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ATOMIC STRUCTURES AND COMPOSITIONS OF INTERNAL INTERFACES

PROGRESS REPORT

for the Period September 1, 1993 to August 31, 1994

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Summary of Progress During Year 02

A detailed atomic scale study was made of the Ag/CdO {222} heterophase interface produced by internal oxidation of a Ag(Cd) alloy. This interface's structure and chemistry were studied employing high resolution electron microscopy (HREM) and atom-probe field-ion microscopy (APFIM). The Ag/CdO {222} interfaces were shown to be, via HREM, semicoherent containing the geometrically necessary misfit dislocations; atomic scale steps at the interfaces were also observed. The chemical sequence of planes across this interface was shown, via APFIM, to be either Ag|Cd|O|... or Ag|O|Cd|...; the probability is approximately 50% that one sequence or the other is observed. It is concluded, based on these experiments, that the CdO precipitates are semicoherent with the matrix and are coarsening via a ledge mechanism, and therefore the terminating plane of the oxide can be either oxygen or cadmium.

A study was commenced of interfacial segregation at metal/metal oxide interfaces. The physical basis of our approach is to internally oxidize ternary metal alloys, where only one of the two solutes can be oxidized. The solute species that is not oxidized must redistribute itself between the matrix and the metal oxide to maintain itself in thermodynamic equilibrium. It is by this means that we create a situation where a metal/metal oxide interface becomes enhanced in solute. The system being studied is the Cu(Ag)/MgO {222} heterophase interface, where Ag is the segregating species. At 950 °C no evidence was found for segregation, and experiments are presently in progress to detect silver segregation for specimens heat treated in the temperature range 400 to 500 °C.

A systematic study was made of the necessary conditions to measure quantitatively the oxygen concentration in MgO precipitates, that are produced by internal oxidation of Cu(Mg) alloys, via APFIM. It was demonstrated that the concentration can be correctly determined for a specimen temperature in the range 30 to 60 K, pulse fraction in the range 0.10 to 0.15, and a pulse frequency of at least 60 Hz; a value of less than 60 Hz yields an apparent oxygen concentration that is significantly less than the actual value. This study is relevant to our study of solute segregation at metal/metal oxide systems in the Cu(Ag)/MgO {222} system.

We are also studying solute-atom segregation at grain boundaries in Ni-Pd alloys via computer simulations and combined APFIM/transmission electron microscope (TEM) experiments. The simulations are performed employing three different methodologies: lattice statics, Monte Carlo, and overlapping distributions Monte Carlo employing embedded atom method potentials developed at Sandia Livermore Laboratory by Baskes, Foiles and Daw. The codes we have were modified to allow a systematic exploration of the effects of the three microscopic degrees of freedom on the possible grain boundary structures, for fixed values of the five macroscopic degrees of freedom, and segregation. The present limitation of the simulation research is the amount of computer time available to us. In parallel with the simulations experiments are being performed. The experimental techniques necessary to study grain boundaries in Ni-Pd alloys via APFIM/TEM have been mastered and experiments were commenced. The experimental results obtained for specific grain boundaries are simulated and the two sets of results compared.

I. Progress During Year 02 of the Grant

Research of Mr. David K. Chan

Metal/ceramic interfaces play an important role in a wide range of materials, for example, metal matrix composites and dispersion hardened alloys. This research focuses on determining atomic scale chemistry and structure of metal/metal oxide interfaces formed via internal oxidation of a dilute binary alloy of cadmium in silver. High resolution electron microscopy (HREM) is used to determine the coherency and atomic sharpness of the interface. Atom-probe field-ion microscopy, in combination with time-of-flight mass spectroscopy, is used to determine the chemistry of the terminating oxide plane at the metal/metal oxide interface -- this is the only presently available technique that can measure chemistry with a spatial resolution of an interatomic spacing.

