

Heat-capacity comparison among the nanocrystalline, amorphous, and coarse-grained polycrystalline states in element selenium

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(Received 5 January 1996)

Nanocrystalline element selenium (nc-Se) samples were synthesized by completely crystallizing a melt-quenched amorphous selenium (*a*-Se). Heat capacities (C_p) of the nc-Se (with a mean crystallite size of 10 nm), a fully relaxed *a*-Se, and a coarse-grained polycrystalline Se were experimentally determined in a temperature range of 225–500 K. Measurement results show that there is no pronounced difference between the C_p values of the nc-Se and the *a*-Se below 250 K. Heat capacities of the nc-Se are found to be only about 2% higher than those of the coarse-grained polycrystalline selenium. The C_p enhancement for the nc-Se, which is much lower than those reported in other nanocrystalline elements, is discussed in terms of the grain-boundary configurations in the nanostructures. [S0163-1829(96)02030-9]

Heat capacity of a material is directly related to its atomic structure, or its vibrational and configurational entropy which is significantly affected by the nearest-neighbor configurations. Nanocrystalline (nc) materials are structurally characterized by the ultrafine crystalline grains, and a large fraction of atoms located in the metastable grain boundaries in which the nearest-neighbor configurations are much different from those in the crystallites. Or in other words, the grain-boundary possesses an excess volume with respect to the perfect crystal lattice. Therefore, heat capacities of the nc materials are expected to be higher than those of the corresponding coarse-grained polycrystalline counterparts.

Experimental measurements of heat capacities at constant pressure, C_p in several nc materials synthesized by means of different methods indicated that C_p values are frequently higher than those for the coarse-grained polycrystalline counterparts, and are even higher than those for the amorphous states as well.^{1–3} For example, the C_p values of a nc-Pd synthesized by consolidation of ultrafine metal powders were reported to be as much as 60% higher than those for the coarse-grained polycrystalline Pd.¹ The heat-capacity values of a ball-milled nc-Ru sample were found to be about 20% higher than those of its coarse-grained polycrystalline counterparts.² Nevertheless, these results should be accepted cautiously because the measured C_p values might be influenced by many factors. Porosity and possible gaseous contamination [e.g., the sample has a density of only 80% and a total impurity content of about 1 at. % in the case of the nc-Pd (Ref. 1)] in the ultrafine-powder-consolidated nc materials may contribute to the enhanced C_p . While in the ball-milled nc specimens, contamination from the milling media and the subsequent consolidation conditions might alter the heat-capacity results. Up to now, solid experimental results of heat-capacity comparison among the amorphous, the coarse-grained polycrystalline, and the nc states are still lacking.

Among the existing synthesis methods of nc materials, the complete crystallization of amorphous solids serves as an effective approach to form dense nc samples without any porosity because no consolidation process is involved.^{4,5} The

grain or interphase boundaries are naturally formed inside the bulk sample during the crystallization process, which can hardly be affected by the external processing factors such as contamination and pressures. So, the nc materials synthesized by using the complete crystallization method provide us a good opportunity to investigate the intrinsic effect of grain or interphase boundaries on heat capacity in nc materials. Furthermore, with the aid of this method, comparison of heat capacities between the amorphous and the nc states with exactly the same composition becomes possible. Up to now, only two cases of heat-capacity measurements were reported for the nc alloys crystallized from the amorphous solids.^{6,7} However, analyses of the C_p enhancements in the nc materials relative to the conventional polycrystalline states are much more complicated because of the multiphase effects as well as the segregation of solute atoms in the grain or interphase boundaries.^{6,7} In order to rule out these influencing factors from the investigation systems, we carried out an experimental measurement on the heat capacities of a nc element selenium sample which was synthesized by completely crystallizing a melt-quenched amorphous selenium bulk sample. The heat capacities of the porosity-free dense nanocrystalline, the amorphous, and the coarse-grained polycrystalline states in the pure element selenium will be compared.

