METAL–CERAMIC INTERFACES STUDIED WITH HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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Abstract—How the core structure of an interface dislocation network depends on both misfit and bond strength across the interface is investigated. It is shown that, in principle at least, it is possible to assess the bond strength by investigating the atomic structure of the dislocation cores. As examples, the misfit-dislocation structures at Ag/Mn3O4, Cu/MnO interfaces formed by parallel close-packed planes of Ag or Cu and O obtained by internal oxidation were studied using HRTEM and lattice static calculations. The lattice static calculations are instrumental in indicating the possible dislocation network and their results served as input for HRTEM image simulations which are then compared with experimental HRTEM images. In addition, the influence of dissolution of a segregating element (Sb) in these systems was also studied using HRTEM. The influence on Mn3O4 precipitates in Ag is distinct, namely: (i) the initial precipitates, sharply facetted by solely {111}, are changed into a globular shape with sometimes also short {220} and (002) facets, (ii) a partial reduction of Mn3O4 into MnO occurs for a part of the precipitates. Further Sb appeared to prevent Oswald ripening of the precipitates.

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1. INTRODUCTION

The importance of interfaces is determined primarily by their inherent inhomogeneity, i.e. the fact that physical and chemical properties may change dramatically at or near the interface itself. As a result of these sharp gradients an isotropic bulk solid may change locally into a highly anisotropic medium. Interfaces between dissimilar materials, such as those between metals and oxides, are of a special kind. Experimental and theoretical work has been carried out in recent years on model systems to understand the basic behavior of metal–oxide interfaces. These model systems are well-defined simple interfaces, that are boundaries with known orientation, high symmetry, between simple, known constituents. The hope is that general concepts governing adhesion, structure, chemistry, mechanical behavior, and their interdependence can be elucidated.

Indeed, an important property of a metal–oxide interface is its free energy per unit area, and the closely related work of adhesion. Thermodynamic and mechanical properties of the interface have been found to depend on these parameters. Experimental determination of the interface cohesive energy (i.e. the reference state has two separated crystals with free surfaces) is an important step towards understanding metal–oxide interfaces. In principle there are several ways in which information on the interface cohesive energy can be extracted from experiments, for example by the measurement of wetting angles or by the study of interface fracture behavior by four point bending tests. The latter provides an idea of the toughness of adhesion, $\Gamma_a$, rather than the energy stored in the system which becomes available when failure occurs. The value of $\Gamma_a$ may be a strong function of the mode mixity, which also depends on geometry and loading details. However, another possibility is to use high-resolution (transmission) electron microscopy, and the information it can provide on the atomic structure of an interface. The link between the atomic structure and the interface cohesive energy is provided by the interaction which takes place at the interface between the bonding across it and the geometrical misfit.

From a theoretical point of view, ab initio calculations based on full-potential LMTO (linear muffin-tin orbital method) within the local density approximation (LDA) have been performed for several metal–oxide interfaces (for a review see Refs [1–3]). An important contribution to the bonding across metal–oxide interfaces is believed to be the Coulomb interaction between the ions in the oxide and the “image charges” in the metal, or rather the charge density that they induce in the metal. Several experimental observations point in this direction, for example the frequent occurrence of polar oxide planes at metal–oxide interfaces.

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However, application of this classical concept at an atomic scale leads to several problems. First of all, the classical interaction diverges for separations approaching zero. Furthermore, the concept does not refer to atoms, and also does not distinguish between (the band structures of) different metals. The main reason that the model does not work at an atomic scale is that the possibilities for charge distribution are unrestricted, whereas in real metal only distributions with a wavelength equal or larger than the Fermi wavelength are permitted. Two ways around this problem have been proposed and applied to model systems with some success [4, 5]. However, the occurrence of a mismatch at metal–oxide interfaces is not considered in these calculations.

The mismatch dislocations at metal–oxide interfaces, unlike the dislocations in the bulk, are not defects but an integral part of the interfacial structure. Their core structure is determined by the bonding across the interface. It is clear that the mismatch at the interface plays an important role, because the elastic strain energy needed to achieve coherence at an interface with large mismatch will in general be higher than for an interface with low mismatch. So, the atomic structure is determined by the interaction between mismatch and bonding. Atomic structure determination of the core structure of mismatch dislocations at metal–oxide interfaces, in combination with atomistic calculations can therefore be expected to lead to a better understanding of interfaces between dissimilar materials. The availability of accurate descriptions of the interatomic forces is of course crucial in these calculations. However, the situation is much less advanced for metal–oxide interfaces, where the nature of the bonding across the interface still needs further clarification. As discussed by Finnis [4], for metal–oxide bonding analogous simple schemes for the description of interatomic forces cannot be easily formulated and those employing image charge effects are not fully atomistic. Hence, studies of mismatch dislocations which fully incorporate atomic structure and bonding in both the ceramic substrate and the metal cannot be made at this stage. For this reason, a simplified model was suggested [6–8] which, while treating the metal atomistically, is similar to the continuum treatment (see Section 2). In particular, in this model the atomic interactions in the metal are described by Finnis–Sinclair type many-body central force potentials. In addition, we carried out both isotropic and anisotropic linear elastic continuum calculations for an array of mismatch dislocations lying at the same interface. These dislocations are of Volterra-type and have singular cores. A comparison of atomistic and continuum results was then made in order to establish whether the structure of the interface could be considered, at least for some combinations of the bond strength and mismatch, as a network of Volterra dislocations. In particular we concentrated on the question of how the core energy and structure depend on both mismatch and bond strength across the interface. In this case, in principle at least, it is possible to assess the bond strength by investigating the atomic structure of the core structure of interface dislocations.