Ag-1.62 at.% Cd foil and wire alloys were internally oxidized in air at 575 °C for 14.5 and 58 hours and 775 °C for 3.5 hours. These oxidizing conditions produced octahedrally-shaped cadmium oxide precipitates that are faceted on the {222} planes, with {002}-type truncations. The precipitates form with a cube-on-cube orientation relationship with the silver matrix. High resolution electron micrographs of these specimens, viewed along a <110>-type projection, yield evidence of misfit dislocations at the interface. Transverse strain field in the silver lattice is readily apparent in a HREM micrograph of the Ag/CdO {222} interface shown in Fig. 1. In a micrograph of another interface shown in Figure 2, the interface is curved and a periodic contrast is seen along the interface. The contrast spacing is 1.14 nm, which is similar to

a dislocation spacing between dislocation lines ($1/2\langle 110 \rangle$ -type) of 1.12 nm. It is not similar to the spacing between Moiré fringes (1.58 nm). Thus, it is concluded that the Ag/CdO interfaces are semicoherent and contain the geometrically necessary misfit dislocations, even though the misfit parameter is large (0.14). In addition, steps at the interfaces (indicated by arrows) are observed in the HREM micrographs – see Fig. 3.

The wire specimens were analyzed via the atom-probe technique along $\langle 111 \rangle$ -type directions in order to determine the sequence of {222} CdO planes across the interface – cadmium oxide has a NaCl-type structure and its {222} planes alternate between pure planes of oxygen and pure planes of cadmium. The periodic nature is readily seen in an integral profile shown in Fig. 4 obtained from an atom-probe analysis. In this case it is clear that the sequence of planes through the interface is O|Cd|Ag|... . A total of 35 interfaces were analyzed, and 19 interfaces had a sequence of planes of Ag|O|Cd|... and 16 interfaces Ag|Cd|O|... . This result was obtained with a spatial resolution of 0.136 and 0.236 nm in cadmium oxide and silver, respectively, without any data deconvolution.

It is concluded from the combined HREM and atom-probe results that the CdO precipitates are semicoherent with the silver matrix and are coarsening via a ledge mechanism, and therefore the terminating plane of the oxide can be either oxygen or cadmium. This conclusion is supported by the coarsening data obtained earlier by Pedder, from which it is calculated that the diameter of the cadmium oxide precipitates are coarsening by 0.2 nm at 575 °C in 14.5 h, and 10 nm at 775 °C in at 3.5 h. In addition, the observed interface structure allows climb of the misfit dislocations.

Research of Dr. Ho Jong

Recently, we have performed quantitative analyses of metal oxide precipitates and metal/metal-oxide interfaces using the atom-probe technique. There are, however, no published systematic investigations of the basic experimental parameters for metal oxides, even though there are several reports of off-stoichiometric metal oxides. The physical properties of metal oxides are different from metals or semiconductors and, therefore, it is essential to understand how they behave in the high electric fields required for atom-probe analysis. A careful examination of the experimental parameters is, therefore, required for the quantitative analysis using APFIM because of the relative evaporation fields of the constituent elements. The critical experimental parameters are: (a) specimen temperature; (b) pulse fraction (ratio of the pulse voltage, V_p , to the steady-state voltage, V_{dc}); (c) field-evaporation rate; (d) the crystallographic planes examined; and (e) the composition of the background vacuum.

We carried out a detailed investigation of the above experimental parameters for nanometer diameter MgO precipitates in a completely internally oxidized Cu-1.86 at.% Mg alloy. Conventional TEM was used to measure the mean diameter and number density of MgO particles. The diameter of the MgO precipitates ranges from 5 to 20 nm, and the average number density of MgO precipitates is $2.6 \cdot 10^{21} \text{ m}^{-3}$. Atom probe quantitation experiments were performed by varying the specimen temperature, pulse fraction ($f = V_p/V_{dc}$), and pulse frequency at a fixed field-evaporation rate and at a background pressure of $3.7 \times 10^{-8} \text{ Pa}$.

