

Grain-size limit of polycrystalline materials

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(Received 28 September 1998)

Through combining an experimental investigation on the isothermal nanocrystallization thermodynamics of bulk amorphous selenium and a theoretical analysis, an easy and reliable way to derive the lower grain-size limit of polycrystalline materials was proposed. The grain-size limit for the polycrystalline selenium was determined to be about 4.0 nm. [S0163-1829(99)00310-0]

Solid polycrystalline materials are composed of crystallites that are separated by grain boundaries, and it has been of general curiosity that whether there is a lower bound of the mean grain size, or a grain-size limit for a polycrystalline material. Up to now, there are indications that there exists a thermodynamics-based grain-size limit (GSL) for each polycrystalline material, below which the amorphous state will be energetically favored.¹⁻⁴ Obtaining the thermodynamics-based GSL is very important, as it can cast light on the understanding of the transition between the polycrystalline and amorphous state; in addition, it can provide guidance to practical manipulation of materials at the atomic level. However, efforts to obtain the GSL for a specific material are rare and far from being successful.

Theoretical considerations on this issue are rare. Through atomistic computer simulations, Wolf *et al.*¹ found that there exists the possibility of a reversible, free-energy based transition between the amorphous and the polycrystalline states with a critical mean grain size (about 1.4 nm in their model material). Veprek *et al.*² made a rough evaluation of the GSL of silicon by assuming the excess energy of the nanocrystalline silicon to be the elastic energy associated with lattice expansion which leads to a transition from the crystalline state to amorphous state. These GSL's are thermodynamics based, as they are controlled only by the thermodynamic parameters of the polycrystalline materials, without regard to the kinetics involved in the particular experimental method.

Experimentally, Veprek *et al.*² reported that the lowest obtainable mean grain size for vapor-phase deposited polycrystalline silicon was about 2.0 nm for films with compressive stress and 3.0 nm for stress-free films through x-ray diffraction (XRD) analysis. Another way to determine the GSL is through mechanical attrition-induced solid-state amorphization, which usually proceeds via a nanocrystalline precursor state with a minimum grain size. However, the minimum grain sizes determined for the same material through the ball-milling method often differ significantly, for example, the minimum grain sizes for the ball-milled silicon are 8 and 3 nm, respectively, in two investigations.^{3,4} Both the deposition method and ball-milling method for determining the thermodynamics-based GSL's are flawed due to the following facts. First, the experimentally available minimum grain sizes obtained through deposition and mechanical attrition are actually the result of the competition between the kinetic and thermodynamic factors, and will change signifi-

cantly with different experimental conditions. Second, when the mean grain sizes of polycrystalline materials approach the minimum grain size, e.g., 2–3 nm, it is rather difficult to distinguish between the amorphous and nanocrystalline states. Third, extended defect structures, voids, and contamination are nearly inevitable in the materials obtained through both the mechanical attrition and deposition methods. All these factors will affect the experimentally obtained minimum grain sizes significantly,²⁻⁴ and result in error in determining the thermodynamics-based GSL. Other methods should be explored to obtain the thermodynamics-based GSL in polycrystalline materials. Here, through combining an experimental study of the nanocrystallization thermodynamics of amorphous selenium and theoretical analysis, a simple and reliable way to obtain the GSL of polycrystalline materials is presented.

Nanocrystallization of amorphous solids provides an effective way to obtain nanocrystalline materials with dense and clean interfaces, low microstrain, and nearly perfect crystallite structures.⁵ The nanocrystalline materials synthesized through this method are excellent model materials for determining the thermodynamics-based GSL. After a systematic study on the thermodynamics of the crystallization process of amorphous selenium, a simple and reliable method to obtain the thermodynamics-based GSL's of polycrystalline materials is presented in this paper.

Bulk amorphous selenium (purity better than 99.999%) was produced by quenching the Se melt that was sealed in an evacuated quartz ampoule into a mixture of water and ice. The obtained amorphous Se was then fully relaxed in a water bath before thermal analysis. Isothermal annealing of the amorphous Se at different annealing temperatures ranging from 373 to 433 K was monitored and recorded by a differential scanning calorimeter (DSC-7, Perkin-Elmmer) to obtain the different grain-sized nanocrystalline Se and to measure the isothermal crystallization enthalpy ΔH^{cryst} of the amorphous Se at the same time. Quantitative x-ray diffraction (XRD) analyses and transmission electron microscopy (TEM) observations were carried out to determine the average grain sizes of the isothermally crystallized Se samples. Measurements of the heat capacity at constant pressure (C_p) were carried on the same differential scanning calorimeter in the temperature range of 223–500 K on the fully relaxed amorphous, nanocrystalline (with a mean grain size of 10

nm), and conventional polycrystalline Se. Details of the experiments are available in Refs. 6,7.