2. THEORETICAL CONCEPTS

2.1. Atomic structures of interfaces and anisotropic linear elasticity theory

A number of theoretical studies have focused on the understanding of the cohesion at metal–ceramic interfaces [9–14], mainly dealing with its chemistry and electronic structure, usually allowing for neither relaxations nor the formation of mismatch dislocations. In our atomistic approach both the metal and the ceramic substrate are represented by rectangular blocks of atoms. They are brought into contact with a chosen orientation relationship along a certain plane. Misfit is introduced by building a block with unequal numbers of unit cells in the metal and the substrate, along one or two directions. The potentials used in the present work to describe the interactions between atoms in the metallic part are of the Finnis–Sinclair type [15]. In this scheme the energy of an atom \(i\) is given by

\[
E_i = \sum_j V(R_{ij}) - \sqrt{\sum_j \Phi(R_{ij})}.
\]  

(1)

The first term is a repulsive component whereas the second term represents an attractive many-body component. The functions \(V\) and \(\Phi\) are short-range pair potentials fitted to reproduce experimental data, such as lattice parameter, cohesive energy, elastic moduli, and vacancy formation energy. Summation is carried out for all atoms \(j\) within the cut-off radius of the applied potentials. The interactions across the boundary, between metal and substrate atoms, are modeled with an effective pair potential [15]. In order to simulate different bond strengths the potential can be multiplied by a factor \(x\), which will be referred to as the “interaction parameter \(x\)” hereafter, and takes the following mathematical form:

\[
U_{MS} = xV_{eff}(R) = x\left[ V(R) - \sqrt{\sum_j \Phi(R_{ij})} \right].
\]  

(2)

For the calculations in this work the atoms in the substrate were kept fixed, so no description of atomic interactions was needed for the atoms of the substrate whereas the semi-empirical many-body potential of the metal was used to describe the metal layer.

For the calculation of the interface cohesive energy the following equation is employed:
The atomic level stress tensor program allows calculation of the components of the stress tensor need not be so. As this value will not change during relaxation in any case, because displacements in the substrate are not allowed, its choice has no effect on calculated interface cohesive energy differences. All other energy values given here are relative to the surface energy of the substrate. Starting from an initial configuration and a chosen value of the interaction parameter \( z \), the block is relaxed using a steepest descent method, moving the atoms in the direction of the resultant force acting on them. Blocks are usually relaxed until no forces larger than 1 eV/Å are found on any atom. The coordinates of the atoms and the energy of the relaxed block are the standard output. Furthermore, the program allows calculation of the components of the atomic level stress tensor \( \sigma_{ij} \). This was done to facilitate comparison with elastic continuum calculations, usually performed in terms of stresses rather than strains [14]. Although the total force on the atoms in the final equilibrium configuration is zero, the components of the stress tensor need not be so. They can be calculated for each atom according to

\[
\sigma_{ij} = \frac{1}{\Omega} \sum \left( R_{ik}^j - R_{ij}^k \right) F^i_k. \tag{4}
\]

Here \( \kappa \) and \( \beta \) refer to the second rank tensor components in a Cartesian coordinate system, and \( i \) and \( j \) indicate atoms. The summation is again over all atoms within the cut-off radius. It should be noted that the term \( F^i_k \), which may be called the partial force on atom \( i \) due to atom \( j \), is not really pairwise because the effects of the many-body terms in the energy are taken into account during its calculation but the force is a central force field. The influence of the starting configuration on the results of the atomistic calculations is expected to be small, especially for small misfits. The misfit at the interface leads to a set of similar but slightly different configurations for the metal atoms near the interface. Changing the starting configuration, by translation of the metal block with respect to the substrate, shifts the position of the misfit dislocation core, but does not change its detailed structure or energy. It should be realized that in the calculations the best continuity of one of the sub-lattices in the ceramic (the oxygen lattice) was taken as the starting configuration and displacements in the substrate were not allowed because of the assumed infinite stiffness of the substrate. This is not generally correct and depends on detailed structural aspects. For example, in perfectly commensurate misfitting (111) interfaces, there are at least three equilibrium configurations (not all of which are necessarily stable), which correspond to starting configurations with one Cu atom in the unit cell (precisely) in (i) the on-top position, (ii) the threefold hollow position [there are two of these, of course, for (pseudo) h.c.p. and f.c.c. stacking], and (iii) a bridge site. The energy barriers between the corresponding relaxed configurations may turn out to be negligible, but that is not necessarily the case.

The misfit dislocation that forms at a particular combination of interaction parameter \( z \) and misfit is clearly detectable. For increasing values of the interaction parameter \( z \), the Burgers vector, which is evenly distributed along a period at the interface for \( z = 0 \), gets more and more localized around the center of the misfit dislocation. Relaxation of the interface structure for various values of the interaction parameter \( z \) and misfit \( \delta \) leads to different values of the calculated interface cohesive energy. These values can be related to the elastic energy in the metal which can also be calculated with the continuum approach. A test of the localization of the resulting atomic configurations can be carried out by calculating the strain energy associated with the interface dislocation. Therefore, we are particularly interested in computing the so-called energy factor \( K \) of an interface dislocation which is related to the elastic self-energy per unit length along the axis of a cylinder of radius \( R \) around the dislocation.

The core energy is usually described by

\[ K \ln(r_c/r_{eh}), \]

where \( r_{eh} \) is the “equivalent hole” radius and \( r_c \) represents the core radius. Further, we are interested to see what is the effect of the approach taken in the atomistic calculations that use an infinitely stiff substrate, i.e. neglecting any elastic field inside the substrate. These fields can be predicted by anisotropic substrate theory as a function of stiffness. In the continuum approach we take the Burgers vector of the interface dislocation parallel to the interface and in the actual calculations it is of perfect edge character. However, the following formulation is still quite general for any type of dislocation near the interface. Further, by means of the introduction of a clamping factor \( \lambda \) which is correlated with the ratio of the elastic constants between the layer and substrate, the solutions can be applied to both rigid and deformable substrate material [16, 17].

The starting point is the displacement field \( u \) of a single dislocation in an anisotropic linear elastic medium, the solution of which can be found in several textbooks on dislocation theory [18]. It is shown that this can be represented in the form of a superposition of partial solutions \( \eta \):
\[ u = \frac{1}{2\pi} \sum_{\eta} D(\eta)A_{\eta} \ln(\xi_1 \cdot r + p_0 \xi_2 \cdot r) \]  

where \( \xi_1, \xi_2 \) and \( \xi_3 \) represent the three mutually orthogonal unit vectors. \( \xi_1 \) lies in the interface, \( \xi_2 \) is perpendicular to the interface and \( \xi_3 \) is parallel to the dislocation line. For each eigenvalue \( p_0 \) an eigenvector \( A_{\eta} \) exists. Matching \( u \) with the displacement discontinuity of the Burgers vector \( b \) in the Burgers circuit and applying the constraint of balancing the external force per unit length yields six equations from which the six unknowns \( D(\eta) \) can be obtained. The stress components are readily obtained from the derivatives of the displacement field with respect to \( r \). From the stress in the interface plane \( \xi_2 \cdot r = 0 \), the elastic energy per unit length is given by (Einstein convention)

\[ E = \frac{1}{4\pi} \sum_{\eta} L_{\eta 0} h_{\eta 0} h_{\eta 0} \ln \left( \frac{R}{r} \right). \]

