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Phase equilibria and phase diagrams of nanoscaled systems

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Abstract

With nanostructured matter advancing from laboratory samples to application-relevant or even applied materials, basic and prevalent issues related to the stability of the nanoscale structures against coarsening need to be addressed. The assembly of nano-composites, where isolated nanoscaled particulates or fibrous components are encased in an inert matrix, gives one important processing option that stabilizes the microstructure against coarsening. However, the impact of heterophase boundaries between the nanoscale structures and the matrix or also between different phases in multicomponent nanoscale systems on the product properties yet remain to be understood.

Keywords: Nanostructures; Surfaces and interfaces; Liquid quenching; Transmission electron microscopy; Calorimetry

1. Introduction

Properties of nanostructured—or nanocrystalline materials are significantly affected by the large fraction of atoms that are situated at or near an external or internal interface, i.e. near the surface or near a grain (or heterophase) boundary [1]. In addition to finite size effects due to the occurrence of similar length scales for a characteristic interaction distance or wavelength and the spatial dimension of the system, the excess free energy associated with interfaces in general accounts for modifications of materials properties at small particle—or grain size. For applications of nanostructured materials, such *interface-controlled* property modifications need to be considered in general, i.e. also for properties that are affected by the reduction of the system size, since the phase stability as well as the stability of the microstructure that determine the performance of materials are interface controlled. Despite the apparent importance of the relation between system size, interface structure and materials properties, the underlying mechanisms that cause the observed modifications remain purely understood.

2. Impact of external interfaces

One example that highlights the importance of the structural details of the particle/matrix interfaces is presented by the melting point shift of pure Pb particles that are embedded in an insoluble and polycrystalline Al matrix [2,3]. It has been shown that Al/Pb composites which were synthesized by mechanical attrition present Pb particles with curved interfaces that melt at size-dependent melting temperatures, T_m, that are lower than the bulk melting temperature, T_m^0, of Pb. Rapidly melt-quenched material of identical composition on the other hand, display Pb-nanoparticles within the grains of the polycrystalline Al matrix with faceted interfaces and – associated with this interface morphology—with $T_\mathrm{m} > T_\mathrm{m}^0$. Thus, the change of the interface morphology modifies the melting behavior of the Pb particles even qualitatively. It is important to note, that reversible microstructure modifications can be performed by plastic deformation of the melt-quenched [4]—or by high-temperature annealing of ball-milled material (Fig. 1) [5]. In these instances, not only the morphology of the particle/matrix interfaces changes from faceted to curved or from curved to faceted, but the respective melting characteristics is also modified qualitatively from $T_\mathrm{m} > T_\mathrm{m}^0$ to $T_\mathrm{m} < T_\mathrm{m}^0$ and vice versa. Just recently, it was shown by HRTEM analysis together with Fourier filtering that specific misfit dislocation arrangements exist for the different morphologies and in the case of faceted particles, even for the different interfaces [6]. These results clearly indicate the importance of interface contributions and also show that the

