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ENERGETICS OF SOLID/SOLID AND LIQUID/SOLID INTERFACES.

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BY

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Introduction

The main thrust of this research was to develop better understanding of the interfacial energetics of crystalline particles of one phase confined (or embedded) in matrices of another phase. Much of the work that motivated this research had been performed on Pb particles embedded in Al. Furthermore, significant contributions to that body of knowledge had emerged from collaborative work between Dr. U. Dahmen of the National Center for Electron Microscopy at LBNL and Prof. E. Johnson of the Neils Bohr Institute of the University of Copenhagen. Thus, the work performed under this Grant benefited from significant input into the design of the research from Dr. Dahmen and Prof. Johnson, who were officially listed as collaborators on the grant.

Beyond interest in interfacial energies, there were several intriguing observations on Pb particles embedded in Al for which understanding was lacking. These included observations of large melting point elevation, or superheating, of embedded Pb particles. The melting temperature of these particles was found to increase with decreasing particle size, and to rise several tens of degrees above the bulk melting temperature for nano-scale particles. Since nucleation phenomena play an important role in melting and freezing, it was clear that the difficulties of interpreting superheating during melting could not readily be addressed without knowledge of the interfacial energies that enter into the formalism used to predict nucleation effects.

The approaches taken in the studies included computer simulations, experimental studies and analytical modeling. Although about half of the work focused on Pb particles embedded in Al, other systems and issues were also addressed.

Research Results

1. Simulations of the free energy of Pb-Al interfaces.

When the research was initiated, there were no data available on the interfacial energies of Pb/Al interfaces. It was known, however, that when face centered cubic (fcc) Pb crystallites are embedded in fcc Al, they adopt a simple cube-on-cube orientation relationship, such that the three principal crystallographic axes of Pb are aligned with those of the Al matrix. In addition, the equilibrium crystal shape of Pb crystallites in Al was known to be cubo-octahedral and bounded exclusively by $\{111\}$ and $\{100\}$ interfaces. Thus, in the context of interfacial energetics, the $\{111\}$ and $\{100\}$ interfaces were of primary interest. Although direct experimental measurement of those energies was part of the research plan, the ability to calculate these energies by atomistic computer simulations was considered important for the purposes of subsequent modeling of melting and freezing.

Atomistic computer modeling of interfacial properties requires the availability of reliable interatomic interactions. Well-tested glue-type interatomic potentials for pure Pb and Al were available in the literature. (Glue potentials are semi-empirical potentials that are quite similar to the widely used embedded atom method potentials). However, a Pb-Al

potential, which would be needed to describe interactions across a Pb/Al interface, had not been constructed. It was therefore necessary to begin the simulation studies by developing the needed Pb-Al interaction. This was performed and reported in a first publication [1]. (Numbers in square brackets in this report refer to papers published under this grant. They are listed at the end of the report in the section on " Publications Acknowledging DOE Support"). The reliability of the Pb-Al interaction potential was tested by reproducing with fair success the known Pb-Al phase diagram [1].

As a second step in this research, calculations were performed to obtain the structure and free energy of the {111} and {100} Pb/Al interfaces [2]. Although there were no experimental values of these energies available for comparison, the interfacial free energy ratio: $\gamma_{(100)}:\gamma_{(111)}$, is known from experiments on the equilibrium crystal shape of Pb in Al near the melting temperature of Pb. The simulations yielded a temperature-dependent ratio, which varied from 1.20 at 300 K to 1.10 at 500 K, in good agreement with the experimental value of 1.15 at 573 K. These results were satisfying in another way. The surface energy ratio, $\gamma_{(100)}:\gamma_{(111)}$, for isolated Pb particles in vacuum is only 1.02, and is given by glue potential calculations as 1.01. Thus, the significant difference in anisotropy between isolated and Al-embedded Pb particles was correctly captured by the glue potential [2]. The results of this study were published together with our collaborators on this project, Dr. Dahmen and Professor Johnson.

2. Modeling the configuration of two phases confined to a cavity of fixed shape

This work was performed in collaboration with Drs. D. Chatain and S. Hagege, both of whom are associated with CNRS laboratories in France. The work was prompted by high-resolution transmission electron microscope (HRTEM) observations by Hagege of 50 nm Pb precipitates embedded in Si that were produced by rapid solidification of liquid Si-Pb alloys. The apparent shape of the embedded Pb precipitates in this case is cubo-octahedral, as it is in the case of Pb in Al. However, careful analysis of the HRTEM images reveals that the Pb particles occupy only part of cubo-octahedral-shaped cavities in the Si matrix, the remainder of the cavity being filled with Pb vapor. The formation of this unusual structure is thought to proceed as follows. During freezing, liquid Pb precipitates form at high temperature in the Si matrix and their shape is cubo-octahedral. When Pb freezes in the confining Si cavity, it contracts due to the specific volume change associated with freezing. At the temperature of Pb solidification, the Si matrix is too rigid to change its shape, and the contraction of the Pb due to solidification leaves behind a void filled with Pb vapor. However, independently of the precise mechanism of formation of the vapor-filled void, there are interesting questions about the factors which control the respective shapes of two phases (Pb solid and Pb vapor in this case) which occupy a cavity of given shape.