The pre-logarithmic factor is called the energy factor \( K \), which was first introduced by Foreman for an isotropic continuum description [19]. Here for a heterogeneous interface, in contrast to a homogeneous interface (grain boundary), it depends both on the various elastic constants and also on the magnitude of the Burgers vector. \( L_{\eta 0} \) and \( A_{\eta k} \) correspond to Lekhnitskii’s representation that is valid for the general anisotropic case [20]. The vector \( L \) is the same vector introduced by Stroh [21], who was the first to mention the orthogonal relation between \( A \) and \( L \) explicitly:

\[ A_{\eta} \cdot L_{\eta 0} + A_{\eta} \cdot L_{\eta 0} = \delta_{\eta 0}. \]

The requirement of balancing the external force \( f \) per unit length at the line leads to the condition for an interface dislocation:

\[ \sum_{\eta} \pm D^{(1)}(\eta) L_{\eta 1}^{(1)} + \sum_{\eta} \pm D^{(2)}(\eta) L_{\eta 2}^{(2)} = 0. \]

Conditions of the continuity of displacements and tractions across the interface mean that \( D^{(1)} \) and \( D^{(2)} \) are interrelated:

\[ D^{(2)}(\beta) = \sum_{\eta} (A_{\eta}^{(2)} \cdot L_{\eta}^{(2)} + A_{\eta}^{(2)} \cdot L_{\eta}^{(1)}) D^{(1)}(\eta). \]

The magnitude of the separate Burgers vector in the substrate and top layer can be calculated by realizing that from the displacement discontinuity \( b \) and the requirement of balancing \( f \) per unit length it follows that

\[ D^{(1)}(\eta) = b_{\eta} \cdot L_{\eta}^{(1)} - f^{(1)} \cdot A_{\eta}^{(1)}. \]

For a homophase interface \( f^{(1)} \) is equal to zero whereas for a heterogeneous interface it is not. Equation (10) expresses mathematically that an interface dislocation between the two elastically dissimilar materials 1 and 2 is equivalent to a dislocation in phase 1 (in the \( \xi_1 \) direction) and a line force (in the \( \xi_2 \) direction) in an infinite medium of phase 1 (see also Ref. [22]). The force term \( f^{(1)} \) should not be confused with the interface bond strength itself since it is the consequence of the continuity of displacements and tractions.

The main significance of this is that from an atomistic approach it can be concluded that the actual atomic structure of misfit dislocations depends on bond strength across the interface as well as on misfit. Next, a simple representation of the interface structure based on linear elasticity theory as an array of bulk-type singular interface dislocations relieving the misfit does not necessarily give the right physical picture. This becomes apparent if elastic energies calculated with atomistics and elasticity are compared. If interface dislocations are formulated, depending on the critical value of the interaction parameter \( z \) across the interface, a comparison with anisotropic elasticity can be made. This comparison indicates a reasonable qualitative agreement of the energy factors. In Fig. 1, some curves are shown of the elastic energy vs misfit \( \delta \) at constant interaction parameter \( z \) and \( K \). The curves are obtained from continuum elasticity calculations using various relevant energy factors. In the latter it is assumed that the equivalent hole radius \( r_{eh} \) is about \( 1/2|b| \) and that \( R \) is equal to \( (1/2)(b/(\delta - \epsilon)) \). The coherency strain contribution \( e \) is neglected since it is not contained in the atomistic energy calculations either. It should be emphasized that in equation (6) and in the comparison of Fig. 1, the interactions between the interface dislocations are neglected. In particular for thin layers the stress fields of the individual dislocations are not completely screened from each other by the surface and interaction terms become important [23–25]. In fact in the anisotropic elasticity calculations of the interface cohesive energy the Volterra dislocations are assumed to be present near the interface, with a very large spacing of the dislocation array.

Fig. 1. Elastic energies from atomistic calculations compared with results from anisotropic elasticity. Solid line: anisotropic elasticity \( (K = 4.0 \) eV/nm). Dashed line: anisotropic elasticity, for Ag/MgO \( (K = 3.31 \) eV/nm). Dotted line: anisotropic elasticity, Ag elastically clamped on to an infinitely stiff substrate \( (K = 4.39 \) eV/nm).
Nevertheless, in a better physical description the long-range logarithmic divergence of non-interacting single dislocations is cancelled out by the homogeneous strain field, so that there is no long-range divergence left in the total energy [24–26]. Nevertheless, the principal message in comparison with the atomistic approach will not change.

The curve of $E$ vs $\delta$ calculated using linear elasticity theory is steeper than any curve for constant interaction $\xi$. In fact, if the interaction between the dislocations, which should be appreciable for 10% misfit and perhaps even for 4% misfit, is taken into account it would be even steeper. In other words, the curve calculated using elasticity theory for single dislocations connects points with different interaction parameters $\xi$, with higher values at higher misfit $\delta$. In contrast, the atomistic description shows that to approach the elastic predictions, different bond strengths for different misfits should be considered.

In addition, the atomistic calculations assume a periodicity imposed by crystallography and this is correct. Dislocation interactions are built in and the elastic calculations are actually approximations; however, if the dislocations are sufficiently isolated, which depends on the value of the misfit, this does not matter too much. Furthermore, these long-range elastic effects will not vary appreciably with the parameter $\xi$ since dislocation separations are determined by geometry. Their position with respect to the interface and their core structure do depend on $\xi$. Hence, atomistic calculations include all the long-range interactions correctly and the elastic calculations are, in this sense, approximations. Nevertheless there is a negligible effect of the long-range interactions on the cores if the misfit is not large. In general, we can conclude that a fair correlation exists between the atomistic and elastic continuum description of interface dislocations. However, it is evident that the elastic continuum approach cannot account for the possible configurations at an interface with misfit, because it does not elucidate the effects of different bond strengths on the interface structure.

