Grain-boundary enthalpy of nanocrystalline materials crystallized from the amorphous state

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An evident inequality between the enthalpy of crystallization of amorphous selenium, ΔH_x, and the enthalpy difference between the undercooled liquid and the conventional polycrystalline selenium, $\Delta H^{l \to c}$, was observed, which is inconsistent with the widely accepted idea that the two enthalpies should be equal. The inequality between the two enthalpies is attributed to the excess enthalpy of the nanocrystallized selenium with respect to the conventional polycrystalline selenium. The maximum excess enthalpy of the nanocrystalline selenium amounts up to 30% of the heat of fusion. Based on the assumption that the excess enthalpy of the nanocrystalline sample is concentrated in the high density of grain boundaries, the grain-boundary enthalpies of the nanocrystalline selenium samples were determined. The obtained grain-boundary enthalpies of the nanocrystalline selenium samples are found to increase from 0.27 to 0.32 J/m^2 with the mean crystallite size increment from 9 to 22 nm. It is predicted that an inequality between the two enthalpies of ΔH_x and $\Delta H^{l \to c}$ will always occur in the nanocrystallization process of an amorphous solid and that the grain-boundary enthalpies of the nanocrystallized products can then be determined. [S0163-1829(97)01933-4]

I. INTRODUCTION

Thermodynamic properties of nanocrystalline materials and/or thermodynamic properties of the grain or interphase boundaries of nanocrystalline materials are crucial in understanding the nature of the boundary structure in nanocrystalline materials and have attracted the interest of a lot of researchers.[1-11]

Up to now, a lot of synthesis methods for the nanocrystalline materials have been developed following the classical method of ultrafine powder (UFP) consolidation,[1] such as mechanical attrition,[4,12] spray conversion processing,[13] electrodeposition,[14] crystallization (of amorphous solids),[15] and so on. Compared with other synthesis methods for nanocrystalline materials, the complete crystallization method possesses some unique advantages:[15]   (a) The synthesized nanocrystalline samples are dense with clean interfaces, and (b) the high density of interfaces in the nanocrystallized products often affects the crystallization kinetics and thermodynamics significantly.[8] So the nanocrystallization process itself provides a unique opportunity to study the thermodynamic properties of the nanocrystalline solids crystallized from the amorphous state.

Investigations on the crystallization thermodynamics of amorphous solids all showed that the enthalpy of crystallization, ΔH_x, of an amorphous solid was equal to the enthalpy difference between the undercooled liquid and the corresponding crystalline phase(s), $\Delta H^{l \to c}$, which was calculated by using the equation

$$\Delta H = \Delta H_f + \int_{T_f}^{T} \Delta C_p^{c \to 1}(T) dT, \qquad (1)$$

where ΔH_f is the enthalpy of fusion and $\Delta C_p^{c \to l}$ is the excess heat capacity of the undercooled liquid with respect to the corresponding crystalline phase(s).[16-18] Chen and Turnbull found agreement between the two enthalpies of ΔH_x and $\Delta H^{l \to c}$ in a Au-Si alloy[16] and later in a Au-Ge-Si alloy.[17] Recently, Klose and Fecht[18] also found agreement between the two enthalpies in a Au-Pb-Sb alloy. Actually, the idea that the two enthalpies of ΔH_x and $\Delta H^{l \to c}$ should be equal has been widely accepted.[19-22] However, in a nanocrystallization process, the average crystallite sizes of the crystallized products are in the range of a few nanometers, and a large amount of energy (enthalpy) exists in the high-density grain boundaries of the nanocrystallized products; then, the calorimetrically measured nanocrystallization enthalpy ΔH_x may be different from $\Delta H^{l \to c}$, the calculated enthalpy difference between the undercooled liquid and the conventional polycrystalline materials. Thus it may be possible to reveal some of the thermodynamic properties of the grain or interphase boundaries of the nanocrystallized products through a study of the thermodynamics of the nanocrystallization process of amorphous solids. In this work, investigations on the thermodynamics of the crystallization process of amorphous selenium were carried out.