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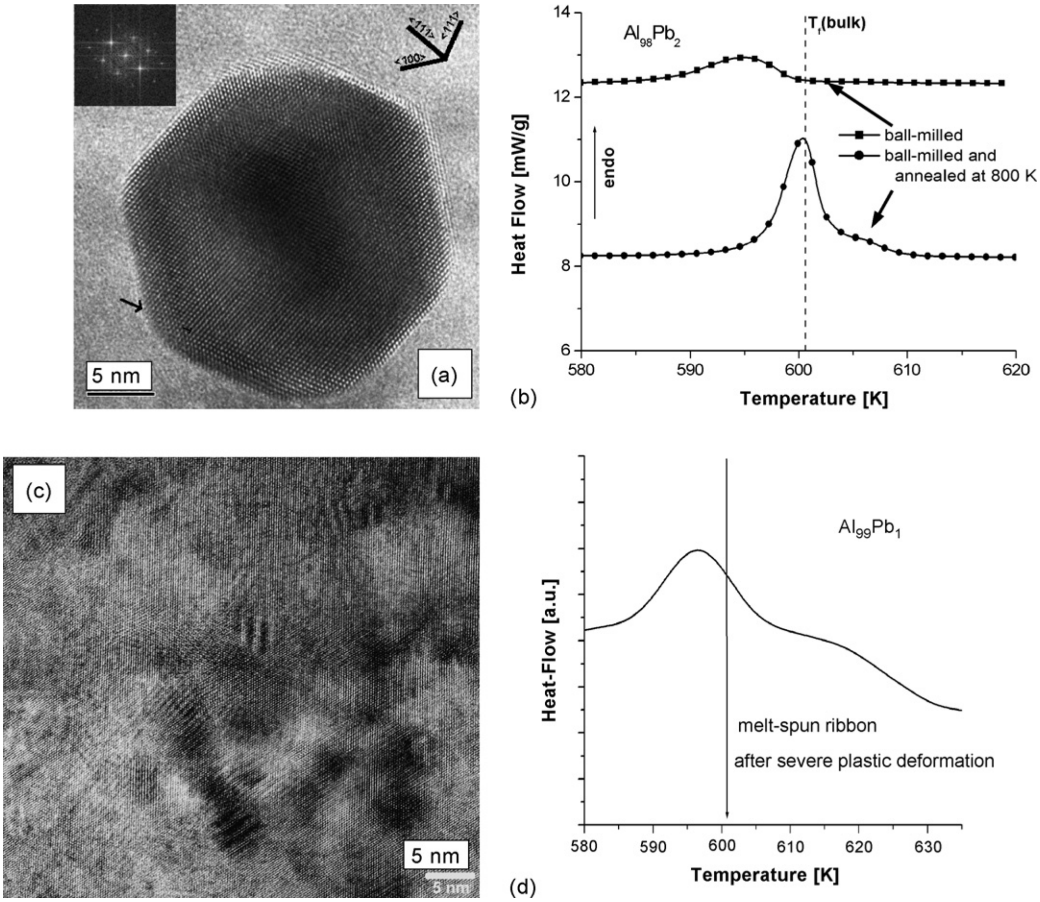

Fig. 1. (a) HRTEM image of a Pb particle in ball-milled material after high-temperature annealing. The arrow on the lower left side of the particle indicates the presence of a dislocation within the particle. (b) Calorimetry results on ball-milled material after high-temperature annealing. The shoulder above the bulk melting temperature is indicated by the arrow. (c) HRTEM image of Pb particles in melt-quenched material after additional high-pressure torsion straining. (d) Calorimetry results on melt-quenched material after the same treatment.

nanoscale size just provides a necessary precondition for interface effects to become significant, but that the atomistic details of the interfaces determine the property modifications even qualitatively. Moreover, the observations support the interpretation of the modifications observed at small sizes being thermodynamic in nature and thus being related to the excess interface free energy rather than to changes of the nucleation kinetics of the phase transformations.

3. Internal interfaces in multicomponent alloy nanoparticles

Aside from the conditions where the actual phase transformations, such as melting or freezing, occur, the majority of nanoscale systems that have been studied concerning the size dependence of phase equilibria or phase transformations, as, e.g. the Pb particles described above, are single component systems. In practice where temperatures are generally not maintained strictly constant, the actual phase transformations represent transient processes that often involve metastable or even unstable states. Thus, in the overwhelming part of temperature-time parameter space, single-component systems are single-phase. The situation is completely different for multicomponent systems where extended stable composition-temperature fields exist that are represented by two or more phases that coexist independent of time and at equilibrium. Thus, multicomponent alloy systems in general entail internal heterophase interfaces in addition to the external surface or the interface of the particles with a matrix. Yet, despite the obvious importance of the extra degree of freedom provided by the composition for materials design and controlled property optimization, only few studies exist on the impact of heterophase boundaries in nanoscale multicomponent systems on the respective phase equilibria and phase transformations, or – in other words – it is generally not well-established if and how alloy phase diagrams change if the size of the alloy structure is reduced to the nanoscale.

In order to systematically address the issue of phase diagram modifications in interface-controlled situations, i.e. for alloy structures that are sufficiently small so that interface contributions to the thermodynamic potentials become significant, we focused our attention on binary alloys that – for the respective bulk system – have a simple eutectic phase diagram between the pure constituents. Real-world model alloys for that situation are given, e.g. by the Bi–Cd system [7]. Yet, since experiments on nanoscale systems almost inevitably involve distributions of size and composition of finite width, an idealized theoretical model eutectic was constructed to analyze the general implications of finite size in detail. A rather uncomplicated case is given by alloys with no solid solubility and an ideal liquid solution, which for the bulk case results in a simple eutectic phase diagram between the pure constituents that is symmetric concerning the equiatomic composition. In a reduced representation, the three materials constants that need to be specified (the atomic volume, melting entropy and interfacial free energy in scaled representations) are similar for most metals. Details of the computation are given elsewhere [8].