The measured excess heat capacity of the undercooled liquid Se with respect to the conventional polycrystalline Se, $\Delta C_p^{c-l}(T)$, can be expressed as⁷ $\Delta C_p^{c-l}(T) = 43.6 - 0.079T$, when $320 \leq T \leq 493$ K. Then, the enthalpy difference between the undercooled liquid Se and the conventional polycrystalline Se, ΔH^{l-c} , can be calculated through the following equation: $\Delta H = \Delta H_f + \int_{T_f}^T \Delta C_p^{c-l}(T) dT$, where ΔH_f is the enthalpy of fusion and T_f is the equilibrium melting temperature of Se. It was found out that the calculated ΔH^{l-c} is evidently not equal to the measured ΔH^{cryst} ; and that the difference between the two enthalpies is actually the excess enthalpy of the nanocrystalline Se with respect to the conventional polycrystalline Se, ΔH^{c-nc} , which can be expressed by the following equation:⁷

$$\Delta H^{c-nc} = \Delta H^{\text{cryst}} - \Delta H^{l-c}. \quad (1)$$

So, the excess enthalpy values of the nanocrystallized products with different mean grain sizes can also be calculated.

It has been widely accepted that at low temperatures, the entropy effects will not be large and the enthalpy can be a good approximation of the Gibbs free energy.⁸ Based on this approximation, a linear extrapolation method to determine the GSL in polycrystalline Se is presented below.

1. Linear extrapolation between ΔH^{cryst} and $1/d$

If we assume that the excess enthalpy of the nanocrystallized Se concentrates in the grain boundaries, then the excess enthalpy of the nanocrystalline Se with respect to the conventional polycrystalline state, ΔH^{c-nc} , can be expressed as follows:⁹

$$\Delta H^{c-nc} = 2\gamma g V_m / d, \quad (2)$$

where γ is the grain-boundary enthalpy, V_m is the molar volume, d is the average grain size, and g is the geometrical factor depending on the shape and size distribution of the grains. Substituting Eq. (2) into Eq. (1), we can get

$$\Delta H^{\text{cryst}} = \Delta H^{l-c} + 2\gamma g V_m / d. \quad (3)$$

If we assume that the enthalpy difference between the undercooled liquid and conventional polycrystalline Se, $\Delta H^{l-c}(T)$, keeps constant [although actually $\Delta H^{l-c}(T)$ is not constant in the temperature range of 373–433 K, such an assumption is acceptable, as can be seen from the following results], and that the product of the grain-boundary enthalpy γ and the geometry factor g does not vary with the mean grain size, then we can obtain a linear relationship between ΔH^{cryst} and $1/d$ according to Eq. (3). Figure 1 shows the measured enthalpy of crystallization of the amorphous Se, ΔH^{cryst} , as a function of $1/d$, the reciprocal of the mean grain size of the crystallized products. It is clear that all the data points are on an approximate straight line. Also, the intercept on the inordinate is about -5.5 kJ/mol, corresponding with the average value of $\Delta H^{l-c}(T)$, where T is the temperature range of 373–433 K. When linearly extrapolating the measured ΔH^{cryst} values to $\Delta H^{\text{cryst}} = 0$, we can obtain the intercept on the abscissa, $1/d_{\text{lim}}$. The implication of d_{lim} is clear, when the mean grain size of the crystallized Se

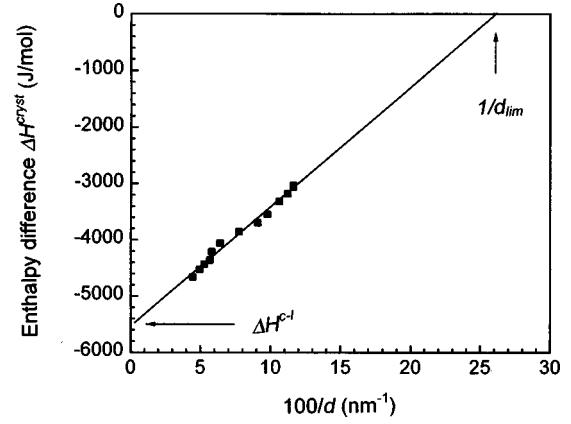


FIG. 1. Linear extrapolation of the experimentally measured enthalpy of crystallization for amorphous Se, ΔH^{cryst} , as a function of $1/d$, the reciprocal of the mean grain size of the nanocrystallized Se.

reaches d_{lim} , the enthalpy, or approximated Gibbs free energy of the nanocrystallized product, the nanocrystalline Se, will be equal to that of the amorphous state. Therefore, the obtained d_{lim} is actually the thermodynamics-based GSL of polycrystalline Se. Here, the obtained GSL is $d_{\text{lim}} = 3.9$ nm.