An amorphous selenium bulk sample (with a purity of 99.999%) was obtained by quenching selenium melt into a mixture of ice and water, and was then fully relaxed in a water bath at 304 K for 400 h before measuring its heat capacity. Nanocrystalline Se samples were synthesized by crystallizing the *a*-Se completely during isothermal annealing treatments. The synthesis procedures were described in detail elsewhere.⁸ In the present investigation, the nc-Se sample was produced by annealing the *a*-Se at 373 K for 280 min. X-ray diffraction (XRD) and transmission electron microscopy (TEM) observations proved that the nc-Se sample was completely crystallized, a mean crystallite size of about 10 nm was obtained from the quantitative XRD and the dark-field TEM experiments. The coarse-grained polycrystalline Se was obtained through an annealing at 205 °C ($0.97T_m$)

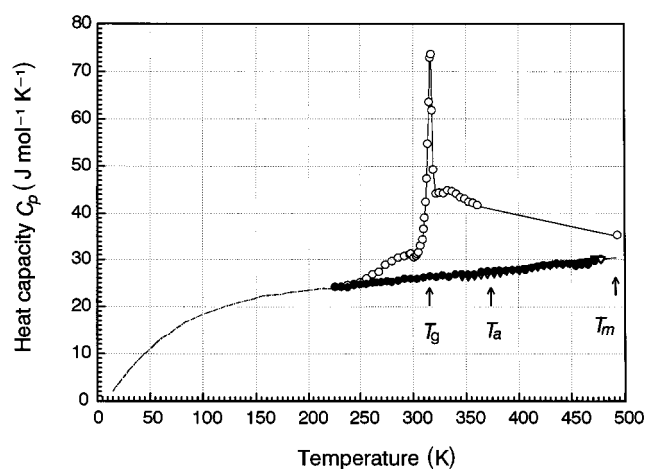


FIG. 1. Comparison of the measured heat capacities of the amorphous selenium (open circles), the nanocrystalline selenium (solid circles), and the coarse-grained selenium (open triangles), and the heat-capacity values for the conventional polycrystalline Se from literature (Ref. 10) (dot-dash line). T_g , T_a , T_m represent the glass transition temperature of the amorphous selenium, the annealing temperature of the nc-Se, and the melting point of selenium, respectively.

for 5 h, and the average grain size was determined to be about 50 nm. The microstructure characterization of the nc-Se crystallized from the a -Se was reported in Ref. 8.

Heat capacity at constant pressure (C_p) measurements were carried out on a differential scanning calorimeter (Perkin-Elmer DSC-7). The temperature and energy measurements were calibrated by means of the pure In and Zn standard samples. Usually, two methods may be employed for measuring heat capacity by using DSC, i.e., the amplitude method and the enthalpy method.⁹ The enthalpy method was employed in the present work because of its better accuracy. This method includes (i) maintaining an energy input to hold a constant temperature, (ii) changing the input to produce a temperature increment, and (iii) again holding constant at a new temperature. A heat-capacity value can be obtained by dividing the energy increment by the temperature increment.

C_p measurements of the selenium samples were carried out in a temperature range of 223 to 500 K, equilibration times at constant temperatures between energy increments were 180 s, the heating rate was 0.033 K/s, and the temperature interval was 4 or 6 K. Seven samples were measured to obtain the statistic average value of the heat capacity. The calorimeter was testified with a sapphire sample in the same temperature range, and the accepted C_p values of the pure sapphire were reproducible within $\pm 1\%$.

