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ATOMIC STRUCTURES AND COMPOSITIONS OF INTERNAL INTERFACES

PROGRESS REPORT
for the Period September 1, 1992 to August 31, 1993

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ABSTRACT

This research program addresses fundamental questions concerning the relationships between atomic structures and compositions of homophase and heterophase interfaces. Metal/ceramic heterophase interfaces are created via the process of internal oxidation of metallic alloys. The interfaces so produced are studied experimentally via a combination of conventional transmission electron microscopy, high resolution electron microscopy, field-ion microscopy and atom probe microscopy. The latter technique is employed to chemically sequence the interfacial region, and to show that the terminating {222} plane of MgO and CdO consists solely of oxygen atoms for the Cu/MgO {111} and Ag/CdO {111} heterophase interfaces, respectively; this is achieved with no deconvolution of the experimental data. The evolution of metal/ceramic heterophase interfaces is studied by following the process of internal oxidation on an atomic scale from its very earliest stages. It is demonstrated that during the early stages of internal oxidation that metal atom clusters as well as hypo and hyperstoichiometric metal-oxygen clusters are present. Solute-atom segregation to grain boundaries is studied in binary metal alloys employing the free energy simulations and the overlapping distribution Monte Carlo methodologies for dilute Pt(Au), Cu(Ni) and Pd(Ni) alloys for both twist and tilt boundaries.

I. PROGRESS

A. THE CHEMICAL COMPOSITION OF A METAL/CERAMIC INTERFACE ON AN ATOMIC SCALE: THE Cu/MgO {111} INTERFACE

Ho Jang, David N. Seidman and Karl L. Merkle

The chemical composition profile across a Cu/MgO {111}-type heterophase interface, produced internal oxidation of a Cu(Mg) single phase alloy at 1173 K, is measured via atom-probe field-ion microscop a spatial depth resolution of 0.121 nm; this resolution is equal to the interplanar spacing of the {222} MgO p In particular, we demonstrate for the first time that the bonding across a Cu/MgO {111}-type heterophase inte along a <111> direction common to both the Cu matrix and an MgO precipitate, has the sequence Cu|O|Mg *not* Cu|Mg|O... ; this result is achieved *without* any deconvolution of the experimental data. Before detern this chemical sequence it was established, via high resolution electron microscopy, that the morphology of an precipitate in a Cu matrix is an octahedron faceted on {111} planes with a cube-on-cube relationship betw precipitate and the matrix.

B. FIRST STUDIES OF ATOMIC SCALE SEQUENCING OF ORDERED CdO: THE Ag/CdO {111} HETEROPHASE INTERFACE

David K. Chan, Ho Jang, David N. Seidman and Karl L. Merkle

The bonding between metal-ceramic interfaces is dependent upon the crystallographic structure and chemical composition of the heterophase interface [1]. In the case of metal/metal oxide interfaces, the chemistry of the interface can control the properties of the bulk material. The metal oxide face of the interfaces can have several configurations--it can be mixed of metal-oxygen, pure oxygen, or pure metal. *Ab Initio* calculations indicate that oxygen is the terminating layer of magnesium oxide in silver and titanium [2]. High resolution electron microscope (HREM) images of cadmium oxide in silver produced by internal oxidation indicate that oxygen is the terminating plane between silver and cadmium oxide [3]. Recent studies of copper/magnesium oxide interfaces produced by internal oxidation using conventional transmission electron microscopy (CTEM), HREM, and atom-probe field ion microscopy (APFIM) have determined the sharpness and chemical nature of the terminating planes [4-6]. It is found that magnesium oxide precipitates have a cube-on-cube orientation relationship with the copper matrix and are octahedral in shape bound by {222} planes. APFIM results show that the interfaces are atomically sharp and the sequence of planes across the interface is Cu-O-Mg and not Cu-Mg-O.

In this study we present the first APFIM results from silver/cadmium oxide interfaces produced by internal oxidation. Internal oxidation is a well studied field, and is based upon preferential oxidation of B solute in an A-B dilute alloy [7-10]. Silver-cadmium internally oxidized alloys are used to switch medium to high currents [11] and have been subject to various studies on strength and electrical properties [12,13]. Previous HREM investigations of silver/cadmium oxide interfaces produced by internal oxidation have determined that the oxides have a cube-on-cube orientation with the silver matrix and are octahedral in shape bound by {222} planes and truncated along <100> directions [3,14,15]. In this study we present evidence that we can field evaporate through a silver/cadmium oxide interface on a plane-by-plane basis. In addition, we demonstrate that it is possible to dissect cadmium oxide along the <111> direction and sequence the ordered planes.

