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To cite this article: Y.H. ZHAO , Z.H. Jin & K. Lu (1999) Mechanical-milling-induced amorphization of Se: A crystallite destabilization model, Philosophical Magazine Letters, 79:9, 747-754, DOI: [10.1080/095008399176814](https://doi.org/10.1080/095008399176814)

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Published online: 14 Nov 2010.



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## Mechanical-milling-induced amorphization of Se: a crystallite destabilization model

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[Received in final form 18 May 1999 and accepted 24 May 1999]

### ABSTRACT

Complete solid-state amorphization has been realized in elemental Se by means of mechanical milling of crystalline Se powder. Quantitative X-ray diffraction and thermal analyses were employed to characterize the amorphization process and indicated that the amorphization onset corresponds to a critical crystallite size and a drop in microstrain. During the major amorphization process, the remaining crystallite size remains unchanged with a constant lattice expansion. A new kinetics model of crystallite destabilization is proposed for the solid-state amorphization which satisfactorily explains the experimental observations.

Amorphous solids can be prepared by means of various quenching techniques from the liquid or vapour state, or alternatively via solid-state amorphization (SSA) from crystalline parent phases (Johnson 1986). SSA has been achieved in many alloy systems with a starting material of either mixtures of elements or intermetallics, by mechanical alloying or milling, irradiation (with electrons or ions), hydrogenation or interdiffusion in multilayer thin films (Johnson 1986, Weeber and Bakker 1998). In some pure elements (such as Si, Ge and Se), partial or complete SSA has also been observed during mechanical milling (MM) or irradiation of powders (Gaffet and Harmelin 1990, Gaffet 1991, Shen *et al.* 1995, Fan *et al.* 1997). From a thermodynamic point of view, SSA can be understood in terms of an accumulation of a variety of defects (point defects, dislocations, grain boundaries (GBs), lattice distortions etc.) in the crystalline phase which raises the Gibbs free energy of the defective crystalline phase above that of the amorphous phase. Most kinetic investigations on the SSA process have been performed on binary alloy systems. A well accepted SSA kinetic model was developed from the amorphization process in diffusion couples in which the amorphous phase nucleates heterogeneously at interfaces or GBs followed by a subsequent thickening of the amorphous layer into the untransformed crystalline phases via atomic interdiffusion (Johnson 1986, Benedictus *et al.* 1996, 1998). This kinetic model has been frequently applied for the amorphization process in various binary systems during mechanical alloying, in which the amorphous phase is assumed to nucleate at intercrystalline regions (forming an amorphous 'shell') and to grow by consuming the crystalline cores (Benjamin and Schelleng 1981, Schwarz

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*et al.* 1985). However, this so-called 'shell' kinetic model is unlikely to be valid for SSA of pure elements, which are the most favourable systems for understanding the intrinsic SSA mechanism and the metastable phase equilibrium. Until now, the kinetic mechanism for SSA in pure elements is least understood.

The objective of the present work is the experimental investigation of the SSA kinetic process in a pure element, Se, during MM. Se provides an excellent opportunity to uncover the intrinsic amorphization mechanism because firstly it is the only known element that can be fully amorphized via MM and secondly the milling-induced amorphization process in Se is very fast so that contamination from the milling media is minor.

MM pure Se powder (99.999%) was carried out in a high-energy vibratory ball mill with stainless steel balls and vial at ambient temperature. The ball-to-powder weight ratio was 10 to 1 and about 4.5 g of powder was used for each run. The loaded vial was sealed by an elastic O-ring in dry Ar with an over-pressure about 3 atm. Wet chemical analysis and energy-dispersive X-ray analysis indicated that, in a sample milled for 250 min, after which the sample was fully amorphized, the O content was 0.1 wt% or less and the Fe content was 0.02 wt% or less.