The merit of the above approach to obtain the d_{lim} is its simplicity, GSL can be obtained just through measuring the ΔH^{cryst} and d . However, this approach has to assume that $\Delta H^{l-c}(T)$ keeps constant during the temperature range where the enthalpies of crystallization of the amorphous state are measured. This is correct for most elemental metals that usually have low $\Delta C_p^{c-l}(T)$,¹⁰ but is not often true for multicomponent alloy systems with comparatively higher $\Delta C_p^{c-l}(T)$.¹¹

2. Linear extrapolation between ΔH^{c-nc} and $1/d$, an improved approach

According to Eq. (2), the excess enthalpy of the nanocrystallized products, ΔH^{c-nc} , will scale linearly with the reciprocal of the mean grain size of the nanocrystallized products with a zero intercept on the inordinate, if we assume the product of γ and g keeps constant with varying d . Figure 2 shows the calculated excess enthalpy of the nanocrystallized product, ΔH^{c-nc} , as a function of the reciprocal of the mean grain size of the nanocrystalline Se. As indicated in Fig. 2, all the data points are on a straight line within experimental error; and also, the intercept on the inordinate is close to zero, just as what is predicated in Eq. (2). When linearly extrapolating ΔH^{c-nc} to $\Delta H^{c-nc} = \Delta H^{c-a}$, where ΔH^{c-a} is the enthalpy difference between the amorphous state and the conventional polycrystalline Se, the enthalpy or the approximate Gibbs free energy of the nanocrystallized product will be equal to that of the amorphous state, and the corresponding mean grain size will be the thermodynamics-based GSL. Here, the enthalpy difference between the amorphous and conventional polycrystalline Se is chosen as $\Delta H^{c-a} = 3.4$ kJ/mol, the nearly constant enthalpy difference between the amorphous and conventional polycrystalline Se when $T < 250$ K, where $\Delta C_p^{c-a}(T) = 0$.⁷ As indicated in Fig. 2, ΔH^{c-nc} reaches ΔH^{c-a} at $d_{\text{lim}} = 4.1$ nm. The two GSL's obtained in the two approaches are very close, in the range of 4.0 ± 0.1 nm, and are comparable with that obtained for Si.⁴

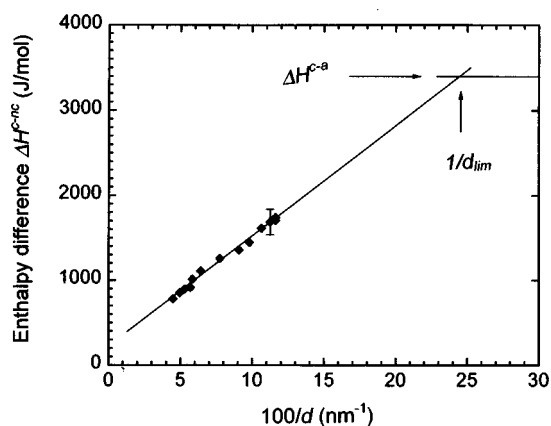


FIG. 2. Linear extrapolation of the excess enthalpy of the nanocrystallized Se, ΔH^{c-nc} , as a function of $1/d$, the reciprocal of the mean grain size. ΔH^{c-a} is the excess enthalpy of the amorphous Se with respect to the conventional polycrystalline Se when $T < 250$ K.

It is notable that in this method for determining GSL, it is assumed that the excess energy of the nanocrystallized product concentrates in the grain boundaries, and that the crystallites have the same lattice structure as those in the coarse-grained counterpart. Generally, a detectable lattice expansion

(with volume expansion less than 1%) often exists in the nanocrystalline materials crystallized from the amorphous state,⁵ and the elastic energy associated with this expansion is negligible (less than 10 J/mol in Se) compared with the other enthalpy values, such as ΔH^{crist} and ΔH^{c-nc} .

Compared with the other methods for determining the thermodynamics-based GSL, this linear extrapolation method possesses its unique advantages. First, the materials which are obtained through annealing the amorphous states have nearly perfect crystallite structure and can serve as excellent model material for accessing their thermodynamic properties. Second, the GSL is obtained by extrapolating the experimental data guided by theoretical analysis, the combination of the experimental results and theoretical analysis distinguishes this method from all the other methods for evaluating the GSL's, which depend on either experimental observation or theoretical calculation. Third, this method is rather reliable. In the two approaches for accessing GSL's, the experimental data are all on a very good line with proper intercept on the inordinate, just as what has been predicated in theoretical analysis. The good agreement between the experimental results and theoretical predication indicates that this method is very reliable.

The support from NSFC and the Chinese Academy of Sciences is gratefully acknowledged.

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