].

There have been few computational studies of surface free energies of Lennard-Jones (LJ) liquids [4] and of LJ solid-liquid interfaces [5,6] but these studies have concentrated on generic LJ systems and to our knowledge there has been no computational work on interphase interfacial excess free energies of systems with different chemistry and physical state. We present here a computational method based on the adiabatic switching formalism [7,8] for computing excess free energies of an interface separating any two phases. Employing this method we have evaluated the excess interfacial free energies in the system Cu-Sn for temperatures in the range 300K - 1200K. The interatomic interactions in this system are described by modified embedded atom method (MEAM) potentials [9]. MEAM has been successfully applied to fcc, bcc, hcp [10] and diamond cubic materials and reproduce quite well diamond α and β -Sn as well as its liquid state [11]. We will discuss the formalism for calculating excess free energies as well as the method employed in fitting Cu-Sn interactions and will present our results on the morphology of the interface with temperature and the excess interfacial free energies values. These values will be compared with solid-liquid Cu and solid-liquid Sn interface energies.

METHODOLOGY AND POTENTIALS

The method employed in the evaluation of the Cu-Sn interfacial free energies is based on calculating the reversible work required to pull apart the surfaces which define the interface. This basic idea has been applied to LJ liquids [4] and to LJ solid-liquid interfaces [5], however in the present case we have eliminated the need of so called external cleaving potentials which are quite cumbersome to use in heterogeneous cases like the present one. The work required to separate the surfaces at the interface can be equated to the energy of adhesion which for our Cu-Sn system can be written as follows:

$$W_{\text{Cu-Sn}} = F_S(\text{Sn}) + F_S(\text{Cu}) - F_I(\text{Cu-Sn}), \quad (1)$$

where $W_{\text{Cu-Sn}}$ is the energy of adhesion, $F_S(\text{Sn})$ and $F_S(\text{Cu})$ are the surface free energies of Sn and Cu respectively and $F_I(\text{Cu-Sn})$ is the interfacial free energy.

The work done in separating the surfaces is evaluated by employing adiabatic switching in a Molecular dynamics (MD) framework [7,8]. Within this method, the free energy difference between two systems whose interactions are described by hamiltonians H_0 and H_1 say, is given by

$$\Delta A = \frac{1}{\tau} \int \langle H_1 - H_0 \rangle dt \quad (2)$$

where ΔA is the free energy difference between system H_0 and H_1 . In the present system, H_0 is a Cu-Sn slab with Cu-Sn interactions and system H_1 is comprised of Cu and Sn slabs with 2 free surfaces each and with no Cu-Sn interactions. This is shown schematically in fig 1. The final system ($H_{\text{Cu}} + H_{\text{Sn}}$) is obtained by adiabatically switching off the Cu-Sn interactions.

FIG. 1. Schematic of Cu-Sn system used to calculate excess free energy. The work done in separating the Cu-Sn surfaces at the interface is given by $\Delta A = (\langle H_{\text{Cu}} \rangle + \langle H_{\text{Sn}} \rangle) - \langle H_{\text{Cu-Sn}} \rangle$.

The surface free energies of Cu and Sn at each sampled temperature were calculated in the same way. Thus, from equation (1) it is straightforward to evaluate $F_I(\text{Cu-Sn})$.

We used slabs of 2000 and 2500 atoms with almost equal number of Cu and Sn types. The Cu side of the interface was Cu(100) which was matched to both β and cubic Sn crystals at 0K. The Z-direction is defined normal to the interface. These configurations were annealed to 900K to create a solid Cu - liquid Sn system. This structure was then equilibrated at various temperatures in

the range 300 - 1200 K and once thermalized, the MD switching runs were done at constant temperature and the excess interfacial free energy was computed. The switching was done over 5 - 10 psec time scales (τ in equation (2)).

MEAM MODEL OF Cu-Sn

The Cu-Sn model was developed using the same methodology as in Baskes et al. [12] for the Ni-Si system. The reference structures for Cu and Sn were taken as the equilibrium structures, fcc and diamond cubic respectively. For convenience the reference structure for the alloy was taken as the L1₂ (cubic) alloy Cu₃Sn even though the equilibrium structure is A3 (hexagonal). The equations for the background electron density and Cu-Sn pair potential are given in Reference [12] and will not be repeated here. The parameters for Cu, Sn, and the reference alloy Cu₃Sn are given in Table 1 using the same definitions as in Baskes [9].

	E_c	r_e	α	A	$\beta(0)$	$\beta(1)$	$\beta(2)$	$\beta(3)$	$t(1)$	$t(2)$	$t(3)$	ρ_0
Cu	3.62	2.50	5.11	1.07	3.63	2.2	6	2.2	3.14	2.49	2.95	1.0
Sn	3.14	2.81	5.09	1	5.0	20.0	10.0	5.0	2.41	5.93	-0.13	1.1
Cu ₃ Sn	3.50	2.68	5.10									

Table 1: Parameters for the MEAM. Values listed are the cohesive energy E_c (eV), the equilibrium nearest neighbor distance r_e (Å), the exponential decay factor for the universal energy function α , the scaling factor for the embedding energy A, the exponential decay factors for the atomic densities $\beta(l)$, the weighting factors for the atomic densities $t(l)$, and the scale factor for the electron density ρ_0 .

Using this model for the Cu-Sn system the properties of Cu, Sn, and Cu₃Sn have been calculated. The results for Cu have been presented previously [9] and will not be repeated here. The results for Sn and Cu₃Sn are presented in Table 2. Agreement with experiment is quite good in most cases. Notable exceptions are the vacancy formation energy and a couple of the elastic constants for β -Sn.