Figure 5 shows the oxygen concentration of MgO precipitates as a function of pulse fraction ($f = 0.1$ and 0.15) and specimen temperature (30 to 60 K) at a fixed pulse frequency of 60 Hz. This result indicates that the weighted mean oxygen concentration is $50.01 \pm 1.03 \text{ at.}\%$ oxygen for the MgO precipitates, and is independent of temperature in the range 30 to 60 K for values of $f = 0.1$ and 0.15 . Figure 6 exhibits the average oxygen concentration of MgO precipitates as a function of pulse frequency at a specimen temperature of 50 K and a pulse fraction of 0.1. The results exhibited in this figure clearly demonstrate that the apparent mean concentration of an MgO precipitate is a strong function of the pulse frequency. It is suggested that the preferential field evaporation of oxygen at V_{dc} is due to the interaction of H_2 in the atom probe's background pressure to form H_2O . This effect decreases with increasing pulse frequency as there is less and less time for the adsorbed H_2 to reach the individual MgO precipitates, as they are dissected by the pulsed field-evaporation process. It is well known that hydrogen that is physisorbed on the shank of an FIM specimen – that is covered with a chemisorbed layer of hydrogen – can diffuse along the shank into the high-field region and react with atoms on the surface of an FIM tip. The reaction of H_2 with oxygen in an MgO precipitate yields H_2O molecules, in the presence of a high electric field, and they are field desorbed in-between the field-evaporation pulses (V_p) while the specimen is maintained at the steady-state voltage (V_{dc}). Thus we could not detect H_2O molecules in the mass spectra. Atom probe experiments on FeO, RuO_2 and NiO all exhibit hypostoichiometric metal oxides, while an APFIM experiment on Rh_2O_3 measured the correct stoichiometry; the metal oxides in these experiments were produced by *in situ* oxidation of elemental metal FIM tips. The effect of pulse frequency on the measured stoichiometry may be quite general, and hence it should be examined carefully when studying metal oxides via the atom probe technique.

Research of Mr. John D. Rittner

Experimental

Mr. Rittner is studying equilibrium grain boundary segregation in nickel-palladium alloys. He is studying this system experimentally using the combined APFIM/TEM approach and computer simulations. During this first year of this project he has been working out the details and completing the preliminary steps necessary to do the experiments and simulations. On the experimental side of his project, the first critical problem he has been working on is the procedure for producing APFIM specimens. This procedure starts with making high-purity alloys by arc melting. The second step involves analyzing the composition and microstructure of the alloys. The final and most difficult step is to draw the alloys down to fine wires and electropolish the ends to very sharp tips. Of special concern with the Ni-Pd alloys is hydrogen charging during electropolishing, thus it was necessary to find a non-acidic solution that works with this binary metallic system. Mr. Rittner has worked out the details and mastered the techniques needed to make APFIM specimens, and is currently trying to determine the proper conditions for quantitative atom probe analyses of Ni-Pd alloys.

Simulations

On the simulation side of his project, there are three different types of simulations being used: lattice statics, Monte Carlo (MC) and overlapping distribution MC employing the embedded atom method potentials developed at Sandia Livermore Laboratory. The computer codes for each of these simulation techniques required several modifications before they could be used in his project. He started by modifying a lattice statics code, so that it can be used to identify the various grain boundary structures that can be detected employing a systematic exploration of the three microscopic degrees of freedom. The simulations using this code are now over half complete and have yielded many interesting results. He has also modified the MC code so that a rigid-body translation jump could be included in the simulations. This code is used to test the stability of the various structures that are found with the lattice statics simulations. The MC simulations are also currently running. The progress on the simulation part of his project is limited only by the amount of computer time available, and hence we propose in a supplementary proposal to upgrade the IBM RS600/53H workstation that we are currently employing.

Research of Mr. Dmitry Shashkov

To investigate interfacial segregation phenomena in a metal/metal oxide system and its effects on the atomic structure of interfaces we employ a model system – Cu/MgO (222). We have studied the atomic structure and chemistry of the Cu/MgO(222) heterophase interface employing TEM, HREM and APFIM. To study interfacial segregation in the Cu/MgO (222) system, appropriate solute elements (segregants) were chosen based on experimental factors, such as feasibility of interface fabrication and APFIM compositional analysis, as well as the chemical nature of the segregant. We concluded that the elements Pd, Ag, Sb, and Au are suitable as segregating species.