We have demonstrated that it is possible to sequence ordered planes of a metal oxide. Twelve planes of CdO along the ordered <111> direction are clearly resolved. In addition, field evaporation through a metal/metal oxide interface is possible without failure of the specimen. The atomic resolution of the composition profile is directly related to the interplanar spacing. In this case, it is 0.136 nm and 0.236 nm in cadmium oxide and silver, respectively, along the <111> direction.

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C. ON THE SIMULATION OF SOLUTE-ATOM SEGREGATION FREE ENERGIES FOR CRYSTALLINE IMPERFECTIONS

John D. Rittner, Stephen M. Foiles and David N. Seidman

The effects of different assumptions made in the simulation of the energetics of free surfaces for face-centered cubic binary alloys are considered. Thirty solvent-solute atom pairs involving the elements Ag, Au, Cu, Ni, Pd and Pt are investigated using embedded-atom method potentials. First, it is demonstrated that the inclusion of local atomic relaxations in lattice statics simulations significantly increases the segregation energy to (111) free surfaces in 14 of the 30 solvent-solute atom pairs investigated. Second, the overlapping distribution Monte Carlo methodology (ODMC) is used to determine the effect of the vibrational entropy contribution on the surface segregation energy for simulations performed at elevated temperatures (1000 K). It is determined that the vibrational entropy term is important for one-third of the pairs. We conclude that for most of the pairs investigated it is necessary to include both local atomic relaxations and the vibrational entropy to obtain accurate results from simulations. Since the ODMC methodology is very computer time intensive, a recently developed quasi-harmonic technique for calculating free energies is tested. Results from this so-called free energy simulation (FES) method are compared to results from the ODMC methodology. It is found that the FES method calculates the segregation free energies of (111) free surfaces accurately for most of the 30 solvent-solute atom pairs, but for some pairs it does not even predict the correct segregant. Detailed segregation free energy profiles for several crystalline imperfections are also calculated employing both methodologies for three of the pairs -- Pt(Au), Ni(Cu) and Ni(Pd). The FES methodology predicts the correct qualitative profile for all but one case. The quantitative agreement is found to vary for the different alloys and crystalline imperfections. The agreement is found to be best for solvent-solute atom pairs that have very similar lattice parameters. It is also found that the FES methodology is not as accurate as the ODMC methodology under conditions of compressive or tensile strains in the bicrystal It is concluded, in general, that care must be taken when applying the FES methodology to study solute-atom segregation to crystalline imperfections.

E. ATOMIC SCALE STUDIES OF THE MECHANISMS OF INTERNAL OXIDATION

Ho Jang, David K. Chan, David N. Seidman and Karl L. Merkle

The phenomenon of internal oxidation of solute atoms, in binary metal alloys, is a venerable one that has been studied off and on since its discovery in 1930 [1]. The diameter and number density of the precipitated metal oxides -- that are the end product of this phenomenon -- depend upon the solute element and its concentration in the alloy, temperature of internal oxidation, external oxygen pressure and time [2,3]. Internal oxidation of alloys has been used to produce dispersion hardened materials in an effort to improve their mechanical properties, and to reduce spallation of alloys, for example, Ag(Cd) alloys, are used to switch medium to high currents [4]. Experimental and theoretical research has demonstrated that to obtain internal oxidation of a solute atom in a solid solution, as opposed to external oxidation of the solvent or solute atoms, several conditions must be met [2,3,5-11]. First, the chemical affinity of oxygen for the solute species must be much greater than for the solvent species. Second, oxygen must diffuse faster in the matrix than does the solute species. The latter can be expressed in terms of the relative permeabilities (D_iC_i) of oxygen and solute atoms in the metal matrix; internal oxidation of a binary alloy results in a ternary system -- solvent, solute and oxygen atoms. Thus internal oxidation may occur if $D_oC_o >> D_sC_s$ -- where D_i represents diffusivity, C_i the solid solubility, and the subscripts o and s indicate oxygen or metal solute atoms. The rate controlling step in internal oxidation is assumed to be the diffusion of oxygen atoms through an alloy, and furthermore the metal oxide that forms is assumed to have a specific stoichiometry. These ideas and assumptions lead to a 'law' for the number of oxygen atoms penetrating unit area of surface (n_o/S) that is parabolic in time (t), as well as Wagner's 'law' for the position of the oxidation front (ξ) in a specimen that is proportional to $t^{1/2}$ [3,5-11].