In order to analyze this problem, energy expressions for several different ways of distributing the solid and vapor phase in a cavity were derived [4]. A few simplifying assumption were made, namely that the walls of the cavity all had the same interfacial energy, and that the two phases were separated by planar interfaces. When two phases are redistributed in a cavity, the only part of the energy that can change is that due to the

interfaces present. Calculations based on the different expressions showed that the manner in which the two phases are distributed depends on only two parameters: the volume fraction of one of the two phases, and a wetting factor analogous to the cosine of the contact angle of the solid phase on the walls of the cavity. This framework was used to construct a stability diagram, which identifies the domains of stability of four different ways of distributing the two phases in a cavity as a function of the two parameters. By using appropriate values of the parameters for the case of Pb in Si, good agreement was obtained between the experimentally observed and predicted shapes of the solid and vapor phases of Pb coexisting in the Si cavities.

In a follow-up paper (which also involved participation of Prof. W.C. Carter of MIT and his graduate student E.J. Siem) some of the assumptions of the previous calculations were relaxed [5]. This included allowing the walls of the cavity to have different energies (i.e. introducing cavity surface energy anisotropy), or allowing the interface separating the two phases in the cavity to have an isotropic energy (as would be the case if one of the phases were a liquid and the other a vapor). Each of these assumptions was tested separately, and each was found to have an effect on the detailed shape of the stability diagrams obtained in the previous paper. The most interesting outcome was obtained when the interfacial energy between the two phases was taken to be isotropic. Whereas in all other cases each of the two phases in the cavity were continuous, making the interface between the two confined phases isotropic leads to stable configurations in which one of the phases becomes discontinuous, i.e. is made up of several particles. This means that certain configurations consisting of several particles of one phase *can be stable with respect to Ostwald ripening*.

3. Measurement of the Pb/Al {111} and {100} interfacial energies

These interfacial energies were measured by a solid-state wetting technique, which had been developed during previous DOE-sponsored research. The method involves the equilibration of small particles of one material (Pb in this case) on a monocrystalline substrate of another material (in this case either Al(111) or Al(100)). The equilibration is performed *in-situ* under ultrahigh vacuum, in a scanning Auger microprobe. After equilibration, the surface compositions of both particles and substrate are obtained by Auger electron spectroscopy, in order to determine the level of adsorption of the particle material at the surface of the substrate, and vice versa. The adsorption on these surfaces can then be used to correct their surface energies by integrating the Gibbs adsorption isotherm. Finally, the corrected surface energies, together with measurements of the contact angle of the particle on the substrate can be used in conjunction with Young's equation to extract the energy of the interface between the particle and the substrate. This is the desired interfacial energy if the particle lies on the substrate in the appropriate epitaxy. Fortunately in the case of Pb on Al substrates, the correct orientation relationship was obtained.

This method had been used before on different particle/substrate combinations (e.g. Pb on Cu) with excellent results. However, in the case of Pb on Al, the application of the solid-state wetting approach turned out to be more complex than expected. The main

difference between Pb on Al and other systems is that the adsorption of Pb on the Al substrate is much stronger, amounting to about 1.8 monolayers. When the adsorption of the particle phase on the substrate is smaller than one monolayer, it is quite simple to integrate the Gibbs adsorption isotherm. However, additional assumptions are necessary in cases where the adsorption exceeds one monolayer, thereby increasing the probable error of the final results. The values obtained were $217 \pm 34 \text{ mJ/m}^2$ and $330 \pm 40 \text{ mJ/m}^2$ for the Pb/Al {111} and Pb/Al {100} interfacial energies, respectively [6, 7]. Although these results do provide values that may be useful for the interpretation of experiments on the Pb-Al system, the probable errors are larger than we would have desired.

4. Melting behavior of nano-scale Pb particles embedded in an Al matrix

In view of the poorly understood melting point elevation of Pb particles embedded in Al, that had been observed experimentally by our formal collaborators (Dahmen and Johnson), it was decided to investigate this phenomenon by computer simulation methods. The major requirement of useful simulations is the availability of reliable potentials, and this problem had already been resolved for the purposes of computing the energies of the {111} and {100} Pb/Al interfaces (described above). The molecular dynamics method was chosen to model the melting behavior of embedded nano-scale Pb particles ranging in size from about 2.5 to 6 nm [9]. All the Pb particles studied were found to melt well above the bulk melting temperature of Pb. Two trends emerged from the simulations. In general, melting point elevation increased with decreasing Pb particle size, as expected from experimental observations. However, a damped oscillation in melting point elevation was found to be superimposed on this trend.