2.2. Misfit-dislocation networks

The theoretical analysis will be compared with HRTEM observations of interfaces between MnO or Mn$_2$O$_4$ and Ag or Cu. The Ag/Mn$_2$O$_4$ interface is special due to the one-dimensional mismatch present along the interface. This mismatch is expected to result in an array of misfit dislocations, which can be observed end-on in HRTEM images, leaving the atomic columns straight and thus causing no problems due to the two-dimensional projective nature of HRTEM. The Cu/MnO interface, characterized by an isotropic mismatch, has already been studied earlier by HRTEM [27] and is a type of interface studied extensively with HRTEM in the past 10 years [28–32]. Nevertheless, these studies were not done in comparison with atomistic calculations. Details of the formation of the interfaces, e.g. that usually tilted close-packed plane interfaces in the Ag/Mn$_2$O$_4$ system occur, are given in separate papers [33, 34].

Different types of semi-coherent interfaces can be proposed for the parallel topotaxy $\{111\}$ interfaces [35] with as extremes a hexagonal misfit-dislocation network with 1/2(110) type Burgers vectors and (112) dislocation-line direction and a trigonal network with 1/6(112) type Burgers vectors and (110) dislocation-line direction. The hexagonal network is compatible with Bollmann’s O-lattice theory by Ref. [36]. The trigonal network can be conceived as a dissociation of the 1/2(110) type misfit dislocations into 1/6(112) type misfit dislocations for the total dislocation-line length in the hexagonal network. Since dissociation of a part of the dislocation-line length in the hexagonal network might occur around specific dislocation nodes, an intermediate type of network between the hexagonal and trigonal is also possible. The three types of networks are schematically depicted in Fig. 2. The O-nodes of the hexagonal network correspond to Cu atoms in a hollow site threefold coordinated by an oxygen atom in the terminating layer in the oxide. Nodes of the dislocation network correspond to Cu atoms on top of oxygen atoms (onefold co-ordination) and Cu atoms in a hollow site threefold coordinated by oxygen atoms, but corresponding to a position corresponding to the intrinsic stacking fault in the metal, i.e. with respect to first-nearest neighbors this node of the dislocation network is identical to the O-nodes and only differs due to second and more distant neighbors. Of course, dissociation in the hexagonal network starts at this last dislocation node corresponding to the threefold coordinated stacking-fault position and triangular...
intrinsic stacking-fault areas develop with the original dislocation node as center, see Fig. 2(b). For a finite stacking-fault energy these triangular areas will always be larger than zero. The lower the stacking-fault energy and the larger the mismatch the relatively larger the triangular stacking-fault areas become, finally completely transforming the hexagonal network into the trigonal one. Here, the interfaces correspond to extremely high misfits and a fully trigonal network is therefore highly probable. Only very high stacking-fault energy could possibly force the network to become hexagonal. However, the use of the concept of stacking-fault energy across a metal/oxide interface is troublesome, because of the generally large differences in lattice constants and the complex interaction mechanisms that take place across the interface. Still, some sense of the value of the stacking-fault energy can be obtained. A direct indication that the stacking-fault energy at parallel \{111\} metal/oxide interfaces is low, comes from the observation of oxide precipitates with parallel as well as twin topotaxy within one metal matrix as observed for Cu/MnO [34], Pd/MgO [28] and Pd/AlO [37, 38]. In all these cases the precipitates are freely formed at relatively high temperatures and apart from kinetic reasons are near to equilibrium structures. Apparently, a reversal of the stacking sequence in the oxide is only of minor importance on the interfacial energy. This indicates that the inter-atomic interactions across the interface are extremely short range, i.e. that second nearest-neighbor interaction can be neglected [37]. An important corroboration for this short range of the interactions comes from \textit{ab initio} calculations for parallel topotaxy \{100\} and \{111\} Cu/MgO interfaces [39]. For both interfaces the region of significant nonzero charge-transfer density appeared to be only slightly greater than the interface separation, indicating the dominance of first-nearest neighbor interaction. Since these arguments make it clear that the stacking-fault energy at parallel \{111\} metal/oxide interfaces is not large in magnitude, only the trigonal misfit-dislocation network at the parallel \{111\} Cu/MgO and Cu/MnO interfaces is conceivable, which is also shown by Ref. [40] using the result of the \textit{ab initio} calculations in molecular dynamics and statics calculations.

3. EXPERIMENTAL

Interfaces between Cu and MnO were created using internal oxidation of Cu–1 at.% Mn alloys. Using this method a large number of oxide precipitates are formed in the metal matrix allowing a large number of interfaces to be investigated. The Cu–Mn alloys were prepared by alloying the pure (99.99% by weight) components in a high-frequency furnace under an oxygen-free protective atmosphere of argon. Slices of about 1 mm thickness of the Cu–Mg ingot were oxidized in a Rhines pack (a package of Cu foil containing the sample together with equal volume amounts of Cu$_2$O, Cu and Al$_2$O$_3$ powder) in an evacuated quartz tube at 1273 K for 17 h. First, the Cu–Mn ingot was homogenized in an evacuated quartz tube for 1 week at 973 K. Subsequently, it was cold rolled from a thickness of about 4 to 0.5 mm. Internal oxidation of the Cu–Mn alloy was performed in a Rhines pack in an evacuated quartz tube at 1173 K for 5 h.

Interfaces formed by parallel \{111\} Cu–MnO, obtained by internal oxidation, were observed using a JEOL ARM 1250 electron microscope at MPI Stuttgart [41]. The point resolution of this microscope is sufficient to resolve the Cu matrix along a \{112\} direction, perpendicular to a \{110\} direction. This enables the possibility for checking an interfacial configuration that was predicted by lattice statics calculations [31]. The resulting structure of these calculations can be fed into an HRTEM image simulation program in order to compare the calculated and experimental images of the interface structure. The Cu–MgO and, to a lesser extent, the Cu–MnO system have been studied before quite extensively using HRTEM [27–30], however, not in combination with atomistic calculations and not along the \{112\} direction of the metal.

Specimen preparation for HRTEM work was straightforward using the standard grinding, dimpling and ion-milling tools. Ion milling was performed in a Gatan dual ion mill at 4 kV and 13° elevation. In most cases some additional ion milling (10–15 min) was done just before observation. For HRTEM the JEOL ARM 1250 in Stuttgart was used with the side-entry objective lens installed (C$_s$ = 2.7 mm, $d$ = 11 nm, divergence = 0.9 mrad [41]) resulting in a point resolution of 0.12 nm. This, in principle, suffices to resolve the Cu $d_{\{220\}} = 0.128$ nm and thus allows atomic resolution images taken along Cu \{112\}. Also, a JEOL 4000 EX/II operating at 400 kV in Groningen (spherical aberration coefficient: 0.97 ± 0.02, defocus spread: 7.8 ± 1.4 nm and beam semi-convergence angle: 0.8 mrad) was used. HRTEM negatives were digitized with a CCD camera and the gray scale was adapted to achieve reasonable contrast. No filtering of the images was performed. HRTEM image simulation was carried out with the computer codes MacTempas [42] and EMS [43] using relaxed atomic configurations of the metal at the interface as obtained by the program described in Section 2 as input.