II. EXPERIMENT

An amorphous selenium (purity better than 99.999%) was produced by quenching the Se melt into a mixture of ice and water, and was fully relaxed in a water bath at 304 K for 400 h before measuring its heat capacity. The 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 (Perkin-Elmer DSC-7) to form the different grain-sized nanocrystalline Se and to mea-
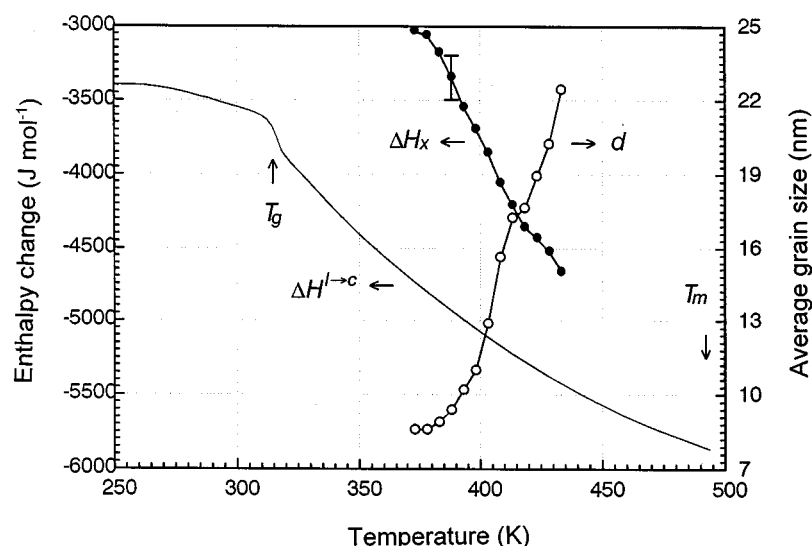
FIG. 1. Calculated enthalpy difference between the undercooled liquid and the conventional polycrystalline Se, $\Delta H^{l\rightarrow c}$, and the enthalpy of crystallization of the amorphous Se, ΔH_x, as a function of temperature, together with the mean grain sizes of the nanocrystallized Se.

sure the isothermal crystallization enthalpy ΔH_x of the amorphous Se at the same time. Nine amorphous Se samples were measured to obtain the statistic average value of the isothermal crystallization enthalpy at a certain temperature. X-ray-diffraction (XRD) analysis and transmission electron microscopy (TEM) observations proved that the amorphous Se samples were completely crystallized after the isothermal crystallization process. Quantitative XRD experiments were carried out to determine the average grain sizes of the isothermally crystallized Se samples. The mean grain sizes were calculated from the half maximum width of the (210), (113), and (104) x-ray-diffraction lines of the crystallized Se according to the Scherrer formula after a correction for $K\alpha$ and instrumental broadening. The mean grain sizes of the crystallized Se samples obtained from the quantitative XRD experiments are approximately in agreement with the results of the TEM observation.[23,24]

III. RESULTS AND DISCUSSION

The heat capacity of the undercooled liquid Se was obtained through an interpolation of the measured specific heat of the amorphous Se near the glass transition temperature and the heat capacity of the liquid Se near the melting point, and the obtained excess heat capacity of the undercooled liquid Se with respect to the conventional polycrystalline Se, $\Delta C_p^{c\rightarrow l}$ (J mol^{-1} K^{-1}), can be expressed by the linear equation[11,24]

$$\Delta C_p^{c\rightarrow l}(T) = 43.6 - 0.079T, \quad 320\ \text{K} \leqslant T \leqslant 493\ \text{K}. \quad (2)$$

The enthalpy difference between the undercooled liquid Se and the conventional polycrystalline Se, $\Delta H^{l\rightarrow c}$, can then be calculated. The obtained $\Delta H^{l\rightarrow c}$ is indicated in Fig. 1 as a function of temperature. The calorimetrically determined crystallization enthalpies of the amorphous Se at different temperatures are also shown in Fig. 1, together with the average crystallite sizes of the crystallized Se samples. The average crystallite sizes of the crystallized Se samples increase monotonically from about 9 nm at a crystallization temperature of 373 K to about 22 nm at 433 K, indicating a nanocrystallization process of the amorphous Se.