Quantitative X-ray diffraction (XRD) measurements of the as-milled samples were performed on a Rigaku DMAX/2400 X-ray diffractometer with Cu K $\alpha$  radiation. The X-ray wavelengths  $\lambda_{K\alpha 1}$  (= 1.540 562 Å) and  $\lambda_{K\alpha 2}$  (= 1.544 39 Å) were selected using a (0002) graphite crystal scattering at the goniometer receiving slit. The divergence, scattering and receiving slits were chosen to have widths of 0.5°, 0.5° and 0.15 mm, respectively. Measurements of  $\theta$ - $2\theta$  scans for the samples were made in the reflection mode at room temperature ( $293 \pm 1$  K) with a small angular step of  $2\theta = 0.02^\circ$  and a fixed counting time of 50 s.

Thermal analysis was performed using a Perkin-Elmer differential scanning calorimeter (DSC-7), with a sensitivity of  $0.04 \text{ mJ s}^{-1}$  for energy measurements. As-milled Se powder compact (weight of ranging from 10 to 25 mg) was sealed in Al pans and measured in a flowing Ar atmosphere at a constant heating rate of  $10 \text{ K min}^{-1}$ . The temperature was calibrated with pure In and Zn standard samples, with an accuracy of  $\pm 0.2 \text{ K}$ .

Figure 1(a) shows the XRD patterns for the unmilled and as-milled Se samples with different milling times  $t_m$ . It is seen that the starting material contains crystalline Se with a trigonal structure (t-Se). The MM evidently decreases the intensities of the XRD Bragg reflections for t-Se, and induces the formation of three broad diffuse scattering haloes characteristic of amorphous Se (a-Se). A significant amount of a-Se was observed after milling for 120 min and the element was fully amorphized after milling for 250 min. This phase transition was verified by differential scanning calorimetry (DSC) measurements, as indicated in figure 1(b). The exothermic peak in the DSC curves corresponding to the crystallization of a-Se appears when  $t_m = 30$  min and becomes more evident with increasing  $t_m$ . The exothermic peak shifts to higher temperatures with an extension of  $t_m$ , which is similar to the observation by Guo and Lu (1998a). When  $t_m = 250$  min, the total enthalpy change for the crystallization of the as-milled a-Se amounts to  $3.2 \text{ kJ mol}^{-1}$ , which is smaller than that of as-quenched a-Se ( $4.9 \text{ kJ mol}^{-1}$ ). This difference originates from different molecular structures of the as-quenched and as-milled a-Se samples (Guo and Lu 1998b).

The pseudo-Voigt function (Cox *et al.* 1986) was used to fit the Bragg reflections of the t-Se and the diffuse scattering haloes from the amorphous phase. The mean grain size  $D$  and the microstrain ( $\epsilon^2$ )<sup>1/2</sup> of the t-Se crystallites were determined by