The initial alloys for this research were fabricated by arc melting of high purity materials in an argon atmosphere. The nominal compositions of the alloys are Cu-2.5 at.% Mg-1.0 at.% Ag (alloy A) and Cu-2.0 at.% Mg-0.7 at.% Sb (alloy B). To produce Cu/MgO interfaces, alloys were internally oxidized by the Rhines pack technique under conditions such that magnesium is selectively oxidized.

Conventional TEM investigations of internally oxidized alloys demonstrated that MgO precipitates were formed in both alloys. The morphology and orientation relationship of precipitates with the matrix were found to be the same as in the undoped Cu/MgO system as previously established. The average diameter of precipitates in both alloys is about 15 nm, and the number density $\sim 10^{22} \text{ m}^{-3}$. Specimens for APFIM investigation of the composition of Cu(Ag)/MgO (222) interfaces (alloy A) were prepared in the shape of sharply-pointed tips by electropolishing of internally oxidized wires. Conventional TEM analysis of needle-shaped specimens showed that alloy A retained the [111] wire texture, which is typical for the Cu/MgO system, and is thus suitable for random-area APFIM analysis.

Twelve specimens of alloy A were analyzed by APFIM. The initial results show that specimens air-cooled from 950 °C, after internal oxidation, retain most of the silver (solute) in the copper matrix. The average composition of the matrix is Cu-1 at.% Ag. No measurable segregation level was observed at the Cu/MgO (222) interface. This fact is consistent with the observation that the interfacial segregation level is usually maximized over a fairly narrow

temperature range -- 400 to 500°C for copper-based alloys. Thus, additional heat treatments are necessary to cause solute segregation at the Cu/MgO interface.

II. Publications Generated on this Grant

1. H. Jang, D. N. Seidman, and K. L. Merkle "Atomic Scale Observations of the Chemical Composition of a Metal/Ceramic Interface," *Scripta Metallurgica et Materialia* 26, 1493-1498 (1992).
2. H. Jang, D. N. Seidman and K. L. Merkle, "The Chemical Composition of a Metal/Ceramic Interface on an Atomic Scale: The Cu/MgO {111} Interface," *Interface Science* 1, 61-75 (1993).
3. H. Jang, D. N. Seidman and K. L. Merkle, "Atomic Scale Studies of the Chemistry of the Cu/MgO {111} Heterophase Interface," *Materials Science Forum* 126-128, 639-642 (1993).
4. H. Jang, D. K. Chan, D. N. Seidman and K. L. Merkle, "Atomic Scale Studies of the Mechanisms of Internal Oxidation," *Scripta Metallurgica et Materialia* 29, 69-74 (1993).
5. D. K. Chan, H. Jang, D. N. Seidman and K. L. Merkle, "Initial Results on the Ag/CdO {222} Interface: Atomic Scale Interfacial Chemistry and Sequencing of Ordered Cadmium/Oxygen Planes," *Scripta Metallurgica et Materialia* 29, 1119-1124 (1993).
6. H. Jang, D. A. Shashkov, D. K. Chan, D. N. Seidman and K. L. Merkle, "Reply to Comment by H. Numakura: On the Quantitative Analysis of Nanometer Diameter MgO Precipitates via Atom-Probe Field-Ion Microscopy," *Scripta Metallurgica et Materialia* 30, 663-668 (1994).
7. D. N. Seidman, B. W. Krakauer and D. K. Chan, "Atom-Probe Field-Ion Microscope Studies of the Chemistry of Internal Interfaces on an Atomic Scale," *MSA Bulletin* 24, 375-388 (1994).
8. H. Jang, D. N. Seidman and K. L. Merkle, "The Composition and Structure of the Cu/MgO {222} Interface on an Atomic Scale," *Materials Science Forum* 154-156, 397-400 (1994).
9. D. K. Chan, B. M. Davis and D. N. Seidman, "New Time-of-Flight Electronics for Atom-Probe Field-Ion Microscopy," *Review of Scientific Instruments* 65 (6) (1994).
10. J. D. Rittner, S. M. Folles and D. N. Seidman, "On the Simulation of Surface Segregation Free Energies," submitted to *Physical Review B*, 4 April (1994).
11. D. K. Chan, H. Jang and D. N. Seidman, "A Quantitative Atom-Probe Analysis of the Composition of a Ag-1.62 at.% Cd Alloy," submitted to *Applied Surface Science* (1994).
12. D. K. Chan, H. Jang, D. N. Seidman and K. L. Merkle, "The Chemistry and Structure of Ag/CdO {222} Interfaces Obtained by Internal Oxidation," in preparation for publication (1994).
13. D. K. Chan, H. Jang, D. N. Seidman and K. L. Merkle, "The Stoichiometry of CdO Precipitates Obtained by Internal Oxidation of a Ag-1.62 at.% Cd Alloy," in preparation for publication (1994).
14. D. K. Chan, "Atomic Resolution Studies of Ag/CdO {222} Interfaces," Ph.D. Thesis, Northwestern University (1994).