The calculated enthalpy difference between the undercooled liquid and the conventional polycrystalline Se, $\Delta H^{l\rightarrow c}$, increases from -5860 J/mol at the melting point 493 K to -4690 J/mol at 373 K, while the nanocrystallization enthalpy ΔH_x increases from -4650 J/mol at 433 K to -2950 J/mol at 373 K. The absolute values of $\Delta H^{l\rightarrow c}$ are larger than those of ΔH_x, exhibiting an evident inequality between the two enthalpies of ΔH_x and $\Delta H^{l\rightarrow c}$, which is inconsistent with the widely accepted idea that the two enthalpies of ΔH_x and $\Delta H^{l\rightarrow c}$ should be equal.[16-22]

In the following section, we will try to resolve the apparent inconsistency above. For the isothermal nanocrystallization process of amorphous Se, the calorimetrically measured enthalpy ΔH_x is actually the enthalpy difference between the amorphous state (or undercooled liquid when the temperature is higher than the glass transition temperature) and the nanocrystallized product, i.e., the nanocrystalline Se, while the calculated $\Delta H^{l\rightarrow c}$ is the enthalpy difference between the undercooled liquid and the conventional polycrystalline Se. So the inequality between the two enthalpies of ΔH_x and $\Delta H^{l\rightarrow c}$ originates from the excess enthalpy of the nanocrystallized Se with respect to the conventional polycrystalline Se. Thus the enthalpy difference between the two enthalpies of ΔH_x and $\Delta H^{l\rightarrow c}$ is actually the excess enthalpy of the nanocrystallized Se with respect to the conventional polycrystalline Se, ΔH^*, i.e.,

$$\Delta H^* = \Delta H_x - \Delta H^{1\rightarrow c}. \quad (3)$$

According to Eq. (3), the excess enthalpies of the nanocrystallized Se samples were calculated. The obtained excess enthalpies of the nanocrystallized Se samples, as a fraction of the enthalpy of fusion, are shown in Fig. 2 as a function of the average crystallite size. It is clear that the obtained excess enthalpies of the isothermally crystallized Se samples decrease monotonically from 30% to 13% of the ΔH_f with the mean grain size increment from 9 to 22 nm, corresponding to 1.74 and 0.78 kJ/mol, respectively.

Generally, nanocrystalline materials are described as a two-component system with a crystalline component and a grain-boundary component with an excess volume, and then the excess thermodynamic properties of the nanocrystalline
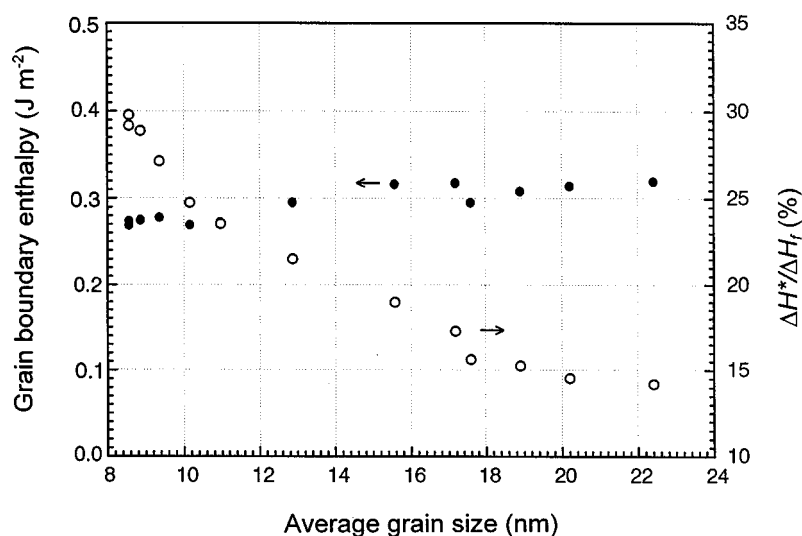
FIG. 2. Obtained excess enthalpy and the grain-boundary enthalpy of the nanocrystallized Se as a function of the average grain size.

materials with respect to the conventional polycrystalline state can be estimated by associating with the excess volume. Alternatively, if we assume that the excess energy (enthalpy) of the nanocrystalline materials is concentrated in the grain boundaries, then the excess energy (enthalpy) of the nanocrystalline materials can be correlated with the specific grain-boundary energy (enthalpy) directly. For example, the excess enthalpy of the nanocrystalline materials with respect to the conventional polycrystalline materials, ΔH^*, can be expressed as follows:

$$\Delta H^* = A_{GB} H_{GB}, \qquad (4)$$

where A_{GB} and H_{GB} are the grain-boundary area and the specific grain-boundary enthalpy of the crystallized product, respectively.

