International Journal of Thermophysics, Vol. 22, No. 4, 2001

Surface Tension of Ni-Cu Alloys: A Molecular Simulation Approach[1]

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The Monte Carlo (MC) method and the embedded-atom method (EAM) are used to calculate the surface tension and the temperature dependence of the surface tension of nickel-copper alloys. The simulation of the surface tension is performed through the calculation of the cohesive work of the alloy. The calculated surface tensions of the alloys are 30 to 40% larger than experimental values, while the changes in surface tension as a function of Cu composition show similar behavior in both calculated and experimental results. The simulation results for the temperature dependence of the surface tension in the undercooled region appear to be identical with that above the melting point, and for the Ni-Cu alloys, the temperature coefficients decrease with an increase of copper concentration.

KEY WORDS: molecular simulation; Monte Carlo method; Ni-Cu alloy; surface tension.

1. INTRODUCTION

The surface tensions of liquid metals and alloys are of particular scientific and technological importance in analysing and understanding many metallurgical processing operations. Its dependence on temperature leads to the well-known Marangoni convection, which plays a central role in some casting and welding situations. Experiments are carried out under most situations when these values are needed. However, liquid metals are difficult to handle due to the high temperatures and their high reactivity. For example, they tend to oxidize which dramatically changes the optical, thermal, and mechanical properties of the surface. Even with the levitation

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[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25–30, 2000, Boulder, Colorado, U.S.A.

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processing and oscillating drop techniques, the experiments often suffer from ambiguities in the interpretation of the resulting frequency spectra [1–3]. As an alternative, many attempts have been made to predict the surface tension of simple liquids and liquid metals over the past several decades. Among the methods, computer simulation with Monte Carlo or molecular dynamics methods is considered to be one of the most promising methods [4].

There are two main routes from the molecular simulation of a finite system to the surface tension of the fluid. The first is to produce a liquid–vapor interface in the simulation and calculate the surface tension from the mechanical expression. For example, via the virial theorem and two-body distribution function the surface tension can be expressed as

$$\sigma A = \left\langle \sum_{i<j} (r_{ij} - 3z_{ij}^2/r_{ij})\, u'(r_{ij}) \right\rangle \tag{1}$$

The second method is from the thermodynamic expression of the surface tension, namely, from the molecular simulation of the free energy needed in forming a new surface. One of these operations was carried out by Miyazaki et al. [4], in which the free energy required to create reversibly a surface in the bulk liquid is obtained from a Monte Carlo simulation. Generally speaking, the first approach suffers from rather high fluctuation and statistical uncertainty, and the second method introduces additional complexity into performance.

An alternative method to calculate the surface tension is to calculate the work of cohesion of the liquid. This method was adopted by Padday and Uffindell in 1968 [5], and used to calculate the surface tension of n-alkanes and the interfacial tension between the n-alkanes and water. The integration of the pair potential is calculated by assuming that the radial distribution function of volume elements is a step function. Lu [6] applied this method to calculate the surface tension of liquid argon, nitrogen and oxygen by summing the interaction energy across an assumed surface in the MC simulation. His work achieved reasonable agreement between the simulation results and experimental data. More recently, we [7] extended this method to simulate a liquid transition metal, nickel. However, the agreement with experimental values was not so satisfactory, with typical deviations of 20 to 40%. Considering that a computer simulation of producing a liquid metal surface can only be used to predict the surface tension of pure liquid copper with an accuracy of 30% [8], this method is considered worthwhile since it provides reasonable results in a straightforward and simple manner. In the present study, this method has been extended to alloys. The surface tensions of Ni-Cu alloys were predicted from the calculation of the work of cohesion in the Monte Carlo simulations.

2. MONTE CARLO SIMULATIONS

The Monte Carlo method has been discussed in detail elsewhere [9]. In short, this method is based on a stochastic process which, by moving molecules one at a time, generates a Boltzman-weighted chain of configuration of a given N-particle system. The quantities of interest are obtained as configurational averages of the generated long chain.

2.1. Embedded-Atom Method

To perform a molecular level simulation for the thermophysical properties of metals, an inter-particle interaction model that is both accurate and computationally simple is needed in order to be able to handle a lager number of particles. The embedded-atom method (EAM) proposed by Daw and Baskes [10, 11] provides such a computationally simple model for simulating metals. It has achieved great success in simulating the structure of liquid pure metals and alloys [12].