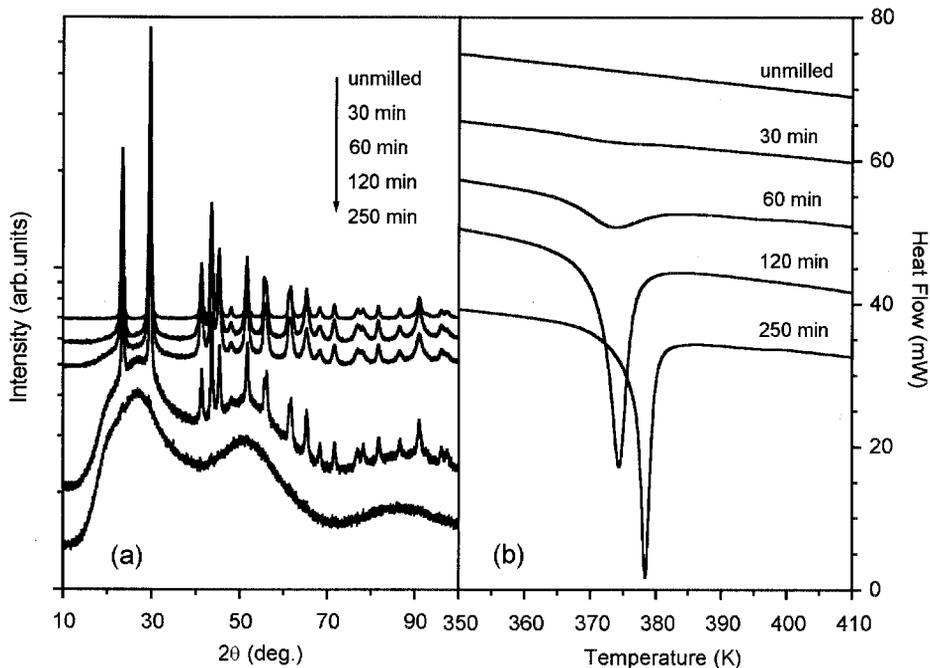


Figure 1. (a) The XRD profiles and (b) the DSC curves for the unground Se and the as-milled Se samples with different milling times (as indicated).

using the Scherrer and Wilson equations, the procedure for which has been previously described in detail (Zhao *et al.* 1997). The variations in  $D$  and  $(\epsilon^2)^{1/2}$  with  $t_m$ , as shown in figure 2(a), indicated that  $D$  decreases monotonically at the early stage of milling and saturates to a constant value of about  $13 \pm 1$  nm when  $T_m > 30$  min. Milling for more than 150 min leads to a further decrease in  $D$  to about 9 nm ( $t_m = 200$  min). On milling, the mean microstrain  $(\epsilon^2)^{1/2}$  increases from about  $0.20 \pm 0.02\%$  ( $t_m = 0$  min) to a maximum value of  $0.39 \pm 0.02\%$  at 30 min, then decreases and tends to zero with further milling.

The volume fraction  $x_a^t$  of a-Se in the as-milled sample is usually taken to be proportional to the enthalpy change from crystallization of a-Se by taking the fully amorphized sample ( $t_m = 250$  min) as 100% a-Se. It can be also estimated from the relative integrated intensity of the XRD Bragg reflections from t-Se:  $x_a^t = 1 - \frac{I_c^t}{I_{c100}}$ , where  $I_c^t$  and  $I_{c100}$  are the sum of the integrated intensities of the Bragg reflection peaks from t-Se in the milled sample and that from the unground sample respectively which can be obtained by means of pseudo-Voigt function fitting. Figure 2(b) shows the variations in  $x_a^t$  and the enthalpy change  $\Delta H_a^t$  for crystallization of a-Se, indicating that the XRD results agree very well with those from DSC. In the early stage of milling ( $t_m < 30$  min; stage I), no visible amorphous phase is detected. Evidently the amorphization process begins at  $t_m = 30$  min. During  $t_m = 30$ –120 min (stage II),  $x_a^t$  increases in an approximately linear relation with  $t_m$ . Afterwards,  $x_a^t$  increases slowly and tends to 100% at 250 min (stage III).

The lattice parameters of t-Se were calculated from the intensity centroid positions by the weighted least-squares method in order to minimize the calculation