In order to explain both the general trends and the oscillatory behavior, a phenomenological model of melting was developed, based on considerations of interfacial energy, volume expansion and lattice mismatch. This model showed that the general trend of increasing melting point with decreasing particle size was directly attributable to the fact that the difference between the liquid Pb/solid Al and the solid Pb/solid Al interfacial energies is positive, i.e. that the liquid/solid interfacial energy is larger than the corresponding solid/solid interfacial energy. This may seem surprising, but is indeed consistent with trends seen in some of our other work on the similar Pb-Cu system. The second result of the simulations consisted of the damped oscillatory change in melting point elevation. In this case, the phenomenological model led to the conclusion that periodic variation of melting point with size is due to an oscillatory strain energy contribution arising from the large size mismatch between Pb and Al atoms.

Lastly, it is worth mentioning that the simulation work also provided an answer to a question that could not be resolved experimentally, namely: where does melting of the cubo-octahedral embedded Pb particles start, i.e. where is liquid nucleated? By inspecting snapshots derived from the simulations, it was possible to conclude that melting occurs via liquid nucleation at the higher energy Pb/Al{100} interfaces.

5. Dependence of grain boundary segregation on grain boundary character

One important issue about embedded particle interfaces is the question of the possible interaction of those interfaces with other interfaces in the material. A good example is an embedded particle residing at a grain boundary (GB) in the matrix. In order to understand the energy balance between the particle interfaces and the GB, and hence the effects of energy balance on particle shape, it is important to know the range over which GB energy can vary. Also, since the systems of interest necessarily consist of two components, solute segregation at GB's can modify the GB energy and therefore the range of GB energies in the material. As a first step in this direction, it was considered useful to investigate the manner in which GB segregation depends of the 5 macroscopic parameters of GB orientation, namely the so-called GB character.

Prior to this work, there was no model available to predict the dependence of GB segregation on character. The approach taken was to adapt a previous model of surface segregation as a function of surface orientation, where only two (rather than five) orientation parameters are needed. However, beyond orientation variables, GB's differ from surfaces in one other important respect: the numbers of "broken bonds" at these two interfaces are quite different. Thus, it was also necessary to make use of a recently developed method for estimating the numbers of broken bonds at a GB.

By modifying the two previous models to make them consistent, it was possible to combine them and to produce a new analytical framework for describing the variation in GB segregation over the five-parameter GB orientation space. This was formulated for the case of fcc metal alloys. Surprisingly, no adequate experimental results were available to test the predictive quality of the model, and it was necessary to compare model predictions against a limited set of computer simulations of grain boundary segregation (performed by other researchers). Excellent agreement was obtained between model predictions and computer simulation results. A paper describing this work has been accepted for publication [10].

6. Review articles

Two review articles were written during the period of this grant [3, 8]. The work described covered topics from DOE-sponsored as well as other research. These papers therefore acknowledge both DOE and other sources of research funding.

Publications Acknowledging DOE Support

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2. A. Landa, P. Wynblatt, A. Johnson and U. Dahmen, Computer Simulation of Pb/Al Interfaces: *Acta Mater.* **48**, 2557 (2000).
3. P. Wynblatt, Effects of Interfacial Segregation on Wetting in Solid Metal-on-Metal and Metal-on-Ceramic Systems: *Acta Mater.* **48**, 4439-4447 (2000).*
4. D. Chatain, P. Wynblatt and S. Hagege, The Shapes of Two Phase Particles: The Case of Trapped Voids in Lead Particles Embedded in Silicon, *Philos. Mag.* **A81**, 1873 - 1886 (2001).
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6. Z. Shi, J. Lowekamp and P. Wynblatt, Energy of the Pb{111}//Al{111} Interface, *Metall. Mater. Trans.* **33A**, 1003-1007 (2002).
7. Z. Shi and P. Wynblatt, A study of the Pb/Al(100) Interfacial Energy, *Metall. Mater. Trans.* **A33**, 2569-2572 (2002).
8. P. Wynblatt, Comparison between Modeling and Experimental Measurements of Interfacial Properties, *Appl. Surf. Sci.* **219**, 39-46 (2003).*
9. Z. Shi, P. Wynblatt and S. G. Srinivasan, Melting Behavior of Nanosized Lead Particles Embedded in an Aluminum Matrix, *Acta Mater.* **52**, 2305-2316 (2004).
10. P. Wynblatt and Z. Shi, Relation between Grain Boundary Segregation and Grain Boundary Character in FCC Alloys, *Interface Sci.*, accepted.

* Review articles that acknowledge DOE as well as other support.