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Coherency strain reduction in particles on a substrate as a driving force for solute segregation

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ABSTRACT

It is well-established that solute segregation to interfaces is driven by the reduction of their energy. Here we propose coherency strain energy reduction due to lattice misfit modification at an interphase boundary, as a distinct driving force for segregation. Our experiments with Fe–Au particles on a sapphire substrate, together with finite element method calculations demonstrated that the elastic energy contribution to the total driving force for Au segregation exceeds its interfacial energy counterpart for particles larger than ~10 nm in size.

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Solute segregation to surfaces and interfaces is a phenomenon known in materials science for nearly 150 years [1]. The thermodynamic driving force for this process is the reduction of the free energy of the surface/interface due to its enrichment or depletion with solute atoms, relative to bulk composition. Quantitatively, the reduction of the surface/interface energy due to segregation is related to the free energy of segregation, which is described by the Gibbs adsorption isotherm in terms of the Gibbsian excess (or deficiency) in solute of a surface/interface. The segregation free energy, which in the case of a substitutional solid solution is defined as a free energy change of the system due to an interchange of a solute atom in the bulk with a solvent atom at the surface/interface, can be split into several contributions, such as the electronic (chemical) energy [2], elastic strain energy [3–5], magnetic energy [6], etc. The chemical term can be estimated by a thermodynamics-based approach [7] or calculated using first-principles methods [2]. The elastic energy contribution resulting from a difference in atomic sizes between solvent and solute atoms was addressed in several segregation models [3,4]. In the framework of the Wynblatt–Ku model [5], the segregation enthalpy is constructed by adding an “elastic term” to the “chemical term”, the latter described by a broken-bonds model. Other works attempt to calculate both quantities separately [8], or to

demonstrate the extent of local elastic energy reduction in the grain boundaries owing to segregation [9].

In addition to atomic size mismatch, the total elastic energy of a system could also affect segregation in multi-phase systems exhibiting a lattice parameter misfit. For example, in heteroepitaxial multi-component thin films on a rigid substrate, the segregation of one species to the film/substrate interface can alter the film's lattice parameter locally at that interface. Under the assumption of fully-strained films (*i.e.* without plastic relaxation *via* misfit dislocations or alternative plastic deformation mechanisms), such segregation could affect the coherency strain in the whole film, rather than only locally at the interface. For a continuous and laterally-infinite thin film interfacial segregation cannot relieve these strains. However, semi-continuous films (*e.g.* those formed by the coalescence of islands during their growth), or isolated particles on a substrate are not constrained laterally. In these cases, segregation may reduce their total elastic energy since any resulting elastic strain gradients in these features could relax in the in-plane (lateral) direction. Such a reduction depends on the geometry of the system and should increase with increasing system volume for a given shape until plastic relaxation mechanisms are activated. This dependence suggests a distinct contribution to the driving force for segregation, which cannot be included simply in the free energy of segregation. Its non-local nature means it cannot be incorporated into thermodynamically-derived segregation isotherms, and should be treated separately for each geometry. The effect described here differs from the depletion effect in

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segregation, since the latter increases with decreasing particle size and becomes significant for particles smaller than ~10 nm in size [10].

Single crystalline metallic particles on ceramic substrates may easily be obtained by agglomeration (“dewetting”) of thin metallic films [11, 12]. These systems offer a good testbed for understanding the effects of elastic energy on segregation, due to the high degree of control over the lattice misfit (*via* the choice of the metal/ceramic pair and their respective crystallographic orientations) and over the particle size and composition (*via* the initial thicknesses of the deposited films). Segregation in such supported single crystalline metallic nanoparticles may be of interest in applications as catalysts for chemical reactions, as employing solute segregation to tailor their catalytic properties is a promising approach [13,14]. While interfacial segregation has been studied in such systems [15,16], the effects of segregation on the total elastic energy were not considered.

Here we address Au segregation in Au/Fe bi-particles, obtained by solid-state dewetting of thin Fe–Au films on a sapphire substrate. In previous works we studied the role of Au segregation to multiple surfaces and interfaces in this system in phase transformations [17], performed quantitative experimental and computational analysis of the segregation layers [18], and employed them for designing core(Fe)-shell(Au) nanoparticles [14]. Langlois et al. studied the effects of elastic energy on the core-shell configuration in Fe–Au nanoparticles [19]. Here we focus on Au segregation to the Fe/sapphire interface and consider the contribution of the lattice misfit at that interface to the driving force for segregation owing to a reduction in the *total* elastic energy of the particles. Au–Fe particles were obtained by annealing thin Fe and Au films, deposited on *c*-plane sapphire substrate. The complete details of sample preparation and characterization can be found elsewhere [18]. Fig. 1a shows a SEM micrograph of a Au-rich particle with two Fe precipitates on opposing sides. A FIB cross-section from this particle, taken along the dashed line in Fig. 1a, is shown in the TEM micrographs in Fig. 1b–d. Au segregation to the Fe/sapphire interface is evident by the thin layer in dark contrast (Fig. 1d). Similar Au segregation to this interface, and to all surfaces of Fe precipitates was quantified in Ref. [18].