Alloys of silver containing 3 at.% Mn and Cu with 1 at.% Mn were formed in a high-frequency furnace by melting the pure constituents (99.99% by weight) in an alumina crucible under an oxygen-free argon protective atmosphere. Ingots were homogenized (1 week at 700°C in an evacuated quartz tube) and subsequently cold rolled from 4 mm down to 0.5 mm. Interfaces between manganese oxides and Ag or Cu were obtained by means of in-
ternal oxidation. Oxidation of Ag–3Mn was performed in air at 900°C for 1 h.

4. RESULTS AND DISCUSSION

4.1. Ag[111]//Mn$_3$O$_4$[111]: a one-dimensional mismatch

An experimental HRTEM image showing an edge-on interface observed Ag[111]//Mn$_3$O$_4$[111] as viewed along the common [110] direction of Ag and Mn$_3$O$_4$ is presented in Fig. 3(a). Mn$_3$O$_4$ has the I4/amd crystal structure with the following lattice constants: $a = 0.575$ nm and $c = 0.942$ nm [44]. This crystal structure can be conceived as a tetragonally distorted spinel structure and then in direct analogy with the cubic spinel, considered with $a'$-axes which are the face diagonals of the true unit $a$, $a' = a\sqrt{2} = 0.814$ nm (the $c$-axis remains the same as above). The oxygen sublattice is thus f.c.t. with half the dimensions of the tetragonal spinel: 0.407 and 0.471 nm. In order to enable an easy and direct comparison between Mn$_3$O$_4$ and the f.c.c. lattices of Ag and Cu the true unit of the I4/amd will not be used in the present work but rather the larger tetragonal spinel unit. Already above for the indication of planes and directions in Mn$_3$O$_4$ this convention is used. The $a'$-axis of the tetragonal spinel is almost exactly twice the lattice constant of Ag (~0.4% mismatch) and the $c$-axis is 15.3% longer than twice the lattice constant of Ag. Hence, all relevant mismatch between Mn$_3$O$_4$ and Ag originates from the $c$-axis of Mn$_3$O$_4$. In the image of Fig. 3(a) the $c$-axis is contained in the plane of projection and the mismatch between Mn$_3$O$_4$ and Ag along the interface shown is thus basically a one-dimensional mismatch of 10.4% in the [112] direction only (i.e. neglecting the mismatch of ~0.4% in [110], which is permissible since the sample thickness is much smaller than the possible period distance between dislocations in this direction). It is important, of course, that these [112] and [110] directions are parallel in Ag and Mn$_3$O$_4$. This is true for the interface shown in Fig. 3, but is not the case in general [33]. The one-dimensional mismatch is likely to give an array of misfit dislocations which can be observed end-on.

A disadvantage of the Ag/Mn$_3$O$_4$ interface, besides the relatively short length of typically 20 nm presently obtained by internal oxidation, is that direct observation of misfit dislocation cores with localized plane bending between coherent-interface regions in the HRTEM image is difficult because that of Mn$_3$O$_4$ does not show a simple direct correspondence to the atom positions (e.g. with black or white dots and the image is rather sensitive to crystal and beam tilt). However, another effect of the mismatch at the Ag/Mn$_3$O$_4$ interface can still be directly observed, although with some difficulty. Viewed along the interface under an acute angle the Ag [111] planes nearest to the interface are not exactly parallel to the interface, but show a periodic undulation. The dark region in between the first and second Ag [111] planes parallel to the interface (atomic columns are imaged as bright dots) becomes periodically wider and narrower along the interface. The period of this undulation corresponds to $(10 \pm 1)/4[112]$ Ag and thus correlates well with the mismatch present along [112] at the Ag/ Mn$_3$O$_4$ interface. To make the existence of these wavy {111} Ag planes clearer, the glancing-angle view is mimicked in Fig. 3(b) by contracting the image parallel to the interface by a factor of three.

In order to be able to interpret these undulations in terms of a misfit-dislocation structure, atomistic (lattice statics) calculations were performed for this Ag/Mn$_3$O$_4$ interface and subsequently used as input for HRTEM image simulation. Since a detailed description of the results of these calculations and simulations are given in Ref. [33], only a short description follows. The results of the atomistic calculations could be interpreted in terms of an array of edge dislocations with line direction [110] and alternating 1/6[112] and 1/3[112] Burgers vectors and evidently the mismatch cannot be relieved by the favorable Shockley partials only. Although a two-dimensional network of dislocations was allowed a formation of a one-dimensional array appears to be more favorable. The most favorable position of the Ag atoms at the interface with respect to the oxide is in the hollow sites with Ag above a triangle of oxygen atoms. (This is also the geometry used in recent ab initio calculations on the polar Cu(111)//MgO(111) interface [39].) The Burgers vector 1/3[112] is located in the middle of two such favorable sites with the Ag atom directly on top of an oxygen atom (least-favorable site). The Burgers vector 1/6[112] is also located in the middle of two favorable threefold oxygen coordinated sites, but now the Ag atom has two nearest neighbor oxygen atoms. The distance between the Ag atoms and the first (111) plane in the oxide clearly reflects these co-ordinations and thus correlates logically with the Burgers vectors. According to the results of the atomistic calculations {111} Ag planes parallel and near to the interface clearly show undulations with an amplitude which can be resolved by HRTEM and the undulations are probably resolved in the experimental image of Fig. 3.