Quite generally, the internal heterophase interface – as any interface – contributes an excess free energy to the total Gibbs free energy and that excess is given as $\gamma\,\Delta A$ (specific interface free energy density of the heterophase interface, γ, multiplied by the change in area of that interface, ΔA), reflecting the change of the relative amount of matter per phase during phase transforma-

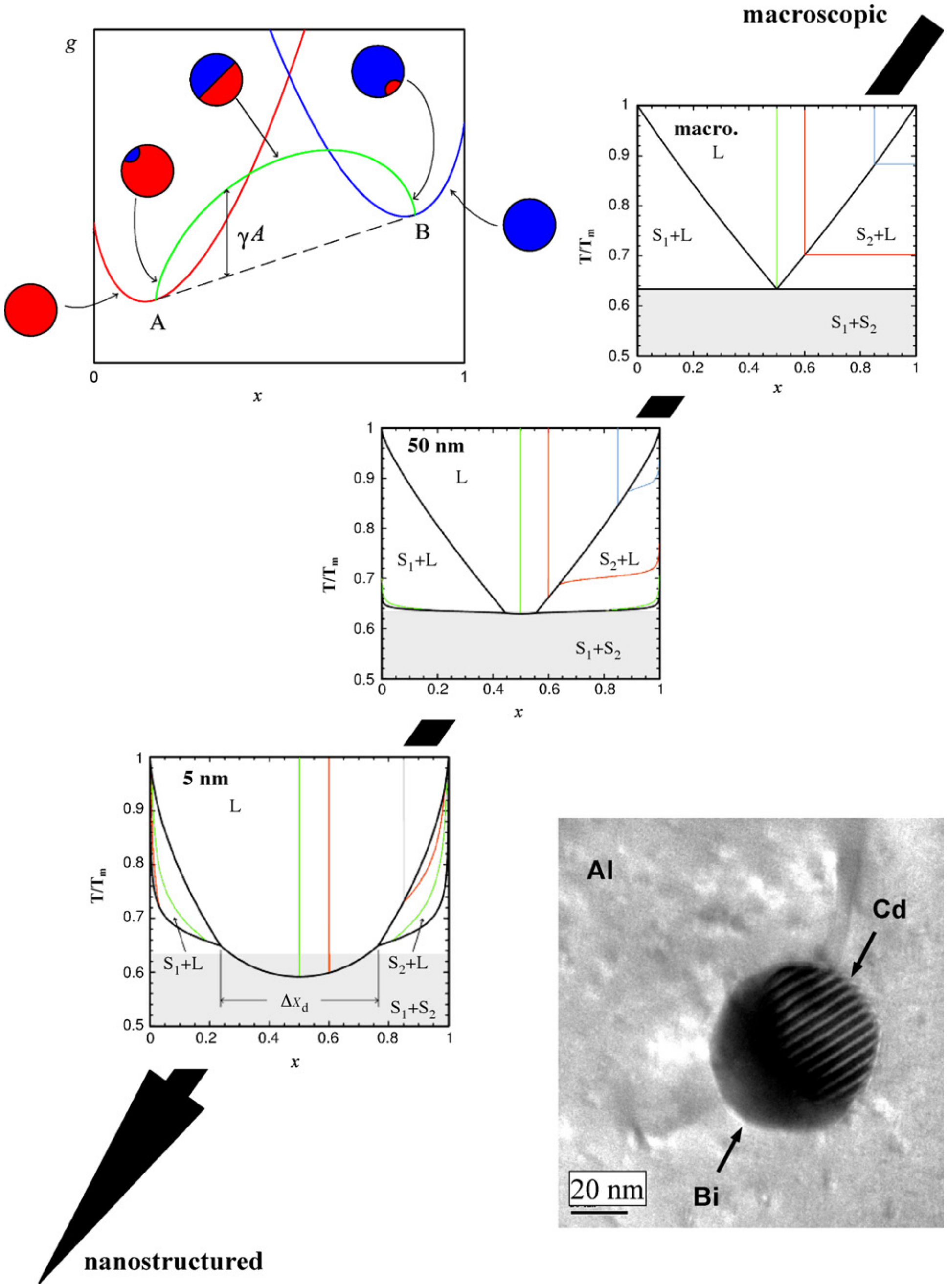

Fig. 2. (upper left) Schematic diagram of molar Gibbs free energies, g, vs. solute fraction x for two phases indicated by concave parabolas (in red and blue). Construction of Gibbs free energy curve for two-phase coexistence of alloys A and B. Dashed: macroscopic system; solid: finite size system. Inserts represent cross-sections through the particle, illustrating the geometric arrangement of the phases and the maximum of the interfacial area A for equal amounts of the two phase. (middle) Calculation results showing the phase diagram of the macroscopic alloy system as well as stability diagrams of nanoscale alloy systems. The lines that start out vertically at high temperatures, represent lines of equal solute fraction in the liquid phase for three arbitrarily chosen values. (bottom right) Representative example of a Bi–Cd alloy nanoparticle embedded in a polycrystalline Al matrix, showing clearly the presence of a heterophase interface within the particle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

tions, which correspondingly changes the interface area between the two coexisting phases. In order to analyze the impact of this internal interface on the thermodynamic equilibrium at different particle sizes, an idealized particle embedded in a solid matrix is regarded where the matrix, as in an experiment, serves to prevent coarsening; this implies that the particle shape and consequently (when volume changes during the phase transition can be neglected) the particle-matrix interface area are fixed. The excess free energy due to the outer surface of the particle is then a constant, which can be ignored altogether since under these conditions it does not affect the phase equilibrium. As shown in detail in [8], the excess term $\gamma\,\Delta A$, which takes on a maximum value for equal atomic fractions of the coexisting phases, removes the linearity of the Gibbs free energy of two-phase states (Fig. 2). Thus, the well-known tangent rule ceases to apply, with important consequences for the phase diagrams, which result from minimization of the total Gibbs free energy at different particle sizes. For instance, the compositions of coexisting phases at constant temperature depend on the nominal composition, i.e. the lever rule is not applicable, and furthermore the composition of the majority phase is not continuous across a phase boundary (indicated by he shaded lines in the diagrams of Fig. 2). The above-mentioned novel features are consistent with the observation by [9], which indicate that the tie lines detach from the phase boundary lines at small size. Thus, it is not possible to obtain the compositions of coexisting phases for a given nominal composition from these phase diagrams, but the temperature-composition fields are given where the respective phase(s) are representing the state of lowest Gibbs free energy.