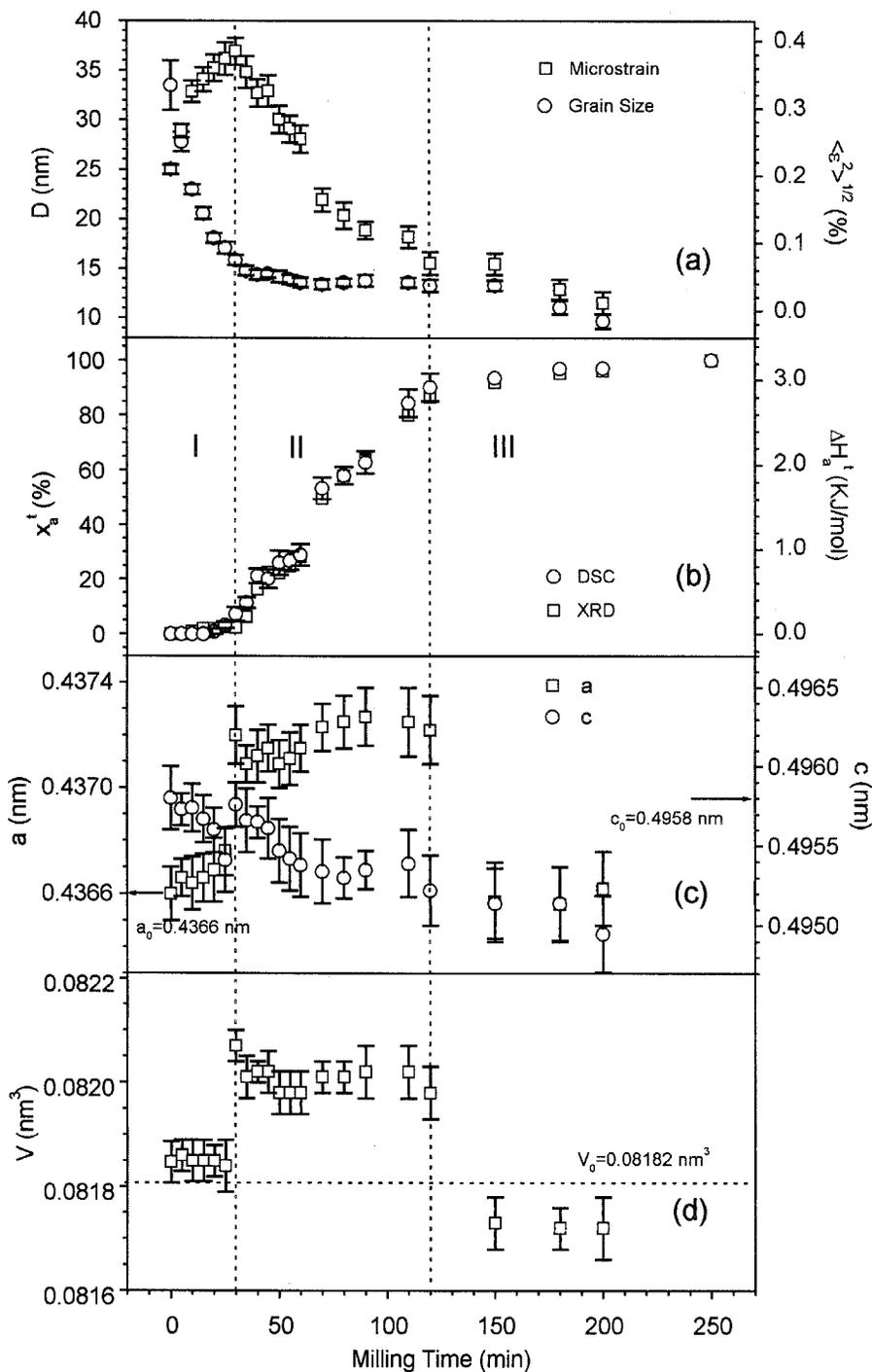


Figure 2. Variations in various structure parameters of crystallite Se with the milling time: (a) the mean grain size  $D$  and microstrain  $(\epsilon^2)^{1/2}$ ; (b) the volume fraction  $x_a^t$  of a-Se determined from XRD and DSC measurements, and the crystallization enthalpy  $\Delta H_a^t$  of a-Se; (c) the lattice parameters  $a$  and  $c$ ; (d) unit-cell volume  $V$  of the crystallite Se against milling time.