To study the effect of Au segregation to the Fe/sapphire interface on the strain distribution in the Au–Fe bi-particles, a model comprised of three subunits was created. These subunits together form a truncated pyramid with a perfect hexagonal base (Fig. 2a). The largest subunit (gold color) in Fig. 2a represents a face-centered cubic (FCC) Au-30 at.% Fe crystal; the smaller subunit (turquoise color) represents a body-centered cubic (BCC) Fe crystal; the intermediate layer (green color) represents a FCC Au–Fe alloy of variable composition. This configuration represents the typical morphology of Au–Fe bi-particles observed experimentally, where the intermediate layer represents the Au interfacial segregation layer [17,18]. The composition of the FCC intermediate layer which minimizes the total elastic energy of the system was sought, assuming for simplicity that it varies continuously from pure Au to pure Fe. We neglected the likelihood that the observed FCC structure of the segregation layer would revert to a BCC structure for low Au concentrations. Instead, the elastic energy of a system without the intermediate layer (replaced by the BCC Fe sub-unit, *i.e.* no segregation) was calculated as a reference. The strain distribution (Fig. 2b) was calculated in the framework of linear elasticity by means of the finite element method (FEM), applying the MSC. Marc code (MSC Software Corporation). We chose this approach since it allows for calculating the elastic energy of the complex particle shapes observed experimentally, whereas formulating explicit expressions for the dependence of the total elastic energy on the segregation layer's composition is only possible for a handful of simple shapes. Hexahedral elements with 8 nodes were used including the “assumed strain” approach. The sapphire substrate was assumed to be much stiffer than the particle materials, so that the particle/substrate boundary was fully constrained in the *x*-*y*-*z* directions. Free boundary conditions were applied on all other faces of the particle. The elements in the Fe subunit and in the intermediate layer were refined relative to the elements in the Au subunit.

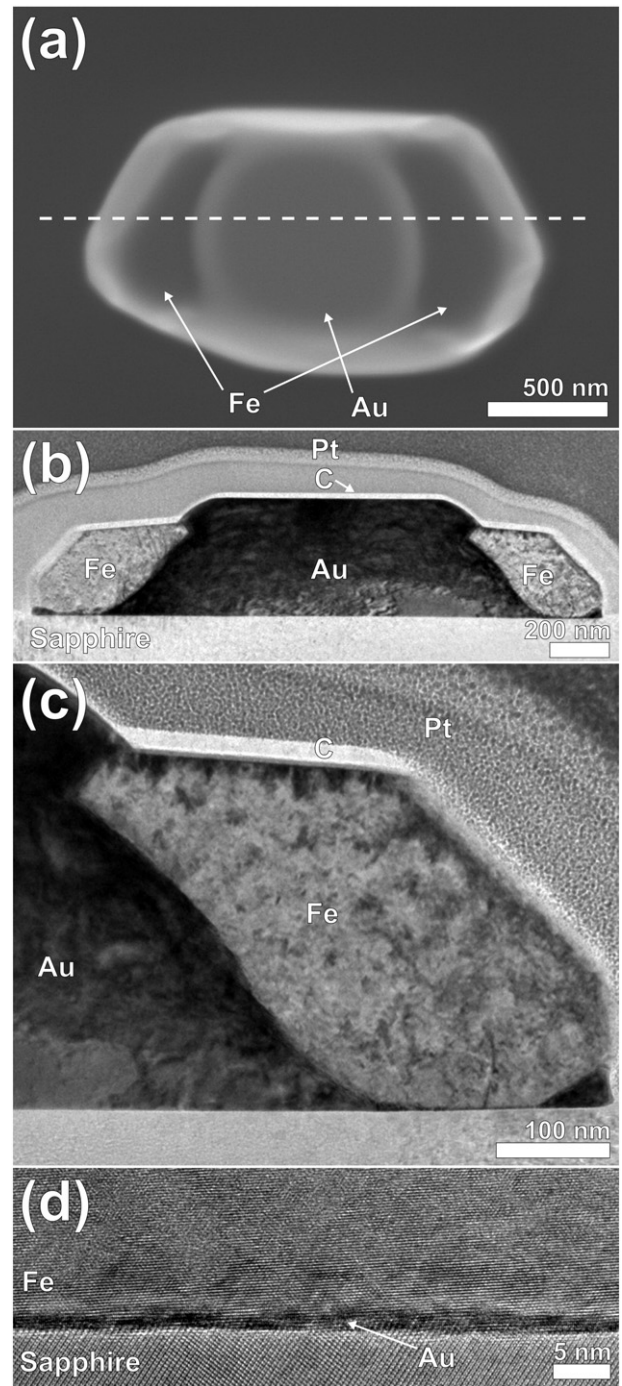


Fig. 1. Interfacial segregation. (a) SEM micrograph of a FCC Au-30 at.% Fe particle with two BCC Fe precipitates on both of its sides. A FIB cross-section was taken along the dashed line. (b) TEM micrograph of the cross-section marked in (a). The C and Pt layers were deposited as part of the FIB preparation process. (c) Magnification of the right Fe precipitate in (b). (d) HRTEM micrograph of the Fe/sapphire interface in (c), showing a Au-enriched segregation layer in dark contrast.

They consisted of 77,760, 16,800 and 179,200 elements, respectively. The orientation relationships (OR) in the system were $(111)_{\text{Au}} \parallel (110)_{\text{Fe}} \parallel (0001)_{\text{sapphire}}$ and $[\bar{2}11]_{\text{Au}} \parallel [1\bar{1}0]_{\text{Fe}} \parallel [11\bar{2}0]_{\text{sapphire}}$ based on experimental observations [17]. These OR are represented in the continuum approach by the orientation of the principle axes of the elastic constants tensor, which are defined in the crystallographic axes of each subunit; and by the misfit strains parallel to the basal planes of the Au–Fe particle, intermediate layer and Fe sub-particle, which were represented in the

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