It may be debated whether or not the graphs of phase stability regions in the temperature-composition domain such as Fig. 2 can still be termed ‘phase diagrams’ or rather ‘stability diagrams’—as compared to the phase diagrams of infinite systems, with which we have become familiar. Yet, although information, e.g. concerning the compositions of the stable phases is not obtained as straight forward as for conventional phase diagrams for bulk systems, these phase diagrams that take the interfacial excess properly into account represent the richer and more general phenomenology at finite size and asymptotically reduce to the familiar ones as the system size tends to infinity. In addition to the above-mentioned modifications at small particle sizes, the topology of the phase diagram changes dramatically, with the most pronounced change being the loss of the invariance of the solidus temperature. Thus, the eutectic point of the bulk phase diagram degenerates to an interval where melting occurs discontinuously without involving a three-phase equilibrium. First calorimetric results obtained on Bi–Cd nanoparticles that are embedded in a polycrystalline Al matrix support the theoretical analysis and actually show a composition-dependence of the solidus temperature at small particle sizes [10]. A TEM image of one representative Bi–Cd alloy nanoparticle is shown in Fig. 2. Additionally, some observations obtained by *in situ* alloying and melting analyses within a TEM [11] agree also with the modeling results.

4. Summary

Interfaces can affect in various ways the properties and the performance or the stability of materials, e.g. by long-range strain fields, by providing paths for rapid diffusion or by providing regions of enhanced solubility or charge accumulation. Yet, even the presence of interfaces that contribute an excess energy can drastically and even qualitatively modify the phase equilibrium. The experimental results on single-component systems, i.e. Pb embedded in an inert Al matrix, emphasize the importance of the local atomic arrangements as well as the details of the defect structure in analyzing the relation between size, morphology and properties. With multicomponent nanoscale alloy particles, modifications at small size are even more pronounced and are affected by internal heterophase interfaces in addition to the impact of the surface of the particle or its interface with a matrix. While even the first results obtained by modeling and also by experiment indicate dramatic changes that affect stability, properties and processing, it seems clear that even more and also more pronounced changes are anticipated for more complex alloy systems with a stronger dependence of the interaction potential on the nominal composition. It will be a crucial step in the development of advanced nanostructured materials to elucidate the rules of nanostructured alloy thermodynamics before properties or processing pathways can be designed.

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