The results of the atomistic calculations were used as input for HRTEM image simulation (MacTempas [42]). For the estimation of the defocus value of about ~6 nm an amorphous edge was used. This edge was very near to the interface (in the same image) and the change from the minimum contrast in the amorphous edge to the defocus value used for imaging could be directly read from the microscope settings. The thickness can also be estimated rather well because the precipitate shape is known to be an octahedron (bounded by [111]
Fig. 3. (a) HRTEM image of a parallel (111) Ag/Mn$_3$O$_4$ interface viewed along the common [110] of Mn$_3$O$_4$ and Ag. Bright dots in Ag correspond to the position of atomic columns. On viewing the image along the interface at grazing angle undulations can be observed primarily in between the Ag planes nearest to the interface. (b) The same image as in (a) but contracted by a factor of three along the interface; solid-lined arrows indicate the position of $\frac{1}{3}$[112] Burgers vectors at the interface and dashed-lined arrows $\frac{1}{6}$[112] Burgers vectors.
planes of Mn$_3$O$_4$ without any significant {001} truncation [14] and is on two sides of the precipitate symmetrically "overgrown" by the Ag matrix (see Fig. 5 in Ref. [33]). The experimental HRTEM images were simulated most accurately if the Mn$_3$O$_4$ was terminated by a close-packed oxygen plane followed by a close-packed manganese plane. The undulations are still clearly present in the simulated image, Fig. 4, and comparison of Figs 3 and 4 indicates that the atomistic calculations probably explain the experimentally observed undulations at the Ag(111)//Mn$_3$O$_4$(111) interface. In order to make this comparison quantitative the distance between the [110] Ag atomic columns in the second {111} plane with respect to the interface and a straight line positioned as correctly as possible at the determined interface plane was extracted from both the experimental and simulated HRTEM images (Figs 3 and 4, respectively).

The results are shown in Fig. 5 as a function of the distance along the interface ([112]) with experimental results and the results based on the simulated image in the top and bottom figure, respectively. The experimental results show minima and maxima in the distance from the Ag columns to the interface with mutual separations, i.e. distances along the interface, which correspond very well with the expected ones. Even the Burgers vectors of type 1/3[112] and of type 1/6[112] can be distinguished well. The Burgers vectors of type 1/6[112] are experimentally barely resolved, but correspond to the maximum differences in the distance to the interface of only 0.01 nm. In Fig. 3 the solid-line arrows denote the core location of the 1/3[112] type misfit dislocations and the dashed-line arrows denote the location of the 1/6[112] type ones.

4.2. Cu[111]//MnO[111]: a two-dimensional mismatch

HRTEM images of edge-on observed Cu/MnO interfaces pertaining to parallel topotaxy of metal and oxide with {111} parallel to the interface are shown in Figs 6 and 7 for viewing along (110) and (112), respectively. The lattice mismatch between Cu and MnO is equal to 22.9%. Either an incoherent or one of the various possibilities of semi-coherent interfaces are in agreement with the experimentally observed interface structures. The different types of misfit-dislocation networks possible for parallel {111} interfaces are described in Section 2.2. Irrespective of the type of interface structure, incoherent or semi-coherent, the lattice mismatch will always determine the period of misregistry along the interface visible in HRTEM images; i.e. 4-5 planes in the MnO match 5-6 planes in Cu. An incoherent interface can be excluded if strain fields at the interface with the predicted periodicity are visible in the experimental images.
images. But because it is not clear a priori what the appearance of these strain fields in HRTEM will be, caution is necessary, since any strain field is expected to have the same periodicity as possible Moiré effects. Still, the first metal and oxide layer at the interface is best excluded in the analysis of strain fields. Strain fields of two-dimensional misfit-dislocation networks are complex. From the point of view of HRTEM imaging it is important to notice that atomic “columns” cannot only be displaced on average, but can also be bent and thereby smear out the projected potential. The analysis of such displacement fields is not advanced in HRTEM since usually atomic columns are assumed to be perfectly straight [45]. Discrimination between the different types of dislocation networks at semi-

Fig. 6. HRTEM image of an edge-on Cu/MnO [111] interface viewed along (110) in the JEOL ARM 1250. Defocus is about −60 nm and atomic columns of Cu correspond to bright dots.

Fig. 7. HRTEM image of an edge-on Cu/MnO [111] interface viewed along (112) in the Stuttgart JEOL ARM 1250. Defocus is about −55 nm and atomic columns of Cu correspond to black dots.
coherent interfaces is more difficult than discrimination between an incoherent and semi-coherent interface, because for all possible misfit-dislocation networks the periodicity of the strain fields is identical. Only if a detailed knowledge of the strain fields is available can it be used, in principle, to distinguish the effects of the different networks in simulated and experimental HRTEM images.

When viewing along the (110) direction it is possible to measure the separation between subsequent bright dots, which correspond to (delocalized) atomic columns, along the interface in a Cu [111] layer. First, a brightness line is determined by integrating over one Cu [111] layer parallel to the interface. Second, the position of each maximum is determined by fitting a third-order polynomial. (The average distance between the bright spots in the Cu[111] layer is about 20 pixels and the number of pixels around the maxima used for fitting the polynomial is 13 on average.) The resulting distance along the interface between subsequent spots ($d_{sep}$) is plotted in Fig. 8(a) for the second and the eighth Cu layers with respect to the interface shown in Fig. 6. The eighth layer is used as a reference and to check for imaging artifacts. In Fig. 8(a) it can be seen that periodically, mostly for only one pair of subsequent spots, $d_{sep}$ is smaller than $d_{sep}^0$ ($d_{sep}^0$ corresponding to the $1/4(112)$ distance in Cu), whereas in between relatively larger parts along the interface correspond to $d_{sep}$ values slightly larger than $d_{sep}^0$. These observed distances clearly resemble the expected distances for an end-on observed array of misfit dislocations. The cores of the misfit dislocations are localized near the periodic smaller

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**Fig. 8.** (a) Separation between subsequent bright spots as a function of distance along the interface for the second and eighth Cu [111] layer with respect to the interface. The results are based on the image shown in Fig. 6 by determining the positions of the bright spots along the interface by fitting third-order polynomials around each maximum of a brightness line profile taken on the second or eighth Cu layer. (b) The same as (a) but now based on a simulated HRTEM image. A defocus of $-55$ nm and a thickness of 5.1 nm is used.
values for $d_{\text{sep}}$, whereas the coherent regions in between correspond to larger values than $d_0$. Although atomic-resolution imaging of Cu/MnO (110) is also possible in the 4000EX (see Fig. 4 in Ref. [33]) it appeared not possible to obtain reasonable results approaching the ones shown in Fig. 8(a). The excess resolution offered by the JEOL ARM 1250 is thus very useful for the accurate determination of displacement of spots in HRTEM images and as such the JEOL ARM 1250 is useful for structures which can also be resolved by microscopes with poorer resolution.