The EAM is based on density functional theory, in which the energy of an arbitrary configuration of atoms is a unique function of the electron distribution. The energy is subdivided into the embedding energy, which is the energy required to "embed" each atom into the local electron density contributed by all other atoms, and a short-range doubly screened pair interaction that accounts for the core-core repulsion. The total energy is written as:

$$E_{\text{total}} = \sum_i F_i(\rho_i) + \tfrac{1}{2} \sum_{ij,\, i \neq j} \phi_{ij}(r_{ij}) \tag{2}$$

$$\rho_i = \sum_{j \neq i} f_j(r_{ij}) \tag{3}$$

where F_i is the embedding energy for placing an atom into that electron density, ϕ_{ij} is a short-range pair interaction representing the core-core repulsion, and r_{ij} is the separation of atoms i and j. ρ_i is the total local electron density at atom i, computed as a superposition of the atomic electron density of the rest of the atoms in the system, $f_j(r_{ij})$ is the atomic electron density of atom j due to atom i. The sums are over all atoms.

For an alloy model, an embedding function $F(\rho)$ and an atomic electron-density function $f(r)$ must be specified for each atomic species, and two-body potentials $\phi(r)$ must be specified for each possible combination of

Table I. Model Parameters. ϕ_e is in eV. f_e acts as a Dimensionless Scaling Factor. α, β, and γ are Dimensionless

Atom	Model parameters					
	E_c	f_e	ϕ_e	α	β	γ
Ni	4.45	0.41	0.74	4.98	6.41	8.86
Cu	3.54	0.30	0.59	5.09	5.85	8.00

atomic species. Note that the embedding energy does not depend on the source of the background charge density. Thus, the same embedding function could be used to calculate the embedding energy of an atom that would be used in the pure metal. This makes this method particularly appealing for studies of alloys.

In this paper, an analytic EAM model developed by Johnson [13, 14] for an alloy was adopted:

$$f(r) = f_e \exp[-\beta[r/r_{1e} - 1]] \tag{4}$$

$$\phi(r) = \phi_e \exp[-\gamma[r/r_{1e} - 1]] \tag{5}$$

$$F(\rho) = -E_c\left[1 - \frac{\alpha}{\beta}\ln[\rho/\rho_e]\right][\rho/\rho_e]^{\alpha/\beta} - \Phi_e[\rho/{}_e]^{\gamma/\beta} \tag{6}$$

$$\phi^{ab}(r) = \frac{1}{2}\left[\frac{f^b(r)}{f^a(r)}\phi^{aa}(r) + \frac{f^a(r)}{f^b(r)}\phi^{bb}(r)\right] \tag{7}$$

where $\rho_e = 12 f_e$, $\Phi_e = 12\phi_e$, and f_e, ϕ_e, α, β, and γ are model parameters. r_{1e} is the equilibrium nearest-neighbor distance in a perfect crystal. All the model parameters used are listed in Table I.

2.2. Methods of Surface Tension Calculation

In Fig. 1, we show the process of producing two new interfaces from a liquid column with a unit cross section. For the separation process,

$$\Delta G = 2\sigma_A = W_{AA} \tag{8}$$

The quantity W_{AA} is known as the work of cohesion, since it equals the work required to pull a column of liquid A apart. This provides us with a possible approach for molecular simulation of the surface tension. Note that during the process of separation, no account has been taken of the equilibration of the surface region. It has been assumed that the bulk

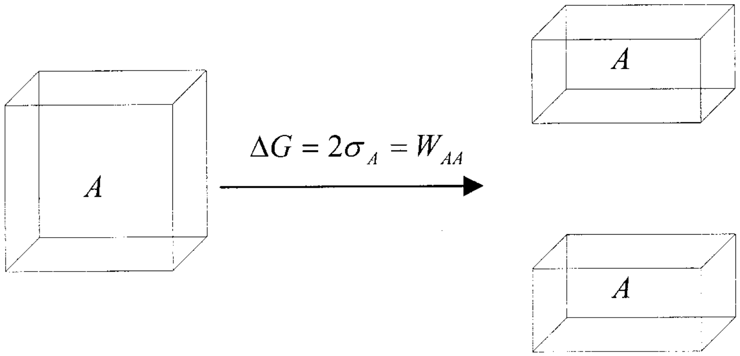

Fig. 1. The process of producing two new interfaces from a liquid column.

