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Progress Report for

EQUILIBRIUM COMPOSITION OF INTERPHASE BOUNDARIES

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by

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DISCLAIMER

The work reported here was initiated in August of 1988, and will come to an end in July 1991. As of this writing, the research program is in its 27th month. The program has employed both modeling and experimental approaches. Most of the objectives of the modeling component of the research have already been achieved. Progress with the experimental phase of the research has been slower. These two aspects of our activities are summarized separately in the following two sections.

Results of Modeling Interphase Boundary Composition

Two modeling approaches have been used to investigate segregation effects at interphase boundaries. The first approach is based on the nearest neighbor bond model, used in conjunction with the regular solution approximation, and is an extension of an earlier framework developed to address segregation phenomena at free surfaces [1]. This approach was first applied to coherent interphase boundaries in two-component systems by Lee and Aaronson [2]. However, in the limit of two-component systems, this approach merely predicts a symmetric composition profile across the interface, and does not yield useful information on segregation effects in the vicinity of the boundary. In order to make this approach useful in the context of segregation phenomena, it must be generalized to multicomponent systems. This was implemented [3] during the present research program, by combining the discrete regular solution bond model approach with the continuum Cahn-Hilliard formalism of gradient thermodynamics [4]. When applied to two-phase, three-component systems, the framework yields analytical expessions for the composition profiles of all three components in the vicinity of the interface, which do not in general display any symmetry across the interphase boundary. In addition, the compositional excess at the interface, and the calculated interfacial energy can be shown to be consistent with the Gibbs adsorption isotherm, indicating that this atomically discrete model is compatible with the thermodynamic limit.

In a follow-on paper [5], we have rederived the results of ref. 3, without recourse to the Cahn-Hilliard formalism. In this work, the model was also exercised for three different Ni-Ag-X alloy systems containing low concentrations of X (where X stands for Cu, Pd or Au) all of which consist of coexisting Ni-rich and Ag-rich phases. This investigation was conducted in order to indentify systems which are likely to display experimentally measureable segregation effects at interphase boundaries. The results showed that Cu segregates strongly, Pd segregates moderately and Au segregates weakly, to the Ni/Ag interface. The prediction that Au segregates only weakly to interfaces in Ni-Ag-Au is consistent with previous qualitative experimental observations obtained in that system [6], and thus validates the predictive abilities of the model, at least in a qualitative sense.

The nearest neighbor bond model approach described above is limited to the treatment of coherent interphase boundaries, and is not expected to provide highly quantitative results in the case of the more common semicoherent boundaries. Coherent boundaries are those where the crystal lattices on both sides of the interface are matched perfectly. In phases with the same crystal structure, this can occur either if the lattice constants of the two phases separated by the interface are identical, or if they are forced to be identical by elastic constraints. The former case is unlikely, and the latter case only prevails when the volume

of at least one of the phases is small. Thus, interphase boundaries are frequently semicohent, i.e. the lattice mismatch between the phases is accomodated at the boundary by the presence of misfit, or interfacial, dislocations. In order to model this more interesting type of interphase boundary, we have employed a second modeling approach, based on Monte Carlo simulation, in conjunction with the embedded atom method (EAM). The EAM is a powerful new method for describing interatomic interactions in metallic systems [7]. Unlike simple pair potentials, it includes certain many-body interactions that depend on the local environment of an atom. It has been applied to the calculation of a broad range of properties in pure metals and alloys [8-10], as well as to the computation of properties pertaining to interphase boundaries [6,11,12,13].

The Monte Carlo approach has been applied to semicoherent interphase boundaries in Cu-Ag-Au alloys dilute in Au. These alloys consist of coexisting Cu-rich and Ag-rich phases, which differ in lattice constant by about 12%, such that good matching across the interface occurs when nine structural units of the Cu-rich phase are opposed to eight structural units of the Ag-rich phase. Thus far, interfaces with two different orientations have been studied: {001}-Cu // {001}-Ag, <110>-Cu // <110>-Ag; and {111}-Cu // {111}-Ag, <110>-Cu // <110>-Ag. These two interfaces will be referred to as the (001) and (111) interphase boundaries, for short.

The study of the (001) interface has essentially been completed, and submitted for publication as two manuscripts [14,15]. The first of these reports the results obtained on the relation between composition and structure at ternary Cu-Ag-Au interfaces, and the second focuses on the interesting structural differences between binary Cu-Ag and ternary interfaces. The highlights of the results are summarized below.