However, we do not have an edge-on observed array of misfit dislocations, but a network which in the case of a trigonal one corresponds to one edge-on array and two 60° inclined arrays (see Section 2.2). To compare the experimentally based result of Fig. 8(a) with the one theoretically expected for the trigonal network, the same procedure as to derive Fig. 8(a) from Fig. 6 is repeated and Fig. 8(b) is derived from a simulated Cu/MnO (110) image for a defocus value of $-60$ nm and a thickness of 5.1 nm. Only the result of the second Cu {111} layer is shown because significant deviations from $d_0$ do not occur in the eighth layer according to the calculations. Also in Fig. 8(b), $d_{\text{sep}}$ is periodically smaller and larger than $d_0$ (indicated again by the dashed line). However, two important differences are present between the results of Figs 8(a) and (b): (1) the asymmetry in the lengths of the dislocation core region and of the coherent region as observed in Fig. 8(a) is absent in Fig. 8(b), (2) the magnitude of the deviations of $d_{\text{sep}}$ from $d_0$ is about four times larger in experiment than in theory. Interestingly, the experimentally observed deviations of $d_{\text{sep}}$ from $d_0$ in the second Cu {111} layer are about of equal magnitude as the deviations in the first Cu {111} layer in the simulation.

Brightness/contrast variations at the Cu/MnO interface when viewed along the (112) direction (Fig. 7), analogous to the observations for Cu/MgO (112) [46], could not be detected. Also displacements of dark or bright spots on or in between the atomic columns of copper at the interface, indicating the presence of misfit dislocations, could not be observed. The small spacing of 0.128 nm between spots along the interface certainly does not allow determination of periodic variations of spot separation along the interface. These observations thus indicate that, if only the Cu/MnO (112) interface is considered, the conclusion would be that the interface is incoherent. However, the observations along the (110) direction clearly indicated the presence of misfit dislocations. Furthermore, image simulation, based on a relaxed structure in which a distinct misfit dislocation network is formed at the interface, indicates that both brightness/contrast variations and periodic variations of displacements of spots along the interface in HRTEM images for viewing along (112) are so small that they are probably not detectable in experimental HRTEM images. The higher mismatch of 22.9% for Cu/MnO compared to the 16.5% for Cu/MgO leaves less room for any modulations due to misfit dislocations to show up in the image. [Here the misfit is calculated with respect to the reference state (Cu) and in the calculations, for example in Cu/MgO, seven layers were put on top of six leading to a mismatch of 16.7%.] In Section 2.1 it was shown that for a certain interaction strength across the interface the degree of localization of the misfit-dislocation cores decreases for increasing misfit, see Fig. 1 [47, 48]. Therefore, for similar interaction strength across the interface, detection of the difference between semi-coherent and incoherent interfaces becomes more difficult for increasing mismatch and in this respect the misfit at the Cu/MnO interface is already extremely large.

For interfaces with relatively high misfit the incorrect conclusion can be easily drawn that the interface is incoherent, because misfit-dislocation networks at these interfaces may hardly leave a trace in experimental HRTEM images. Discriminating between a semi-coherent and an incoherent interface is important for a correct understanding of the bonding of metal/oxide interfaces.

4.3. Segregation of Sb at metal–oxide interfaces

Solute segregation to the hetero-interfaces is known to affect the adhesive strength at interfaces [49]. However, in contrast to segregation at grain boundaries only very few studies have addressed segregation at metal/ceramic interfaces [50]. In the present study a segregating element, Sb, is dissolved in similar systems as were addressed in the previous sections. To analyze the effect of the Sb dissolution, first the oxide precipitates were grown in the pure metal matrix using internal oxidation. Subsequently the Sb was dissolved in the metal matrix by annealing the composite in an evacuated quartz tube, also containing a small amount of Sb, at a temperature just above the melting point of Sb. The Sb vapor pressure allows transport of the Sb to the metal matrix using solid state diffusion provided the relative amount of Sb present corresponds to a concentration lower than the solubility limit of Sb in the metal. Since this process of introducing Sb in the alloy generally takes 1 week at a temperature of 650 or 700°C, the influence of Sb on the precipitates can only be determined if a comparison is made with the effect of annealing the sample under identical conditions but without the presence of Sb. So, three types of samples are compared: as-grown, Sb-dissolved and vacuum annealed.

The dissolution of 4 at.% of Sb in the Ag matrix showed according to HRTEM observations two major effects on the Mn$_3$O$_4$ precipitates: (i) a change from a precipitate sharply facetted by solely
to a globular shape with sometimes also short {220} and (002) facets and (ii) a partial reduction of Mn$_3$O$_4$ in MnO for a part of the precipitates. An HRTEM image showing both effects is presented in Fig. 9. The lower interfacial strain energy for Mn$_3$O$_4$/Ag with respect to MnO/Ag [50] is probably responsible for the tendency to keep the outer core of the precipitate Mn$_3$O$_4$. The reduction of Mn$_3$O$_4$ into MnO can be understood since annealing in Sb vapor will result in equilibrating the sample with respect to the dissociation pressure of Sb–oxide and this pressure is significantly lower than the original oxygen partial pressure used for internal oxidation. 

To test this explanation, a pure Ag/Mn$_3$O$_4$ sample was annealed in Zn instead of Sb vapor. The dissociation pressure of ZnO is in between these pressures for MnO and Mn$_3$O$_4$ and therefore full reduction of Mn$_3$O$_4$ in MnO is expected. This expectation was indeed confirmed: only MnO precipitates with {200} truncated octahedral shapes were observed in the Zn treated sample; see Fig. 10.

Vacuum annealing of the Ag/Mn$_3$O$_4$ under identical conditions as used for the introduction of Sb also resulted in some differences with the as-grown case, however, completely different from the changes due to the Sb dissolution: (i) next to the {111} facets of the Mn$_3$O$_4$ which remained predominant also {200} and (002) facets developed during the anneal for precipitates which did not exhibit growth (see Fig. 11), (ii) regions where these precipitates without growth were observed adjacent to regions where large (several 100 nm) non-faceted, sometimes polycrystalline Mn$_3$O$_4$ clusters had “consumed” by Oswald ripening all original small precipitates. In the Sb dissolved samples, such growth of the Mn$_3$O$_4$ precipitates was never observed and thus Sb prevents this process. These results also make it clear that Sb is responsible for the spheroidizing effect on the precipitates.