Analysis of x-ray-diffraction line broadening indicated that the lattice microstrain was as low as $0 \sim 0.05\%$ in an $FeZr_2$ nanophase crystallized from the amorphous state[24] and about $0 \sim 0.04\%$ in a TiO_2 nanophase.[7] The corresponding lattice strain energy of such a low microstrain is less than 1 J/mol, which is negligible compared with the total excess enthalpy in nanocrystalline materials. So we can believe that the excess energy (enthalpy) of nanocrystalline materials is concentrated in the high-density grain boundaries. Actually, Eq. (4) has been widely used to calculate the specific grain-boundary energy (enthalpy) values of nanocrystalline materials according to the experimentally determined excess energy (enthalpy).[4,6,7,25]

The calculation of the specific grain-boundary energy (enthalpy) from the total excess energy (enthalpy) requires an accurate determination of the total grain-boundary area. The grain-boundary area A_{GB} in a mean volume share can be calculated by using the equation

$$A_{GB} = g V_m / r, \qquad (5)$$

where V_m is the molar volume, r is the average grain radius, and g is the geometrical factor depending on the shape and size distribution of the grains.[25] The geometrical factor g in Eq. (5) will be $g = 1.5$ for identical spherical grain shape, $g = 1.65$ for identical tetrakaidekahedral grain shape, and $g = 1.86$ for identical cubic grain shape. The geometrical factor will be reduced by a factor of 0.7–0.9 if the grain size distribution is taken into account.[25] In the present calculation, $g = 1.65$ is used. It should be noted that the error of choosing such a geometrical factor ($g = 1.65$) will be no less than 30%.

By combining Eqs. (3), (4), and (5), we can then calculate the specific grain-boundary enthalpies of the nanocrystallized Se samples. The obtained specific grain-boundary enthalpies of the nanocrystallized Se samples are also indicated in Fig. 2. The obtained grain-boundary enthalpies for the nanocrystalline Se samples are in the range of 0.27–0.32 J/m^2 and decrease slightly from 0.32 J/m^2 at a mean grain size of about 22 nm to 0.27 J/m^2 at the mean grain size of about 9 nm. However, it should be noted that the error of the obtained mean grain-boundary enthalpies of the nanocrystalline Se may be significant, as the geometrical factor g in Eq. (5) is actually assumed to be constant with different mean grain size, while the three-dimensional (3D) shapes of the grains will evolve as the grain size increases. Thus a change in g is likely.

Measurements of the (excess) grain-boundary enthalpies of nanocrystalline solids with different average crystallite sizes often show a strong crystallite size dependence of the grain boundary enthalpies, and the obtained (excess) grain-boundary enthalpies often increase with the average grain size within the measured crystallite size range.[7,8] The average grain-boundary enthalpies of different grain-sized nanocrystalline solids, wherever available, are compared in Table I. The mean interfacial enthalpy H_{GB} for Ni/Ni_3P interfaces in a nanocrystalline Ni-P alloy decreases from 0.47 to 0.16 J/m^2 when the mean crystallite size decreases from 60 to 6.5 nm, with an average slope of $\delta H_{GB}/\delta d = 5.8 \times 10^6$ J/m^3, although the interfacial enthalpies may be affected by the presence of dual phases and the segregation effect of phosphorous atoms in the interfaces.[8] The H_{GB} values for UFP-consolidated TiO_2 nanophase samples decrease from 1.55 to 1.28 J/m^2 with the reduction of the crystallite size from 76 to 34 nm, with the slope of $\delta H_{GB}/\delta d = 6.4 \times 10^6$ J/m^3,[7] while for nanocrystalline Se the H_{GB} values also decrease from 0.32 to 0.27 J/m^2 with the reduction of the mean grain size from about 22 to 9 nm, with the slope of $\delta H_{GB}/\delta d = 4.0 \times 10^6$ J/m^3. All the above values of the mean

TABLE I. Comparison of the grain-boundary enthalpies of different grain-sized nanocrystalline solids.