Measurement results of C_p in the temperature range of 225–500 K for the as-crystallized nc-Se, the fully relaxed a -Se and the coarse-grained polycrystalline Se samples are presented as a function of temperature in Fig. 1, together with the C_p values for conventional polycrystalline Se from the literature.¹⁰ No significant difference can be identified from Fig. 1 between the C_p values of the as-crystallized nc-Se and the coarse-grained polycrystalline Se. The C_p values of the nc-Se are also found to be rather close to those of the a -Se below 250 K. When $T > 250$ K, C_p of the a -Se increase rapidly with the increase of temperature due to the

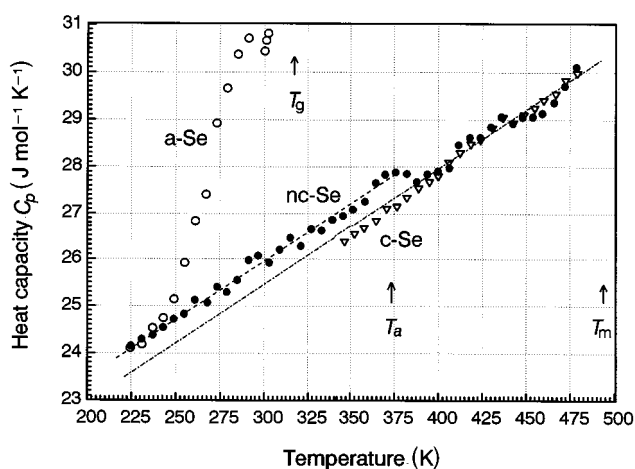


FIG. 2. A magnified part of Fig. 1, showing the relationship among the heat capacities of the amorphous selenium (a -Se), the nanocrystalline (nc-Se), and the coarse-grained polycrystalline selenium (c -Se).

relaxation process and the subsequent glass transition.

Figure 2 is a magnified part of Fig. 1, showing the heat-capacity comparison among the three states: the nc-Se, the a -Se, and the coarse-grained polycrystalline Se. From Fig. 2, one may find that below 250 K, C_p values of the nc-Se are overlapped with that of the a -Se before its relaxation and glass transition. The measured C_p values for the coarse-grained polycrystalline Se coincide well with those in the literature.¹⁰ The heat capacity of the nc-Se is found to be an approximate linear relation with temperature within 225 to 375 K, and the C_p values of the nc-Se are about 2% higher than those of the coarse-grained polycrystalline Se below 375 K. Considering that the measurement accuracy of C_p is about 1% in the present work, such a C_p difference may reflect the intrinsic property of the nc-Se sample, that the nc-Se exhibits a higher C_p than the coarse-grained polycrystalline Se. When $T > 375$ K, the difference between the specific heats of the nc-Se and the conventional polycrystalline Se diminishes. Quantitative XRD measurements of the nc-Se indicated that a significant grain-growth process took place when $T > 375$ K. The mean crystallite size of the as-crystallized nc-Se samples increases from the initial value of 10 nm up to about 21 nm after the C_p measurement at 425 K. But no grain growth was detected in the nc-Se and the coarse-grained polycrystalline Se below 370 K. These results implied that the nc-Se underwent a grain-growth process and/or a relaxation process which may account for the depression of the C_p difference between the nc-Se and the coarse-grained polycrystalline Se above 375 K. In addition, one may also conclude that the C_p values of a nc-Se with an average grain size larger than 21 nm are rather close to those of the coarse-grained polycrystalline Se with a mean grain size of about 50 nm.

The heat-capacity enhancement in the nc-Se with respect to that of the coarse-grained polycrystalline Se, being in the range of 2%, is much smaller than those of the nc elements reported in the literature.^{1–3} Table I lists a comparison of C_p values among the nc, the amorphous, and the coarse-grained polycrystalline states in various materials. From Table I one may find that the C_p enhancements are quite large (as much

TABLE I. Comparison of the typical heat-capacity values of the nanocrystalline, the coarse-grained, and the amorphous states in various materials. (The values in the brackets are the excess heat capacities of the nc state with respect to the coarse-grained polycrystalline states).