III. Current Graduate Students and Dates of Graduation

1. David K. Chan: He is taking his Ph.D. final examination on 9 June 1994 and has been offered a position at Lawrence Livermore National Laboratory, Livermore California.
2. John D. Rittner: He has a DOE Simulation Science Fellowship which has one more year to go. John should be able to finish his Ph.D. thesis by June 1996.
3. Dmitry Shashkov: He passed his qualifying examination this past fall. Dmitry should be able to finish his Ph.D. thesis by June 1997.

IV. Current Federal Support

Source of Support	Project Title	Award Amount (annual figure)	Period covered by the award	% Effort per calendar year
NSF/DMR	Atomic Resolution Studies of Solute Atom Segregation and Phase Transitions at Internal Interfaces	\$186,291	1 March 1994 to 28 February 1995	43.78%
DOE/BES	Atomic Structures and Compositions of Internal Interfaces	\$149,833	1 September 1993 31 August 1994	35.21%
Materials Research Center at Northwestern University (NSF funded)	Chemistry on an Atomic Scale of Semiconductor Interfaces	\$89,406	1 March 1994 to 23 February 1995	21.01%

Figure 1: A silver/CdO (111) heterophase interface viewed along the [110] direction. The d_{111} lattice spacings of the Ag matrix and the CdO precipitate are indicated.

Figure 2: Another silver/CdO [111] heterophase interface viewed along the [110] direction. Note the interface is curved in the upper portion of the figure. Also note the presence of periodic contrast along the interface; the periodicity of this contrast is 1.14 nm, and this corresponds to the calculated dislocation spacing of 1.12 nm that is required by the presence of the geometrically necessary misfit dislocations.

Figure 3: Yet another silver/CdO [111] heterophase interface viewed along the [110] direction. The arrows indicate the presence of steps at the interface.

Figure 4: An integral profile across a CdO|Ag (222) interface obtained by atom probe field-ion microscopy. First note that the silver signal inside the CdO precipitate is very tiny, and then becomes, of course, significant once the interface is crossed. Finally note that the terminating (222) plane of the CdO is pure Cd in this case.

Figure 5: The oxygen concentration of MgO precipitates as a function of pulse fraction ($f = 0.1$ and 0.15) and specimen temperature (30 to 60 K) at a constant pulse frequency of 60 Hz. The average field-evaporation rate was maintained at 0.005 events per pulse to prevent excessive evaporation during data collection. The error bars on each data point represent plus or minus one standard deviation for a total length of two standard deviations. The weighted mean oxygen concentration for all the measurements is 50.01 ± 1.03 at.% O.

Figure 5

Figure 6: The oxygen concentration of MgO precipitates obtained from atom-probe experiments as a function of pulse frequency (10 to 60 Hz) at a constant pulse fraction (f) equal to 0.1, and a specimen temperature of 50 K. The error bars on each data point represent plus or minus one standard deviation for a total length of two standard deviations. The results exhibited clearly indicate surprisingly that the apparent oxygen concentration of an MgO precipitate is a strong function of the pulse frequency.

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