error. The intensity centroid positions were calibrated by an external standard method using a pure Si polycrystal to minimize the systemic error. The detailed procedure for the lattice parameters determination was described by Zhao *et al.* (1997). Measured lattice parameters  $a$  and  $c$  for t-Se in the as-milled samples as a function of  $t_m$ , are shown in figure 2(c). The value of  $a$  is found to increase monotonically from the tabulated value  $a_0$  ( $= 4.3655$  Å (Parthasarathy and Holzapfel 1988)) to  $a = 4.3720 \pm 0.0011$  Å ( $\Delta a = (a - a_0)/a_0 = 0.15\%$ ) in stage I. In stage II,  $a$  remains unchanged at about  $4.3719 \pm 0.0009$  Å ( $\Delta a = 0.15\%$ ). In stage III,  $a$  is found to decrease to  $a_0$ . The value of  $c$  is found to be close to  $c_0$  ( $= 4.9576$  Å (Parthasarathy and Holzapfel 1988)) when  $t_m = 0$  min and shows a decreasing tendency with increasing  $t_m$ . The unit-cell volume  $V$  of t-Se can be calculated from  $V = (3^{1/2}/2)a^2c$ , as shown in figure 2(d). It is seen that  $V$  for the t-Se crystallites increases during MM. In stage II,  $V$  remains unchanged at a value about 0.3% higher than  $V_0$  while, in stage III,  $V$  decreases close to the tabulated value.

The above results indicated that MM of t-Se element powders causes a grain refinement, and an increased  $(\varepsilon^2)^{1/2}$  as well as a lattice distortion in the t-Se crystallites in stage I. When  $t_m = 30$  min, the grain size tends to a constant value  $13 \pm 1$  nm, and  $(\varepsilon^2)^{1/2}$  reaches a maximum value which corresponds to the onset of amorphization. Stage II is a major amorphization process ( $x_a^t = 0-90\%$ ) corresponding to a drop in  $(\varepsilon^2)^{1/2}$ , while the remaining t-Se crystallite size remains unchanged at 13 nm with a constant lattice expansion of 0.3%. Further milling up to 250 min leads to complete amorphization, a further decrease of  $D$  to 9 nm,  $(\varepsilon^2)^{1/2}$  to zero, and  $V$  close to  $V_0$ .

The thermodynamics of the amorphization process in Se can be considered by a comparison of the Gibbs free energies of the a-Se and the crystalline t-Se phases. Assuming that a spherical crystallite with a diameter  $D$  is transformed into an amorphous phase, the Gibbs free-energy change will be

$$\Delta G_{(T)} = \frac{4\pi}{3} \left(\frac{D}{2}\right)^3 (\Delta G_v - \Delta E_1 + \Delta E_2) + 4\pi \left(\frac{D}{2}\right)^2 (\gamma_{ca} - \gamma_{gb}), \quad (1)$$

where  $\Delta G_v$  is the Gibbs free-energy difference per unit volume between the amorphous and crystal states, which can be approximated as  $\Delta H_m(T_m - T)/T_m$  (Turnbull 1950).  $\Delta E_1$  is the elastic energy density change (per unit volume) due to the lattice expansion  $(V_{nc} - V_c)/V_c$  ( $V_{nc}$  and  $V_c$  are the nanocrystalline and crystalline volumes respectively) and  $(\varepsilon^2)^{1/2}$  induced by milling, that is  $\Delta E_1 = [(V_{nc} - V_c)/V_c]^2 B + ((\varepsilon^2)^{1/2})^2 B$  (where  $B$  is the bulk modulus for the solid) (Kittel 1971).  $\Delta E_2$  denotes the change in strain energy density resulting from the volume change due to amorphization. According to Allen *et al.* (1980),  $\Delta E_2 = (18\mu B \varepsilon'^2 f)/(4\mu + 3B)$ , where  $\mu$  is the shear modulus for the solid and  $f$  is a factor to account for the effect of a free surface on the strain energy density, which is taken to be 1.0 in the present case.  $\varepsilon'$  is the hydrostatic strain associated with the fractional volume change during amorphization,  $\varepsilon' = \frac{1}{3}(V_a - V_c)/V_c$  ( $V_a$  is the volume of the amorphous state).  $\gamma_{gb}$  and  $\gamma_{ca}$  are the energy of the GBs and the crystalline–amorphous interfacial energy respectively. A critical grain size  $D^*$  can be deduced for the amorphization process when  $\Delta G_{(T)} = 0$ :

$$D^*(T) = \frac{6(\gamma_{gb} - \gamma_{ca})}{\Delta G_v - \Delta E_1 + \Delta E_2}. \quad (2)$$