Alloy system	Nanocrystalline			Amorphous C_p^a (J mol ⁻¹ K ⁻¹)	Coarse-grained C_p^c (J mol ⁻¹ K ⁻¹)	Temperature T (K)
	Synthesis method	d (nm)	C_p^{nc} (J mol ⁻¹ K ⁻¹)			
Pd (Ref. 1)	UFP consolidation	6	37 (48.0%)	27 ^a	25	250
Cu (Ref. 1)	UFP consolidation	8	26 (8.3%)		24	250
Ru (Ref. 2)	Ball-milling	15	28 (21.7%)		23	250
Ni ₈₀ P ₂₀ (Ref. 6)	Crystallization	6	23.4 (0.9%)	23.4	23.2	250
Se	Crystallization	10	24.5 (1.7%)	24.7	24.1	245

^aExtrapolated specific-heat value for pure Pd-based on values for the amorphous Pd₇₂Si₁₈Fe₁₀ alloy.

as 48% in nc-Pd at 250 K) for nc samples synthesized by consolidation of ultrafine powders or by ball milling; while the enhancements are rather small (1–2 %) for the nc samples (Ni-P and Se) crystallized from the amorphous solids. The crystallized nc samples and the amorphous solids with the same composition have approximately comparable C_p values. The relatively lower C_p enhancements for the crystallized nc samples, compared with those in the nc samples synthesized by use of other methods, might be attributed to the following reasons. Firstly, the crystallized nc samples are free of porosity and gaseous contamination in the grain boundaries. Porosity inside the nc materials creates considerable internal free surfaces which may enhance the configurational and vibrational entropy of the samples. Secondly, because the nanostructures are obtained through an annealing heat treatment at relatively high temperatures (in the case of the nc-Se, the annealing temperature is about $0.7T_m$), the crystallites as well as the grain boundaries are well relaxed during the annealing, leading to a relaxed nanocrystalline state with extremely low microstrain (as small as 0.05% in a crystallized nc FeZr₂ samples¹¹). Therefore, these nc materials may exhibit lower heat capacities compared to the unrelaxed nc materials with the same grain size. This was verified by the facts that the C_p enhancements in the consolidated nc-Pd and the ball-milled nc-Ru decrease from 50 and 20 % down to 5 and 7 %, respectively, after annealing the nc samples. Such a drastic depression in the C_p values implies that the microstrains, lattice defects, and grain-boundary dislocation densities might be significantly reduced during the thermal annealing.

Nanocrystalline samples can be generally described as a two-component system consisting of the nanocrystallites and the grain or interphase boundary components. The atomic fraction of the grain-boundary component can be approximately estimated to be $3\delta/d$, where δ is the thickness of the grain boundary and d is the average crystallite size. For the nc-Se with $d=10$ nm, about 30% of the atoms are on the grain boundaries. Keeping in mind that the excess heat capacity of the nc-Se is about 2% of the conventional polycrystalline Se, then, the excess heat capacity of the grain-boundary component should be 7% relative to the C_p of the conventional polycrystalline Se, which is much lower than those proposed in other nc materials.^{12,13}

The heat-capacity enhancements in the nc materials are usually associated with an increase in the configurational and vibrational entropy of the grain boundaries, which constitute a large volume fraction of the material. Hence, the grain-boundary configurations or the grain-boundary energy should be responsible for the C_p enhancements. Theoretical calculations^{12,13} indicated that C_p of the grain boundary increases with an increment of the grain-boundary excess volume, and hence with an increment of the grain-boundary energy. A low excess specific heat of the grain-boundary component would correspond to a small excess volume of the grain boundary, and therefore a low grain-boundary enthalpy.^{12,13} In fact, grain-boundary enthalpy of the nc-Se has been determined to be about 0.27 J/m²,¹⁴ much smaller compared with those obtained in other nc materials (e.g., the obtained grain-boundary enthalpy for platinum is as much as 1.1 J/m²).^{2,3,15,16} Therefore, nc materials may possess much lower excess volume than what has been expected.