Recently, thermogravimetric measurements of the ratio of oxygen-to-magnesium atoms have been made as a function of time during internal oxidation of a Ag-0.4 at.% Mg alloy between 280-550°C [12,13]. These measurements demonstrate that the oxidation fixation process occurs in three stages at constant temperature -- as a function of internal oxidation time -- and that significant deviations from Wagner's 'law' exist. The atomic mechanisms for the three stages are suggested to be the following: (1) sub- or hypostoichiometric (oxygen poor) metal-oxygen species are initially formed; (2) these elementary species evolve toward irregular clusters that are oxygen rich; and (3) a portion of the excess oxygen is released and the clusters evolve toward a more compact structure [13]. During the second stage the quantity n_o/S is proportional to $t^{1/2}$; the fixation of oxygen, however, is greater than predicted by Wagner's theory [13]. In summary, the thermogravimetric measurements show that the classical picture of internal oxidation is considerably more complicated than had been envisaged, and that the specific atomic mechanisms by which metal oxide precipitates evolve are uncertain.

Also recently internal oxidation has been used as a means to produce metal/metal oxide heterophase interfaces for study via high resolution transmission electron microscopy [14-20] or atom-probe field-ion microscopy (APFIM) [18-20]. The technique of internal oxidation is a convenient method to control the diameter and number density of metal oxide precipitates, and thereby obtain a reasonable probability of finding these heterophase interfaces -- with a high frequency -- employing high-resolution microscopic studies. Many of the metal oxides produced by internal oxidation have a simple cube-on-cube orientation relationship with the matrix. For example, MgO precipitates in a Cu matrix have an octahedral morphology with the facets of the octahedra being {111}-type planes [18-20]. Much theoretical [21,22] and experimental effort [14] has focused on the nature of the chemical sequence across metal/metal oxide heterophase interfaces. Employing APFIM we have demonstrated that the chemical sequence is Cu|O|Mg|... across the {111}-type planes that form heterophase interfaces in the Cu/MgO system.

During the course of the above investigation -- and research on internal oxidation of Ni(Cr) to form Cr_2O_3 precipitates -- we discovered that it is possible to detect directly nonstoichiometric clusters of metal oxides utilizing APFIM, and thereby study the nucleation and growth of metal oxide precipitates in ternary alloys -- two metal species plus oxygen. In this paper we present the first atomic scale evidence -- based on APFIM observations of the Cu-Mg-O system -- of the nucleation and growth phenomena for metal oxide precipitates in a metal matrix. The results demonstrate that it is possible to follow the complete evolution of metal oxide precipitates starting with the smallest elemental clusters formed from metal solute-atoms and oxygen -- that is, metal solute-atom or metal-oxygen dimers.

The APFIM results presented demonstrate, in a very direct and vivid manner, that the process of internal oxidation does **not** result directly in the nucleation and growth of metal oxide precipitates that are exactly stoichiometric -- in the case presented MgO -- at the earliest stages of the formation of a metal oxide precipitate. Rather both hypo- and hyperstoichiometric clusters form as well as the clustering of magnesium atoms. The clusters that we observe are clearly precursors to larger precipitates (>1 nm diameter) that are observed via field-ion [18-20] or high resolution electron microscopy [14-20]; For example, Fig. 2 in reference [18] exhibits a field-ion micrograph of a 7.3 nm diameter MgO precipitate in a Cu matrix. Our results also demonstrate that the entire process is considerably more complicated than had been envisaged in the widely used classical model of internal oxidation [3,5-11]. Furthermore, our results lend credence to the results of the thermogravimetric measurements [12,13], reviewed in the *Introduction*, where indirect evidence was presented for hypo- and hyperstoichiometric MgO clusters in an internally oxidized Ag-0.4 at.% Mg alloy. In addition, our results demonstrate that the Mg solute atoms can cluster prior to being internally oxidized, and that both hypo- and hyperstoichiometric clusters of magnesium oxide form as the position of the oxidation front (ξ) moves through a specimen. Thus, we have demonstrated that the atomic mechanisms for internal oxidation of a solute atom, such as Mg, occurs as a result of series of reactions that involve the formation clusters of Mg atoms that are internally oxidized to produce both hypo- and hyperstoichiometric metal oxide clusters. The latter must evolve in time towards dense precipitates with a specific mean stoichiometry or perhaps a range of stoichiometries. Any deviation from exact stoichiometry can, of course, be accommodated by the formation of Schottky-type point defects. Our experiments also demonstrate that it is now possible to follow, on an atomic scale, the process of internal oxidation from its very earliest stages to the point where metal oxide precipitates are visible by different high resolution microscopies.

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