structure of the liquid phase is maintained right up to the surface and is retained at all stages of surface formation. However, the structure of the surface region is unlikely to be the same as the bulk due to the imbalance of attractive force, therefore, further energy must enter or leave the system as the freshly formed surface approaches equilibrium. Thus, to obtain the surface free energy, it is necessary to know the quantity of heat entering the system to obtain equilibrium, Q (a quantity almost impossible to measure), and the entropy increase during the surface formation, S.

$$\Delta G = 2\sigma_A = W_{AA} + Q - TS \tag{9}$$

In the calculation of the surface tension of n-alkanes [5], it has been found to be reasonable to omit the last two terms in the Eq. (9), implying that the quantities Q and TS are numerically equal and cancel each other. There is no evidence that for liquid metals this approximation is still reasonable. However, we have to make the same assumption as a necessary condition for a simple method of estimating the surface tension.

2.3. Calculation of Work of Cohesion

The simulated system is in a cubic box with periodic boundary conditions. It is assumed that there exists an interface in the box, which is parallel to the x and y axes and perpendicular to the z axis. Then the work of cohesion can be calculated through the statistics of the interaction between the atoms belonging to different sides of the interface.

However, the surface tension calculated with the above method is the surface tension between the simulated liquid metal and vacuum. In this paper, the surface tensions between the liquid alloys and argon are obtained by taking into account the surface tension between gaseous argon and vacuum.

3. RESULTS AND DISCUSSION

In the present simulation, the system starts in a cubic box with a face-centered configuration, consisting of 500 atoms. Periodic boundary conditions are applied in the *x*, *y*, and *z* directions. Simulations are carried out in NVT ensembles because they have less fluctuation than NPT ensembles. In each run, the size of the system was rescaled after a primary equilibrium, so that the pressure of the system is maintained at 0 to 1 atm. In order to achieve a fully equilibrated liquid phase, each simulation runs for up to 4×10^5 Monte Carlo steps, and generates 2×10^8 configurations. After equilibrium is achieved in the system, 2×10^4 Monte Carlo steps are used to calculate the surface tension and other properties of the system.

Surface tensions of liquid nickel-copper alloys in the temperature range of 900 to 1743°C are obtained. For the Ni-20% Cu alloy, these temperatures correspond to an undercooling of 230°C and to a superheating of 568°C.

Figure 2 shows comparisons between the predicted and measured [15] surface tensions of Ni-Cu alloys of different Cu composition at a fixed temperature of 1743°C. It can be seen from the figure that our simulation results lie 30 to 40% higher than the experimental data. Although the predicted surface tensions are always higher than the experimental values,

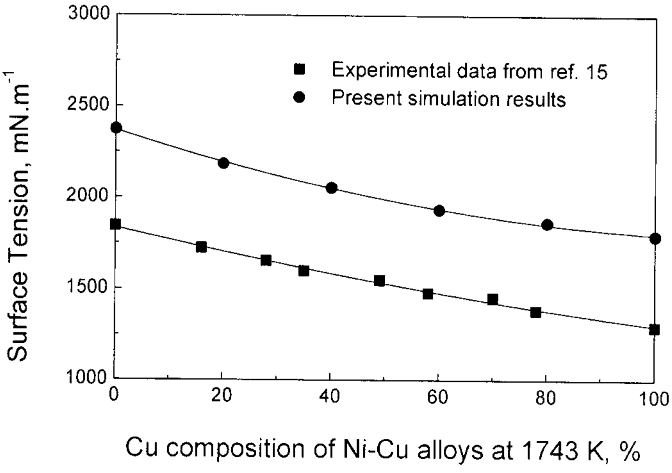

Fig. 2. Comparison between simulation results and experimental data.

the changes in surface tension as a function of Cu composition show a similar behavior for both experimental and calculated results.

In a previous study by the authors [7], the surface tensions of a pure transition metal are calculated. The results lie 20 to 40% below the experimental values when an effective pair potential developed from EAM is adopted. In that simulation, the equilibrium electron density in the pair potential model is assumed to have no contribution to the inter-particle interaction across an interface, considering that the inter-particle interaction across an interface is dominated by the pair forces. In the present study, an analytic EAM model instead of an effective pair potential model is employed, and the calculated surface tension of pure transition metals are 30 to 40% higher than experimental data, implying that the equilibrium electron density should have significant contributions to the calculation of the work of cohesion.