Nanocrystalline solids	Synthesis method	Grain size (nm)	Grain boundary enthalpy (J/m^2)	$\partial H_{GB}/\delta d$ (10^6 J/m^3)	References
Ni-P[a]	Crystallization	6.5–60	0.16–0.47	5.8	8
TiO_2	UFP consolidation	34–76	1.28–1.55	6.4	7
Se	Crystallization	9–22	0.27–0.32	4.0	This work

[a]Grain-boundary enthalpies for the Ni/Ni_3P interphase boundaries are calculated from the corresponding values in Ref. 8 by use of the same method as for nanocrystalline Se in this work. The H_{GB} values for the nanophase TiO_2 are obtained through calorimetrically measuring the heat release for the grain growth during a linear heating process (Ref. 7).

grain/interphase boundary enthalpy of the nanocrystalline materials decrease with the average grain size.

In the following we will discuss the effect of the average grain size d of the crystallized product on the crystallization enthalpy of an amorphous solid. In the crystallization process of a metallic glass, we can assume the grain or interphase boundary enthalpy H_{GB} to be about 1 J/m^2 (the typical grain-boundary energy values for equilibrated high-angle grain boundaries of refractory metals),[26] and the molar volume V_m to be 1×10^{-5} m^3 mol^{-1} (for pure iron $V_m=7.1\times10^{-6}$ m^3 mol^{-1}). Then, if in a normal crystallization process, the average crystallite sizes of the crystallized products are in the range of a few micrometers, for example, the mean grain radius $r=5$ μm, then the total grain-boundary enthalpy in the nanocrystallized product is about 3.3 J/mol, which is in fact negligible compared with $\Delta H^{l\rightarrow c}$ (the values of $\Delta H^{l\rightarrow c}$ are often in the range of several kilojoules per mole). Therefore, the crystallization enthalpy ΔH_x would be equal to $\Delta H^{l\rightarrow c}$, just as what has been experimentally observed and widely accepted.[16–22] However, if in a nanocrystallization process the average grain sizes of the crystallized products are in the range of a few nanometers, for example, $r=5$ nm, then the total grain or interphase boundary enthalpy of the nanocrystallized product will be about 3.3 kJ/mol, which is nearly comparable to $\Delta H^{l\rightarrow c}$. So the nanocrystallization enthalpy ΔH_x will not be equal to $\Delta H^{l\rightarrow c}$, just as what has been observed in the nanocrystallization process of amorphous Se in this work.

Lu et al.[8] also found that the enthalpy of an eutectic nanocrystallization process of an amorphous Ni-P alloy, ΔH_x, is not equal to $\Delta H^{l\rightarrow c}$, the excess enthalpy of the corresponding liquid alloy. In fact, agreement between the enthalpies of ΔH_x and $\Delta H^{l\rightarrow c}$ only occurs in a crystallization process in which the mean grain size of the crystallized product is so large (for example, on the order of micrometers) that the excess enthalpy exists in the grain boundaries of the crystallized product is negligible compared with $\Delta H^{l\rightarrow c}$, while an inequality between the two enthalpies of ΔH_x and $\Delta H^{l\rightarrow c}$ will always occur in a nanocrystallization process of amorphous solids. Therefore, the thermodynamic properties of the grain or interphase boundaries of the nanocrystallized products can then be obtained. This actually provides a way to obtain the thermodynamic properties of the grain or interphase boundaries of the nanocrystalline materials crystallized from the amorphous state.

IV. CONCLUSION

Conclusively, an evident inequality between the enthalpy of crystallization of amorphous Se, ΔH_x, and the enthalpy difference between the undercooled liquid and the conventional polycrystalline Se, $\Delta H^{l\rightarrow c}$, was observed, which is inconsistent with the widely accepted idea that ΔH_x and $\Delta H^{l\rightarrow c}$ should be equal. The difference between ΔH_x and $\Delta H^{l\rightarrow c}$ originates from the high-density grain boundaries of the nanocrystallized product, the nanocrystalline Se. Accordingly, the excess enthalpies of the nanocrystalline Se samples were calculated to be in the range of 0.78–1.74 kJ/mol, corresponding to 13%–30% of ΔH_f. With the assumption that the excess enthalpy of the nanocrystallized product is concentrated in the high-density grain boundaries, the grain-boundary enthalpy values of the nanocrystalline Se samples were also calculated, which decrease from 0.32 to 0.27 J/m^2 with the reduction of mean grain size from 22 to 9 nm. It is predicted that an inequality between the two enthalpies of ΔH_x and $\Delta H^{l\rightarrow c}$ will always occur in a nanocrystallization process of amorphous solids, and the grain-boundary enthalpies of the grain or interphase boundaries of the nanocrystallized products can then be obtained.