By means of the available data for  $V_{nc}$ ,  $V_c$ ,  $(\epsilon^2)^{1/2}$ ,  $\gamma_{ca}$  (Kelton 1991),  $\gamma_{gb}$  (Lu and Sun 1997),  $\Delta H_m$ ,  $T_m$ ,  $\mu$ ,  $B$  and  $V_a$  for Se, we obtained  $D^*(293\text{ K}) = 15\text{ nm}$  which coincides with our observed grain size in which amorphization occurs. The size of the remaining crystallites during the major SSA process, which remains unchanged at about 13 nm, is also very close to the calculated  $D^*$ . The agreement between the calculated and measured  $D^*$  implies that the SSA in Se can be satisfactorily understood on the basis of thermodynamics by considering the interfacial and bulk energies. However, the SSA kinetics in Se seems to be different from the feature that the ‘shell’ kinetic model predicts. In the ‘shell’ model, an amorphous layer is formed at GBs (or junctions) followed by a thickening process into the crystallite interior, as schematically illustrated in figure 3; one may expect a shrinking crystallite size with the development of the amorphous phase. However, this is not observed in our experiments.

The observed constant crystallite size during the development of the amorphous phase in Se leads us to propose a different kinetic model, namely that crystallites smaller than  $D^*$  are amorphized instantly when they are activated by MM, while those larger than  $D^*$  remain crystalline. This crystallite destabilization model, as schematically shown in figure 3, implies that the transformation of nanocrystallite Se into an amorphous phase is a process in which the amorphous–crystalline interface does not move gradually via atomic diffusion. In other words, the amorphization process during milling does not proceed via a continuous movement of the amorphous–crystalline interface from the GBs into the remaining crystallites, but via an abrupt phase change in individual remaining crystallites.

Clear evidence supporting this crystallite destabilization model is the variation in  $(\epsilon^2)^{1/2}$  in the sample during MM, which represents the stress within or between the

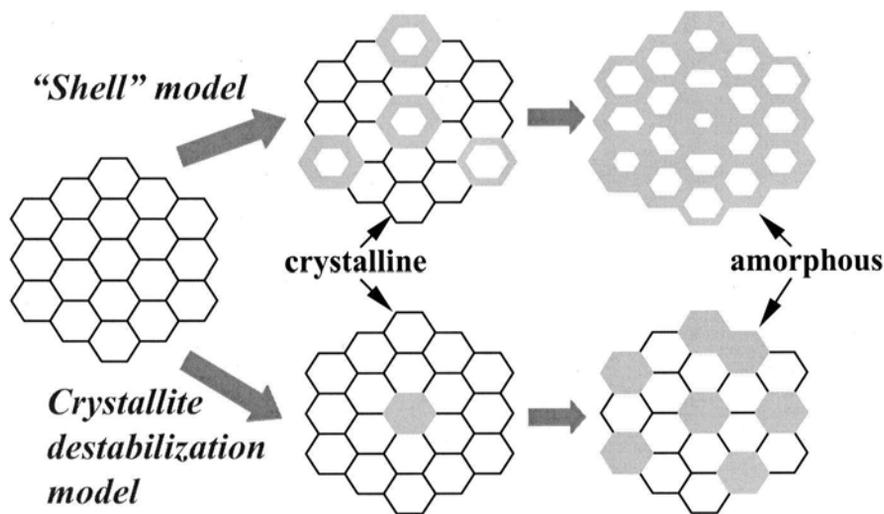


Figure 3. Schematic representations of the ‘shell’ model (upper) in which the amorphous phase nucleates heterogeneously at GBs followed by a subsequent thickening of the amorphous layer into the untransformed crystalline phase via atomic interdiffusion, and the crystallite destabilization model (lower) in which crystallites smaller than the critical grain size are transformed completely into an amorphous phase while those larger than the critical size remain crystalline.