In order to conduct Monte Carlo simulations of a given interface, it is first necessary to determine the compositions of the coexisting bulk phases which are consistent with the interatomic interactions dictated by the EAM. This can be accomplished by finding the values of the chemical potentials of the components for which the bulk phases coexist, and using those values in subsequent interface simulations. It is worth noting that the compositons predicted by the EAM for the bulk phases at two temperatures, as well as the slopes of the related tie-lines, are generally consistent with the experimentally known values. This favorable comparison with experiment lends credibility to the results of these EAM-based simulations. Simulations of the (001) semicoherent boundary showed that Au segregates to the interface, and that silver penetrates into the Cu side of the boundary. In addition to compositional information, the Monte Carlo simulation provides configurational, i.e. structural, information about the interface. An important finding of these simulations is that the penetration of Ag into the Cu side of the interface is associated with an instability of the (001) interphase boundary, which tends to break up into pyramidal Ag protrusions into the Cu phase, bounded by {111} facets. The phenomenon is different from conventional faceting in that the periodicity of the facets is determined by the period of the misfit dislocations present at this semicoherent interface, and appears to be driven by the minimization of both interfacial energy and misfit dislocation strain energy. Two factors can control the interfacial energy component of the driving force for faceting. The interfacial energy of {111}

interphase boundaries might be lower than that of {001} boundaries, and the segregation of Au to the boundaries might further reduce the interfacial energy. Previous calculations do indeed suggest that the energy of {111} interfaces is lower than {001} interfaces in binary Cu-Ag alloys [16]. In order to test the role of Au segregation on the predicted faceting, Monte Carlo simulations were also performed on binary Cu-Ag alloys [15]. While Ag also penetrates into the Cu side of the interface in the binary alloy, this penetration is less marked, and the protrusions take the form of truncated pyramids having both {111} and {100} facets. These results show clearly that the fully pyramidal structure of the interface in the ternary Cu-Ag-Au alloy is stabilized by Au segregation. Furthermore, the results indicate, as mentioned earlier, that compositional and structural features of interphase boundaries are intimately connected, and that methods which address both of these attributes of interfaces, such as Monte Carlo simulation, are particularly suitable for this type of study.

As of this writing, the computations on (111) interphase boundaries in both Cu-Ag and Cu-Ag-Au are well under way. In the binary alloy, the (111) interface is stable in the sense that no faceting takes place. Some penetration of Ag into the Cu side of the interface is seen, but is much less marked than in the case of the binary (001) interface. In addition, the same type of interaction between the two components and the interfacial dislocations is observed as in the binary (001) boundary, i.e. higher concentrations of the smaller Cu atom are seen where the atom displacements due to the interfacial dislocations lead to local compression, and vice versa. In the ternary alloy, Au segregates to the interface, and the penetration of silver into the Cu side of the interface is increased in relation to the binary (111) interface. However, convergence of the Monte Carlo results is slower in the ternary alloy, and it is premature to draw any major conclusions on the behavior of (111) interphase boundaries in the Cu-Ag-Au system at this time. The modeling results on (111) interphase boundaries will however be completed before the end of the current grant, and will be the subject of at least one additional publication which will describe the behavior of the (111) interface and compare it with that of the (001) interface.

Experimental Studies of Interphase Boundary Composition

The original plan for the experimental component of the research, under the current grant, was to develop a quantitative interface analysis method by perfecting a technique which had been developed previously to obtain qualitative interphase boundary compositions [6,11]. The method consisted of sequentially growing doped epitaxial thin films of each of the two phases of interest on rock salt single crystal substrates, equilbrating the thin film couple, and then measuring the equilibrium composition profile across the interphase boundary in a scanning Auger microprobe (SAM) by a crater edge profiling technique. That method had shown that whereas Au tends to segregate to interphase boundaries separating Cu-rich and Ag-rich phases in Cu-Ag-Au [11], no comparable segregation of Au could be observed in and Ni-Ag-Au [6]. The problems with the initial implementation of this approach were that: (a) the apparent widths obtained for the interfaces were too high, and (b) that the integrated excess of Au at Cu-Ag-Au interfaces was about an order of magnitude too large. These problems were attributed to difficulties in maintaining a high degree of

interface planarity during film growth and subsequent equilibration, and to artifacts introduced by the sputtering process associated with crater edge profiling [17]. It was felt that these difficulties could be overcome by more careful control of the thin film growth conditions, and by deconvolution of the sputtering damage through careful calibration by means of specially prepared standard specimens.