ACKNOWLEDGMENTS

[1]H. Gleiter, Prog. Mater. Sci. **33**, 223 (1989).

[2]H. J. Fecht, Phys. Rev. Lett. **65**, 610 (1990); Acta Metall. Mater. **38**, 1927 (1990).

[3]M. Wagner, Phys. Rev. B **45**, 635 (1992).

[4]E. Hellstern, H. J. Fecht, Z. Fu, and W. L. Johnson, J. Appl. Phys. **65**, 305 (1989); H. J. Fecht, E. Hellstern, Z. Fu, and W. L. Johnson, Metall. Trans. A **21**, 2333 (1990).

[5]J. Rupp and R. Birringer, Phys. Rev. B **36**, 7888 (1987).

[6]A. Tschöpe, R. Birringer, and H. Gleiter, J. Appl. Phys. **71**, 5391 (1992).

[7]C. D. Terwilliger and Y. M. Chiang, in *Nanophase and Nanocomposite Materials*, edited by S. Komarnen, J. C. Parker, and G. J. Thomas, MRS Symposia Proceedings No. 286 (Materials Research Society, Pittsburgh, 1993), p. 15.

[8] K. Lu, R. Lück, and B. Predel, Scr. Metall. Mater. **28**, 1387 (1993).

[9] D. Wolf, J. Wang, S. R. Phillpot, and H. Gleiter, Phys. Lett. A **205**, 274 (1995).

[10] R. Birringer, G. E. Krill, and M. Klingel, Philos. Mag. Lett. **72**, 71 (1995).

[11] N. X. Sun and K. Lu, Phys. Rev. B **54**, 6058 (1996).

[12] C. C. Koch, Nanostruct. Mater. **3**, 109 (1993).

[13] B. H. Kear and L. E. McCandlish, Nanostruct. Mater. **3**, 19 (1993).

[14] U. Erb, A. M. El-Sherik, G. Plumbo, and K. T. Aust, Nanostruct. Mater. **2**, 383 (1993).

[15] K. Lu, J. T. Wang, and W. D. Wei, J. Appl. Phys. **69**, 522 (1991); Scr. Metall. Mater. **24**, 2319 (1990); K. Lu, Mater. Sci. Eng. R Rep. **16**, 161 (1996).

[16] H. S. Chen and D. Turnbull, J. Appl. Phys. **38**, 3646 (1967).

[17] H. S. Chen and D. Turnbull, J. Chem. Phys. **48**, 560 (1968).

[18] G. Klose and H. J. Fecht, Mater. Sci. Eng. A **179/180**, 77 (1994).

[19] L. Greer, J. Less-Common Met. **145**, 131 (1988).

[20] B. Predel, Key Eng. Mater. **40&41**, 17 (1990).

[21] K. Ohsaka, E. H. Trinh, J. C. Holzer, and W. L. Johnson, Appl. Phys. Lett. **62**, 2319 (1993).

[22] B. Zappel and F. Sommer, Mater. Sci. Eng. A **179/180**, 283 (1994).

[23] H. Y. Zhang, Z. Q. Hu, and K. Lu, J. Appl. Phys. **77**, 2811 (1995); Nanostruct. Mater. **5**, 41 (1995).

[24] N. X. Sun, Master thesis, Institute of Metal Research, Chinese Academy of Sciences, 1996.

[25] L. C. Chen and F. Spaepen, Nature (London) **336**, 366 (1988); J. Appl. Phys. **69**, 679 (1991).

[26] W. Gust, B. Predel, and K. J. Stenzel, Z. Metallkd. **69**, 721 (1978).