The relationships between the temperatures and the simulated surface tensions of Ni-20% Cu, Ni-40% Cu, and Ni-60% Cu alloys are given in Fig. 3. It can be seen from Fig. 3 that the simulation results for the temperature dependence of surface tensions in the undercooled region appear to be identical with those above the melting point. For Ni-Cu alloys, the temperature coefficients decrease with an increase in copper composition. Experimental values of the temperature dependence of Ni-Cu alloys are not available. Even for pure liquid nickel and copper, these quantities are not well known experimentally, because the available experimental values have considerable discrepancy [7, 16]. Thus, the simulation results for the

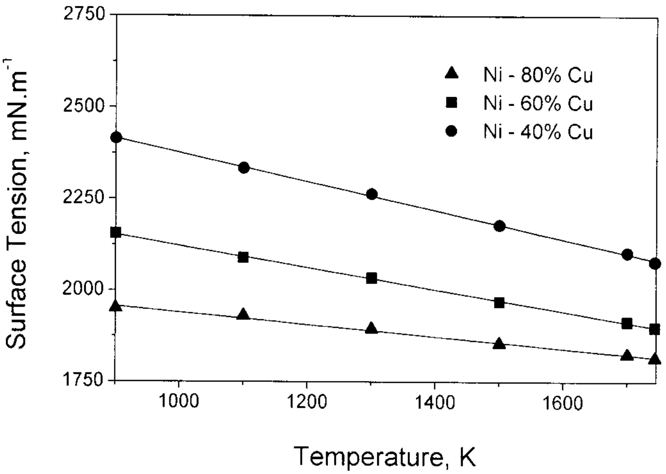

Fig. 3. Temperature dependence of surface tensions of Ni-Cu alloys.

temperature dependence of the surface tensions of Ni-Cu alloys are not compared with experiment in this paper.

4. CONCLUSION

Surface tensions of liquid nickel-copper alloys have been predicted with a Monte Carlo simulation through the calculation of the work of cohesion. The temperature ranges from 900 to 1743°C. For the Ni-20% Cu alloy, these temperatures correspond to an undercooling of 230°C and to a superheating of 568°C. When compared with available experimental data, the simulated surface tensions of the alloys are 30 to 40% larger, while the changes in surface tension as a function of Cu composition show similar behaviors for both experimental and calculated results. As to the temperature coefficient of the surface tension, the simulated value in the undercooled region appears to be identical with that above the melting point, and for the Ni-Cu alloys, the temperature coefficients decrease with an increase of copper concentration.

ACKNOWLEDGMENTS

Support from the National Natural Science Foundation of China under Grand Number 59876016, the High Technology Research and Development Program of China (863 program), the Tongfang High Performance Computation Foundation, and the Fundamental Research Foundation of Tsinghua University is gratefully acknowledged.

REFERENCES

1. S. Sauerland, G. Lohofer, and I. Egry, *J. Non-Crystalline Solids* **156–158**:833 (1993).
2. K. C. Mills and R. F. Brooks, *Mat. Sci. Eng.* **A178**:77 (1994).
3. J. Egry, G. Lohofer, and S. Sauerland, *Int. J. Thermophys.* **14**:573 (1993).
4. J. Miyazaki, J. A. Barker, and G. M. Pound, *J. Chem. Phys.* **64**:3364 (1976).
5. J. F. Padday and N. D. Uffindell, *J. Phys. Chem.* **72**:1407 (1968).
6. Z. Lu, *J. China Textile Univ.* **17**:88 (1991).
7. M. Chen, C. Yang, and Z. Y. Guo, *Mat. Sci. Eng.* **A292**:203 (2000).
8. L. M. Holzman, J. B. Adams, S. M. Foiles, and W. N. G. Hitchon, *J. Mat. Res.* **6**:298 (1991).
9. M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987).
10. M. S. Daw and M. I. Baskes, *Phys. Rev. Lett.* **50**:1285 (1983).
11. M. S. Daw and M. I. Baskes, *Phys. Rev.* **B29**:6443 (1984).
12. S. M. Foiles, *Phys. Rev.* **B32**:3409 (1985).
13. R. A. Johnson, *Phys. Rev.* **B37**:3924 (1988).
14. R. A. Johnson, *Phys. Rev.* **B39**:12554 (1989).
15. K. Nogi, W. B. Chung, A. McLean, and W. A. Miller, *Mat. Trans., JIM* **32**:164 (1991).
16. N. Eustathopoulos, B. Drevet, and E. Ricci, *J. Crystal Growth* **191**:268 (1998).