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Prepared by:

Paul Wynblatt
Department of Materials Science and Engineering
Carnegie Mellon University

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Table of Contents

1. Introduction 1
2. Results of Modeling Research 1
3. Results of Experimental Research 2
4. Publications Resulting from the Grant 4
5. Bibliography 5
1. Introduction

Funding under this grant was initiated on 8/1/88, and terminated on 7/31/97. The principal thrust of this research was to develop improved understanding of the factors which control interfacial segregation at interphase boundaries in metallic alloy systems. The work consisted of both modeling as well as experimental components.

2. Results of Modeling Research

We begin with a description of the results obtained from the modeling component of the work. The project was initiated by developing a nearest neighbor bond model, which made use of the regular solution approximation to calculate the composition profile across an interphase boundary in ternary two-phase alloys [1]. This approach had been applied before by Lee and Aaronson to interphase boundaries in binary two-phase alloys [2]. However, in two-component systems, this approach merely predicts a symmetric composition profile across the interface, and does not yield useful information on segregation effects near the boundary. For the case of ternary systems, the equilibrium conditions are more complex, and the approach used involved a combination of the discrete lattice method of Lee and Aaronson [2] with the continuum gradient thermodynamics formalism of Cahn and Hilliard [3]. When applied to three-component, two-phase systems, this framework yields analytical expressions for the composition profiles of all three components, which do not in general display any symmetry across the interface. In addition, it was demonstrated that the compositional excess at the interface and the calculated interfacial energy were consistent with the Gibbs adsorption isotherm, indicating that this atomically discrete model was compatible with the thermodynamic limit. In a follow-on paper [4], the results were rederived without recourse to the Cahn-Hilliard formalism, and the model was exercised for several alloy systems.

This modeling approach is too simple to lead to highly reliable quantitative results. First, any model which limits interatomic interactions to first neighbors and pairwise interactions does not reproduce all of the properties of alloys, and second, this approach can only deal with coherent interfaces, whereas many important interfaces are semicoherent, i.e. the misfit across the interface is accommodated by the presence of interfacial dislocations. Nevertheless, this model proved to be a valuable tool for identifying systems likely to display segregation effects worthy of further study, either by experimental approaches or by more precise modeling techniques. The earliest system identified in this manner was Cu-Ag-Au (dilute in Au). This system consists of co-existing Cu-rich and Ag-rich phases over a substantial range of composition and
temperature, thus offering the opportunity for studying the interaction of Au with the Cu/Ag interface. While the segregation of Au to the Cu/Ag interface was predicted to be only weak to moderate, further study of this system was undertaken because of the availability of a well-established ternary phase diagram. Two other potentially interesting systems were identified; Ni-Ag-Cu (dilute in Cu) which consists of coexisting Ni and Ag phases, and in which strong segregation of Cu at the Ni/Ag interface was predicted; and Cu-Pb-Au (dilute in Au), expected to consist of coexisting Cu and Pb phases, with a prediction of moderate segregation of Au at the Cu/Pb interface.

A more quantitative modeling approach, based on the embedded atom method (EAM) in conjunction with Monte Carlo simulation, was also developed. The application of this type of modeling for interfaces in binary alloys had been developed in some earlier work [5]. In this project, we extended this approach to the more complex (and more interesting) case of ternary alloys. The usefulness of this approach was validated by demonstrating that it produced reliable predictions of the ternary Cu-Ag-Au phase diagram, including tie-lines [6]. Interface simulations were performed for a cube-on-cube orientation relationship (OR) between the Cu- and Ag-rich phases. Very interesting results were initially obtained in simulations of the (001) Cu/Ag interface, with and without Au additions [6,7]. These showed a significant reconstruction of the binary Cu/Ag (001) interface, which is further modified by the presence of Au, indicating that even weak segregation effects can lead to significant restructuring of interphase boundaries. Such effects had not been reported before. Later simulations of the (111) Cu-Ag interface showed a weak segregation of Au, and indicated that boundaries of that orientation do not undergo reconstruction [8].

Simulations of the (001) and (111) interfaces in the Ni-Ag-Cu system [9] produced results that were generally similar to those obtained for Cu-Ag-Au, except that the segregation of Cu at the Ni/Ag was found to be stronger than that of Au at the Cu/Ag interface, in agreement with the trends predicted by the simple bond model. No Monte Carlo simulations were performed for the case of the Cu-Pb-Au system, as EAM potentials for Pb were not available.