During the first one-and-a-half years of this research program, a great deal of effort was devoted to the improvement of the above method, with only marginal success. It was finally concluded that whereas this method was useful for a qualitative identification of interface segregants, the quantitative compositional characterization of interphase boundaries required the development of other approaches. As a result, three different experimental concepts were evolved, and preparatory work has been performed to test each of them. Briefly, the first approach entails measurements of the solid state wetting characteristics of one phase by another. By performing experiments with and without segregants at the interface, this approach should yield a quantitative, though indirect, assessment of the concentration of segregant at the interface. A second approach entails imaging of the interphase boundary by means of atomic resolution transmission electron microscopy. Since the contrast in the atomic resolution image depends on both the configuration and the species of the atoms present, this approach is capable of yielding information on both the structure and the composition of the interface. Finally, quantitative measurements of grain boundary compositon have been obtained by atom probe field ion microscopy [18]. While the equipment necessary for this approach is not available at CMU, Professor D. N. Seidman of Northwestern University has agreed to give us access to his equipment for conducting experiments on interphase boundaries. It is expected that firm conclusions on the usefulness of at least two of these new avenues, in the form of preliminary results, will be reached before the end of the current grant.

Publications under the Current Grant

Published

P. Wynblatt and S. A. Dregia, "Equilibrium Composition of Interphase Boundaries", chapter in the Proceedings of the International Congress on Intergranular and Interphase Boundaries in Materials, Colloque de Physique (Supplement to J. Physique) 51, C1-757 (1990). (Full manuscript reviwed by organizing committee before publication).

Accepted for Publication

S. A. Dregia and P. Wynblatt, "Equilibrium Segregation and Interfacial Energy in Multicomponent Systems", accepted for publication in Acta. Metall. Mater.

Submitted for Publication

P. Bacher, P. Wynblatt and S. M. Foiles, "A Monte Carlo Study of the Structure and Composition of (001) Semicoherent Interphase Boundaries in Cu-Ag-Au Alloys", submitted for publication in Acta Metall.

Mater.

G. Rao and P. Wynblatt, "A Survey of Segregation at Interphase Boundaries in Ternary Alloys", submitted for publication in the proceedings of an MRS symposium on Kinetics of Phase Transformations, November 1990.

P. Bacher and P. Wynblatt, "Monte Carlo Modeling of Interphase Boundaries in Cu-Ag and Cu-Ag-Au Alloys", submitted for publication in the proceedings of an MRS symposium on Kinetics of Phase Transformations, November 1990.

Manuscripts in Preparation

S. A. Dregia and P. Wynblatt, tentative title: Effects of Segregation at Interphase Boundaries on Nucleation.

P. Bacher and P. Wynblatt, tentative title: Modeling of Segregation at (111) Interphase Boundaries in Cu-Ag-Au.

Oral Presentations

P. Wynblatt and S. A. Dregia, "Equilibrium Composition of Interphase Boundaries", invited paper at the International Congress on Intergranular and Interphase Boundaries in Materials, Paris, September 1989.

P. Wynblatt, "Equilibrium Composition of Interphase Boundaries", Distinguished Visitor Seminar, Ford Motor Company, Dearborn, November 1989.

P. Wynblatt, "Structure and Composition of Interphase Boundaries", invited papaer at a workshop on Tailored Interfaces for High Temperature Metal-Ceramic Composites, Aurora (NY), September 1990.

P. Wynblatt, "Segregation Effects at Interphase Boundaries", invited seminar at the Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, October 1990.

G. Rao and P. Wynblatt, "A Survey of Segregation at Interphase Boundaries in Ternary Alloys", contributed paper, MRS symposium on Kinetics of Phase Transformations, Boston, November 1990.

P. Bacher and P. Wynblatt, "Monte Carlo Modeling of the Stucture and Composition of Interphase Boundaries in Cu-Ag-Au Alloys", contributed paper, MRS symposium on Kinetics of Phase Transformations, Boston, November 1990.

Project Personnel

In addition to the PI, one graduate student and one post-doctoral fellow have received support from the current grant. The graduate student, Gayathri Rao, has been primarily responsible for the experimental component of the research. She entered graduate school at CMU in Sepember 1988, and is pursuing studies towards a Ph.D. degree. She successfully passed the Ph.D. qualifying examination in June 1990, and has devoted herself to full time research since that time. The post-doctoral fellow, Dr. Patrice Bacher, received his Ph.D. in Grenoble (France) before joining CMU in January 1989. He has been responsible for the modeling component of the work. From October to December 1989, he participated in the Visiting Scientist Program at Sandia National Laboratory (Livermore) where he engaged in collaborative research with Dr. Stephen M. Foiles.

Dr. S. A. Dregia, one of the PI's former students, and currently Assistant Professor at Ohio State University, has collaborated on certain aspects of the research, at no cost to the grant.

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