crystallites induced by atomic interaction between neighbouring crystallites. The existence of a significant amount of  $(\varepsilon^2)^{1/2}$  (0.1%) when  $x_a^t = 90\%$  means that some crystallites are connected by GBs rather than that all remaining crystallites are isolated in the amorphous matrix. If a crystallite is surrounded by an amorphous phase, as described in the 'shell' model,  $(\varepsilon^2)^{1/2}$  of the crystallite will be released into the viscous amorphous phase.

The lattice distortion (expansion) of nanocrystallites originates from the strong interaction between GBs and the crystallites, and it was found that the lattice distortion increases significantly with a reduction in grain size (Zhao *et al.* 1997). The observed constant lattice expansion, which agrees with the constant grain size during the major amorphization process (stage II), implies that GBs still effectively exist between the crystallites, which again supports the detectable  $(\varepsilon^2)^{1/2}$  for crystallites. When most of the samples were transformed into amorphous phase ( $x_a^t > 90\%$ ) so that all crystallites are isolated in the amorphous matrix, the lattice distortion and  $(\varepsilon^2)^{1/2}$  will decrease, just as we observed in stage III. When the GBs disappear,  $(\varepsilon^2)^{1/2}$  and lattice distortion will be relaxed by the surrounding amorphous phase, which possesses a rather lower viscosity than that of the crystalline phase.

It is known that t-Se consists of helical [Se-]<sub>n</sub> chains in which the Se atoms are covalently bonded. The [Se-]<sub>n</sub> chains are bonded by van der Waals forces (Ungar and Cherin 1969). The as-milled a-Se was verified to consist of [Se-]<sub>n</sub> chains which are randomly arranged (Guo and Lu 1998b), but the bonding length within [Se-]<sub>n</sub> is the same as that in crystalline t-Se (Zhao *et al.* 1999). This means that the SSA of t-Se induced by MM is basically a disordering process of the ordered [Se-]<sub>n</sub> chains without structural change within [Se-]<sub>n</sub> chains. It is understandable that MM may easily break the relatively weak van der Waals forces between [Se-]<sub>n</sub> chains while the strong covalent bonds within the chains remain unchanged. The distance between [Se-]<sub>n</sub> chains t-Se, which equals the lattice parameter *a*, increases significantly upon milling of t-Se before the onset of the amorphization process and is unchanged during the major SSA. This suggests that the amorphization process of the t-Se crystallites might be initiated by the fact that the chain spacing is dilated to a critical value so that the ordering of the [Se-]<sub>n</sub> chains is destroyed, leading to catastrophic transformation from ordered [Se-]<sub>n</sub> chains into disordered (amorphous) chains. This lattice destabilization in Se was verified by extended X-ray absorption fine-structure results which showed that the second-nearest coordination shell begins to disappear when the amorphous phase develops (at  $t_m = 30$  min) (Zhao *et al.* 1999). The decreasing  $(\varepsilon^2)^{1/2}$  during the major SSA also implies that it is not the driving force for the SSA process, at least in the present case.

In conclusion, we have observed a complete amorphization process in Se induced by MM, which can be well understood on the basis of thermodynamics. The amorphization kinetics can be explained in terms of the crystallite destabilization model rather than by the classical 'shell' kinetic model. The intrinsic mechanism for the crystallite destabilization in pure elements needs further investigations in different systems and theoretical modelling, which are in progress.

#### ACKNOWLEDGEMENTS

The financial support from the Chinese Academy of Sciences and National Science Foundation of China (grants 59625101, 59771019 and 59431021) is acknowledged. The authors appreciate discussions with Professor J. Xu.

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