RESULTS

In what follows, we will take the Z-direction to be the direction normal to the interface and the XY plane as the plane parallel to the interface. Figure 2 shows both side and top view profiles of a small cross section ($25 \times 25 \text{ Å}^2$) of the Cu-Sn interface at 300 K and 900 K. No miscibility between Cu-Sn were observed in any of the equilibration or switching runs. This is found to be true for a number of binary metal systems [13]. We find an effective higher density of Sn atoms at the interface which seems to increase with temperature. The interface also appears smoother at higher temperatures. This might be a result of solidification of Sn below 500K and subsequent crystallization for which a higher strain in the Sn is expected due to the large misfit between Cu and Sn. Figure 3 shows the "layer" density (number of atoms as a function of Z) around the

interface at 300K and 900K. The separation between Cu layers does not change appreciably with temperature except for thermal expansion. The contact layer of Sn with Cu at 900K has a density 20-30% higher than at 300K.

PROPERTY	α -Sn	β -Sn	L-Sn	hex-Cu ₃ Sn
a	6.483 (6.483)	5.78 (5.83)		2.69 (2.76)
c		3.13 (3.18)		4.26 (4.32)
$\Delta E^{x \rightarrow \text{ref}}$		-0.03 (-0.03)		0.02 (0.02)
B	0.27 (0.27)	0.404 (0.356)		1.01
C_{xy}	0.12 (0.12)	0.040 (0.042)		0.51
C_{xz}		0.755 (0.134)		0.53
C_{11}		0.740 (0.458)		
C_{66}	0.20 (0.23)	0.126 (0.149)		
E_{1v}^f	2.07	1.31 (0.52)		
α_T		37.5 (23.5)		
ρ_L			6.54 (7.00)	
$d\rho_L/dT$			-0.68 (-0.61)	

TABLE 2. Comparison of MEAM model of Sn with experimental values. Values listed are the lattice constants a and c (Å), energy relative to the reference structure $\Delta E^{x \rightarrow \text{ref}}$ (eV), bulk modulus B (eV/Å³), shear elastic constant in the x-y plane C_{xy} (eV/Å³), shear elastic constant in the x-z plane C_{xz} (eV/Å³), elastic constants C_{11} and C_{66} (eV/Å³), relaxed vacancy formation energy E_{1v}^f (eV), thermal expansion coefficient at room temperature, α_T (10⁻⁶ K⁻¹), liquid density at 900 K ρ_L (g/cm³), and temperature derivative of the liquid density $d\rho_L/dT$ (g/cm³-K). Experimental values in parentheses are taken from Reference [14].

The thickness of the interface can be assessed by plotting the average potential energy per atom as a function of Z. Figure 4 shows such a plot of the potential energy per atom at two different temperatures (300 and 900 K). The dashed line is a guide to point at the ideal location of the interface (at Z=0). Values in the Z < 0 region are those in the Cu slab while Sn-values are found in the Z > 0 region. On the Cu side, only the contact layer shows appreciable variation in the energy per atom relative to bulk values. For Sn, the energy variation with Z is small but larger than for Cu, with values decaying back to nominal bulk values within 4 Å of the ideal interface.

FIG. 2. Side and top view of Cu-Sn interface at both 300 and 900 K. There is a noticeably higher density of Sn atoms at the interface at 900K than at 300K.

FIG. 3. Number of Cu and Sn atoms as a functions of Z around the interface (dotted line). The effective density of Sn atoms around the interface increases with temperature.

FIG. 4. Energy per atom as a function of distance from interface. Cu-atoms are located at $Z < 0$, while Sn atoms are located at $Z > 0$.

FIG. 5. Cu-Sn Interfacial free energy ($\text{eV}/\text{\AA}^2$) as a function of temperature. The dashed line is a guide to the eye.

The calculated interfacial energy as a function of temperature is shown in figure 5. The calculated values are in the range 480-200 ergs/cm^2 . The variation with temperature can be calculated from a fit to the data. We obtain a value of $d\gamma_{\text{SL}}/dT = 0.25\text{-}0.50$ ($\text{ergs}/\text{cm}^2\text{-K}$). As a guide, the experimental value for the solid-liquid interface free energy of Cu and Sn are $\gamma_{\text{SL}}(\text{Cu}) = 177 \text{ ergs}/\text{cm}^2$ (1356 K) and $\gamma_{\text{SL}}(\text{Sn}) = 55 \text{ ergs}/\text{cm}^2$ (500K)..

CONCLUSIONS

We have calculated excess free energies of Cu(S)-Sn(S) and Cu(S)-Sn(L) interfaces as a function of temperature by evaluating the reversible work required to pull the surfaces apart at the interface. This work was calculated using the method of adiabatic switching in a Molecular Dynamics framework. We have employed the MEAM formalism to obtain the potentials describing the interactions in the system. The agreement with experimental properties of Cu and Sn and Cu₃Sn is quite good in most cases. Notable exceptions are the vacancy formation energy and a couple of the elastic constants for β -Sn.

No miscibility or alloying of Cu-Sn was observed in the time scale of our thermalization runs. The calculated interfacial free energy values are 480-200 ergs/cm² corresponding to temperatures in the range of 300-1200K respectively. Work on liquid Sn solid Cu-Sn alloys (Cu₃Sn) is currently in progress.

This work was supported by the Department of Energy under contract No. DE-AC04-94AL85000.

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