THE ROLE OF LENGTH SCALES IN PHASE DIAGRAMS: A TOOL FOR DESIGNING COMPOSITES

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Introduction

When selecting the materials from which a composite is to be fabricated, it is important to know how the fineness of the phases affects the properties of the materials. For example, it is known that the melting temperature of most solid elements decreases when the size of the phase decreases. Less well known is that the solubility of the phase can also change but typically it increases with decreasing size even to the point of reaching complete miscibility at sizes as large as 10nm. These structural changes in the properties of phases can be determined from phase diagrams displayed as a function of size, especially at the nanoscale. In this paper we point out how the length scale of the embedded phases alters the phase diagram from that of bulk phases.

Modeling considerations

The fundamental basis of phase diagrams is classical thermodynamics, which has been extended to nanosized phases by adding surface terms [1]. The equations for equilibrium between nanosized phases a and b having interfacial radii of curvature r_a and r_b , surface stresses f_a and f_b , and surface energies γ_a and γ_b , respectively, have been shown to be given by the following relationships where T is temperature, P pressure, $_i\mu$ chemical potentials of species i, and atomic volumes $v_a = v_b = v$.

These equations are based on a constant temperature throughout the multi-phase particle and discontinuities in the pressures and chemical potentials across the interfaces in agreement with Gibbs [2]:

Thermal Equilibrium: $T_a = T_b = T$

Mechanical Equilibrium: $P_a = P_{ext} + 2\frac{f_a}{r}$,

$$P_b = P_{ext} + 2\frac{f_b}{r_b}$$

Chemical Equilibrium: $_{i}\mu_{a} = _{i}\mu_{ext} + 2(f - \gamma)_{a}\frac{\upsilon}{r_{a}},$

$$_{i}\mu_{b}=_{i}\mu_{ext}+2(f-\gamma)_{b}\frac{\upsilon}{r_{b}}.$$

with bulk phases, the temperature-As composition phase diagram of nanoparticles shows an area in which two phases coexist in equilibrium. A band of compositions that represent the ends of the tie lines that connect the compositions of each of the two equilibrium phases is also represented on the phase diagram. The discontinuous jumps in pressure and chemical potential lead to a gap between the two-phase region and the band of compositions of the two phases [1]. The purpose of the present paper is to experimentally determine the extent of the two-phase and one-phase regions as a function of size of individual nanoparticles and the existence of any gap in the diagram.

Experimental details

Tin and bismuth of 99.99% purity were simultaneously evaporated from separate tungsten baskets in a vacuum of about 10^{-5} Pa onto amorphous carbon substrates. Isolated alloy nanoparticles were obtained with size and composition determined by the respective temperatures of the tungsten baskets and the substrate temperature. The samples were annealed for 90 minutes at about 375 K to achieve equilibrium structures independent of

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the deposition conditions. An example of the deposited nanoparticles is shown in figure 1. Analytical transmission electron microscopy was used to characterize the samples. Nanodiffraction applied to individual particles determined the structure and energy dispersive spectrometry, the composition using standards to calibrate the spectra.



Figure 1 Transmission electron micrograph of alloy particles of Sn-Bi showing solid solution particles and two-phase particles exhibiting a flat interface between the Sn-rich phase and the Bi-rich phase.

Results and discussion

An isothermal slice through the threedimensional phase diagram of temperaturecomposition-size was constructed by plotting individual points on a map of reciprocal radius and composition. Single phase and two-phase particles were given different symbols in order to determine the boundary between these two regions. These points are shown in figure 2 where it is seen that the one-phase region overlaps with the two-phase region. This overlap is believed to arise because the shape and strain state of the particles differ significantly from particle to particle. The overlap area is not large.

Sn and Bi become completely soluble in one another when the diameter of the particle is below ~10 nm. Other elements exhibit similar behavior. This implies that composites with a nanosized, embedded phase may become a solid solution at elevated temperatures.

Average compositions of individual two-phase alloy nanoparticles were measured as well as



Figure 2. Map of reciprocal size and composition of individual Sn-Bi alloy nanoparticles. The two-phase region is bounded by a dashed line and the one-phase region, by a solid line. These two regions overlap.

compositions of the Bi-rich and Sn-rich phases. According to the thermodynamic modeling the two-phase region should define a range with a gap between it and the bands of compositions of the individual phases. Figure 3 shows this data but no gap.



Figure 3 Map of reciprocal size and the compositions of individual two--phase particles and composition of the Sn-rich side and composition of the Bi-rch side. The lines from figure 2 are redrawn here.

Conclusion

The size dependence of the solubility limits of multi-phase nanoparticles offers an additional degree of freedom in composite deign.

References

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