Very recently, Wolf *et al.*¹⁷ reported their computer simulation results on the thermodynamic properties of the nc materials and glasses, indicating that the heat-capacity values of the nc material might be below or above those of the glass depending on its grain size. The nc material with a critical grain size (in their study system it is 1.4 nm) may have an identical C_p as the glass. These simulation results, to some extents, agree well with our experimental observations that a fully dense, relaxed nc solid and the corresponding amorphous solid with exactly the same composition have comparable specific heats, as observed in Ni-P (Ref. 6) and Se.

In conclusion, heat capacities of the nc, the amorphous, and the coarse-grained polycrystalline Se were measured in the temperature range of 225–500 K, and were compared with the C_p data for conventional polycrystalline Se from literature.¹⁰ No evident C_p difference was found between the nc-Se sample (with a mean grain size of 10 nm) and the amorphous Se sample below 250 K. The heat capacity of the nc-Se was found to be only 2% higher than that of the coarse-grained polycrystalline Se.

The authors would like to thank Professor Q. Jiang for helpful discussions. The financial support from the National Science Foundation of China and the Chinese Academy of Sciences are acknowledged.

- ¹J. Rupp and R. Birringer, *Phys. Rev. B* **36**, 7888 (1987).
- ²E. Hellstern, H. J. Fecht, F. Zhu, and W. L. Johnson, *J. Appl. Phys.* **65**, 305 (1989).
- ³H. J. Fecht, E. Hellstern, F. Zhu, and W. L. Johnson, *Metall. Trans.* **21A**, 2333 (1990).
- ⁴K. Lu, J. T. Wang, and W. D. Wei, *J. Appl. Phys.* **69**, 522 (1991); *Scr. Met. Mater.* **24**, 2319 (1990); K. Lu, *Mater. Sci. Eng. Rep.* **R16**, 4 (1996).
- ⁵M. L. Sui, K. Lu, W. Deng, L. Y. Xiong, S. Patu, and Y. Z. He, *Phys. Rev. B* **44**, 6466 (1991); *J. Appl. Phys.* **69**, 4451 (1991).
- ⁶K. Lu, R. Lück, and B. Predel, *Z. Metallkd.* **84**, 740 (1993).
- ⁷J. Li and T. M. Wang, *Appl. Phys. Lett.* **66**, 1774 (1995).
- ⁸H. Y. Zhang, Z. Q. Hu, and K. Lu, *J. Appl. Phys.* **77**, 2811 (1995); *Nanostruct. Mater.* **5**, 41 (1995).
- ⁹J. F. Smith, Q. Jiang, R. Lück, and B. Predel, *J. Phase Equilibria*, **12**, 538 (1991).
- ¹⁰R. Hultgren, P. D. Desai, D. T. Hawkins, M. Glesier, K. K. Kelley, and D. D. Wagman, *Selected Values of the Thermodynamic Properties of Elements* (ASM, Metals Park, Ohio, 1973).
- ¹¹N. X. Sun, X. D. Liu, and K. Lu, *Nanostruct. Mater.* (to be published).
- ¹²H. J. Fecht, *Phys. Rev. Lett.* **65**, 610 (1990); *Acta Metall. Mater.* **38**, 1927 (1990).
- ¹³M. Wagner, *Phys. Rev. B* **45**, 635 (1992).
- ¹⁴N. X. Sun, and K. Lu (unpublished).
- ¹⁵A. Tschöpe, R. Birringer, and H. Gleiter, *J. Appl. Phys.* **71**, 5391 (1992).
- ¹⁶C. D. Terwilliger and Y. M. Chiang, in *Nanophase and Nanocomposite Materials*, edited by S. Komarneni, J. C. Parker, and G. J. Thomas, MRS Symposia Proceedings No. 286 (Materials Research Society, Pittsburgh, 1993), p. 15.
- ¹⁷D. Wolf, J. Wang, S. R. Phillpot, and H. Gleiter, *Phys. Lett. A* **205**, 274 (1995).