In the case of Sb dissolution in a Cu matrix the MnO and MgO precipitates in pure Cu were obtained by internal oxidation of Cu–1 at.% Mn, Cu–3 at.% Mn and Cu–2.5 at.% Mg with the so-called Rhines pack method (see Section 3). Both MnO and MgO precipitates currently of interest show parallel topotaxy with Cu and have {200} truncated octahedral shape and have average sizes of 200 and 40 nm after 1 week vacuum anneal at 700°C, respectively. Assuming that this anneal results in precipitates with equilibrium shapes the ratio of the {200} and {111} interfacial energy $\gamma_r$ can be obtained from the relative {200} and {111} facet lengths using the Wulff theorem. For Cu/MnO $\gamma_r = 1.64 \pm 0.04$ is obtained from the average of ten precipitates and for Cu/MgO $\gamma_r = 1.27 \pm 0.1$. During the 1 week anneal at 700°C about 2.5 at.% Sb is dissolved in the Cu matrix and the ratio $\gamma_r$ appears to be significantly affected, namely $\gamma_r = 1.30 \pm 0.06$ for Cu(Sb)/MnO (average of 16 precipitate shapes) and $\gamma_r = 1.07 \pm 0.14$ for Cu(Sb)/MgO (average of 14 precipitates). For instance, for Cu/MnO this corresponds to an increase of the relative length of the {200} facet with a factor of 3. It is interesting to note that previous experiments with 2.5 at.% Au dissolution in Cu/MgO showed a decrease of the relative length of the {200} facet, i.e. an effect opposite to that of the Sb dissolution [50].

The general picture that arises from the Sb dissolution in the systems Ag/Mn$_3$O$_4$, Cu/MnO, Cu/MgO
for the present metal/oxide interfaces than for f.c.c. metal/metal interfaces. This difference originates from the two f.c.c. sublattices, one for the anions and one for the cations present in the oxide compared to one f.c.c. lattice in the metals. The ratio of the number of atoms in the terminating layer of the oxide and in the adjacent first metal layer is, for the parallel close-packed plane interface, equal to the ratio of the lattice constants of the metal and the oxide. For parallel non-polar metal/oxide interfaces, such as parallel \{200\}, \{220\} in NaCl structure-type oxides, this ratio is a factor of two higher. This factor of two comes from the fact that only one of the two sublattices in the oxide tends to continue in the metal at the non-polar interface and this results in relatively more free volume experienced by the metal layer at the non-polar interface compared to at the polar close-packed interface. Hence, segregation is expected to occur much more strongly to the non-polar than to the parallel close-packed plane interface.

5. CONCLUSIONS

The scientific message of this paper is that from the atomistic calculations it can be concluded that the actual atomic structure of misfit dislocations depends on the bond strength across the interface as well as misfit. A simple representation of the interface structure as an array of bulk-like interface dislocations relieving the misfit does not necessarily give the right physical picture. This becomes apparent if we compare elastic energies calculated with atomistics and elasticity theory. If interface dislocations are formed, depending on a critical value of the interaction parameter across the interface, a comparison with anisotropic elasticity can be made, showing reasonable quantitative agreement of the energy factors. The total elastic energy is, however, a different case. The curve calculated with elasticity theory is steeper than a curve for constant interaction. In fact, it will be even steeper if the interaction between the dislocations is taken into account, which should be appreciable for 10% misfit, and perhaps even for 4% misfit. In other words, the elasticity curve connects points with different interaction parameters, i.e. with higher values at higher misfit. This is in agreement with the results of Fig. 1. There we found that at higher values of misfit \( \delta \), it takes a higher interaction constant to arrive at dislocation-like structures. Although elasticity does not assume anything about bond strength we can state that when not considering the bond strength and using an elasticity approach is effectively like assuming that the bond strength increases with misfit.

As an example, the misfit-dislocation structures at Ag/MnO\(_4\) and Cu/MnO interfaces formed by parallel close-packed planes of Ag or Cu and O obtained by internal oxidation were studied using...
HRTEM and lattice statics calculations. The lattice statics calculations are instrumental in indicating the possible dislocation network and their results serve as input for HRTEM image simulations which are then compared with experimental HRTEM images. The essentially one-dimensional mismatch between Ag and Mn$_3$O$_4$ of 10.4% along the (111) interfacial plane appears to be accounted for by an array of dislocations with line direction [110] and alternating Burgers vectors 1/6[112] and 1/3[112]. The presence of this dislocation structure is based on a periodically varying distance between the [110] Ag atomic columns and the (hypothetically straight) interface.

Distinction between the hexagonal network of the edge dislocations with Burgers vector 1/2(110) and the trigonal network of 1/6(211) dislocations at the f.c.c.-metal/f.c.c.-oxide (111) interfaces on the basis of experimental HRTEM images is difficult due to the projective nature of HRTEM. It requires a comparison with atomistic calculations of the relaxed configuration of (metal) atoms at the interface. Periodic variations in separation between the average position of atomic columns along the interface were detected at the Cu/MnO interface when viewing along [110] and also clearly indicated the presence of misfit dislocations. When viewing along (112), brightness variations or displacements of the average position of atomic columns are difficult to detect for Cu/MnO. The ability of the JEOL ARM 1250 to resolve the 0.018 nm [220] fringes of Cu is not a guarantee that the subtle effects of misfit dislocations are observed. For interfaces with high mismatch, such as Cu/MnO, the present study indicates that misfit-dislocation networks hardly leave detectable effects in HRTEM images and indicates that easily the incorrect conclusion can be drawn that the interface is incoherent.

The influence of dissolution of a segregating element (Sb) in these systems was also studied using HRTEM. The influence on Mn$_3$O$_4$ precipitates in Ag is distinct: (i) the initial precipitates, sharply faceted by solely [111], are changed into a globular shape with sometimes also short [220] and (002) facets, (ii) a partial reduction of Mn$_3$O$_4$ into MnO occurs for a part of the precipitates. Further Sb appeared to prevent Oswald ripening of the precipitates. The influence on MnO and MgO precipitates in Cu is more subtle: only a small but significant increase of the facet lengths of the {200} (and {220}) relative to the {111} occurs. The influence of Sb can be explained by a large decrease of the energy of steps at Ag/Mn$_3$O$_4$ interfaces and by a stronger tendency for segregation of Sb to {200} and {220} than to {111} facets of the Ag/Mn$_3$O$_4$, Cu/MnO and Cu/MgO interfaces.

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