3. Results of Experimental Research

We now turn to the experimental component of the previous work performed in metallic systems. One important reason for the lack of extensive work on segregation at interphase boundaries has been the difficulty of making reliable quantitative measurements of boundary composition. Two different experimental approaches were used: solid state wetting studies, and atomic resolution transmission electron microscopy (ARTEM).
The solid state wetting approach was developed during this research program. Conceptually, it is an extension of the so-called sessile drop technique used in the measurement of the surface tension of liquid metals and alloys, but is quite different in the details of its application, in that the experiments are conducted on micron-sized solid particles under ultrahigh vacuum (UHV) conditions in a scanning Auger microprobe (SAM). This ensures that the compositions of both droplet and substrate surfaces can be monitored, not only to establish freedom of contamination by random impurities, but also to correct the energies of these surfaces for any adsorption or segregation of deliberate alloying additions. The technique also allows measurement of interfacial energies, as discussed in more detail in reference [10].

This approach was used to measure the Pb/Cu interfacial energy in the presence and absence of Au [10]. The measurements were performed on polycrystalline as well as mono-crystalline pure Cu and Cu-Au alloy substrates. The changes in interfacial energy resulting from the presence of Au allowed calculation of the Au excess at the Pb/Cu interface by means of the Gibbs adsorption isotherm. While this is an indirect method for obtaining interfacial composition, our measurements demonstrated that it is both quantitative and reliable. In addition, the moderate segregation of Au observed at the Cu/Pb interface was generally consistent with the predictions of the simple bond model, thus providing a validation of the usefulness of that model. As a bonus, this approach is able to provide values of interfacial energies, which are sorely lacking in the literature.

The ARTEM approach for determination of interfacial composition is based on contrast effects expected to arise in alloys such as Cu-Ag-Au from strongly scattering gold atoms segregated at the Cu/Ag interface. The basic approach required comparisons of ARTEM photomicrographs with simulated images produced from the results of our Monte Carlo modeling. For example, simulated images of (111) interfaces using the Monte Carlo modeling results from Cu-Ag binary and Cu-Ag-Au ternary alloys show extra contrast effects in the vicinity of interfacial dislocations [11].

ARTEM was applied first to the (111) Cu/Ag interface separating phases with a cube-on-cube orientation relationship (OR) in Cu-Ag-Au alloys [11]. This interface is one which occurs naturally in these alloys when precipitates of the Ag-rich phase are produced in a Cu-rich matrix. (The Ag-rich precipitates also display a twin OR to the matrix, as discussed below). The results obtained showed, among others, that this interface is planar with regularly spaced interfacial dislocations, as expected from the earlier Monte Carlo simulations [8]. Comparisons between simulated atomic resolution images derived from the Monte Carlo results, and ARTEM images of the (111) interface in Cu-Ag-Au, indicate that periodic contrast effects associated with the clustering of Au
in the vicinity of interfacial dislocations are indeed present. We discovered, fortuitously, that the Cu/Ag interface is mechanically weak and easily fractured. As a result, a sample of the ternary alloy was fractured in situ in a scanning Auger microprobe, yielding a direct measurement of Au at the Cu/Ag interface. This confirmed the weak segregation of Au inferred from the ARTEM results, and increased our confidence in the predictions of the Monte Carlo simulations. We also investigated the structure of the Cu/Ag interface in a binary Cu-Ag alloy, to verify that the periodic contrast, interpreted to be the result of Au segregation in the ternary alloy, disappears when Au is absent. This work has confirmed our expectations, by demonstrating the lack of comparable periodic contrast in the binary alloy [12].

As mentioned above, two types of Ag precipitates arise in Cu-Ag-Au alloys; one type has a cube-on-cube OR with the Cu-matrix, and the other is in a twin-related orientation. This is also the case in binary Cu-Ag alloys. In both binary and ternary systems, the cube-on-cube OR is associated with a \{111\} habit, whereas the precipitates with a twin orientation have a different habit, close to but not exactly on \{112\}. We have pursued this interesting difference by ARTEM studies on the twin-oriented variant in the binary alloy. These studies [13] showed that the interface consists of periodically spaced ledges, and that this structure essentially obviates the need for the presence of interfacial dislocations at the twin-oriented interphase boundary. This type of OR and interfacial structure is quite rare and has only been reported before at metal silicide/Si interfaces; e.g., in [14]. Our work reported in ref. [12] and benefited from collaboration with Professor J. M. Howe of the University of Virginia.

4. Publications Resulting from the Grant


5. Bibliography