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Amorphization of selenium induced by high-energy ball milling

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Structural changes occurring in the crystalline element selenium upon high-energy ball milling has been studied. Milling experiments have been performed at the ambient temperature and at a cryogenic temperature of $-100\ ^\circ\mathrm{C}$, respectively. The final milling products under both conditions were found to be a fully amorphous phase after several hours of mechanical milling. Calorimetric evidences indicate that during cryogenic-temperature milling amorphization procedure is faster than that at ambient temperature. Our experimental results suggest that amorphization of the crystalline element selenium is driven by defects created by frequent mechanical deformation. [S0163-1829(97)02218-2]

Amorphization by mechanical alloying (MA) of a mixture of elemental powders and mechanical milling (MM) of intermetallic compounds has become an active subject during the past decade. In the former case, the gain in free energy resulting from mixing of the elements is suggested to be the driving force for amorphization. In the latter case, however, when the free energy of the intermetallic compound is raised by frequent mechanical deformation above that of the amorphous counterpart, a polymorphous phase transformation from crystal to glass may occur.[1] The increase in the free energy of an intermetallic system may be caused by the increase of defects (dislocations, grain boundaries) and atomic disorder.[2–5] Which one can be considered as a major source of energy storage is still controversial. Jang and Koch have attributed the observed partial amorphization of Ni_3Al to the creation of defects upon high-energy ball milling.[2] Bakker, Zhou, and Yang have systematically studied the phase transformation in some intermetallic systems induced by ball milling.[5] They found that the observed amorphization can be attributed to atomic disorder.

Besides amorphization of a mixture of elements by MA and intermetallic compounds by MM, the amorphization of a pure crystalline element upon high-energy ball milling is still of sufficient scientific interest. Previous studies have demonstrated that high-energy ball milling can modify the structure and magnetic properties of the crystalline and amorphous solids, which is somewhat the same as the irradiation effect in condensed matter.[1,6–8] However, it is well known that several covalently bonded systems can be amorphized by irradiation. It is therefore interesting to know whether these systems can be amorphized by high-energy ball milling. Gaffet and co-workers have reported that the partial amorphization of Si and Ge may occur after mechanical milling.[9–11] They found that the obtained amorphous Si phase had a higher crystallization temperature and a higher crystallization activation energy when compared with the one prepared by ion implantation or vapor deposition. These results have been recently verified by Shen *et al.*[12] However, Bokhonov, Konstanchuk, and Boldyrev argued that the observed partial amorphization of Si can be attributed to the combination of silicon and oxygen during milling such that the amorphous phase is SiO.[13] In this paper, we will demonstrate that a fully amorphous element Se can be obtained by high-energy ball milling under various milling temperatures. The amorphization mechanism for the transformation will be discussed.

The bulk crystalline selenium (99.999%) was crushed into powders and sealed in a stainless vial (80 ml in volume) together with eight stainless balls (10 mm in diameter). The initial ball-to-sample mass ratio was about 10:1. The milling process was carried out under flowing Ar gas ($0.8\ \mathrm{ml/s^{-1}}$) at room temperature, using a high-energy vibrating ball mill (Super-Misuni, NEV MA8, Nisshin-Giken, Japan) equipped with a rotary pump and a gas-flow system. The vial was cooled by flowing water. In order to perform the milling process at a cryogenic temperature, a liquid-nitrogen vessel was bathed in a mixture of dry-ice and ethyl-alcohol and liquid nitrogen was continuously poured into this mixture. A K thermocouple was fixed on the bottom of the ball-mill vessel. The temperature can be kept at $-100\pm5\ ^\circ\mathrm{C}$. After some selected milling times, the milling process was interrupted, and small amounts of the milled materials were taken out for analysis. Structural evolution during the milling process was studied using a Rigaku x-ray diffractometer equipped with a graphite monochromator and Cu $K\alpha$ radiation ($\lambda=0.15405$ nm). Thermal analysis was performed using a differential scanning calorimetry (Perkin-Elmer DSC-7). A heating rate of $20\ ^\circ\mathrm{C/min}$ is employed to obtain the value of the enthalpy releases. A continuous pure argon flow was used to avoid possible oxidation during DSC. Temperature and peak-area calibration was carried out periodically with Zn and In standard samples.

Figure 1 shows the x-ray-diffraction (XRD) patterns for the element Se after various milling times at the ambient temperature. It is well known that the element Se exists in one of four major allotropes: amorphous, trigonal (hexagonal), α- and β-monoclinic allotropes, of which the trigonal selenium is the most stable crystal form. Trigonal selenium consists of helical $[\mathrm{Se}\text{-}]_n$ chains, and α- and β-monoclinic selenium of Se_8-ring molecules.[14] Se atoms in the same chain or ring are bonded with covalent bond, and the chains or rings are bonded with van der Waals forces.[15] The XRD for the unmilled Se shows the hexagonal structure. After 2 h of milling, some diffraction lines disappear and an amorphous phase emerges. With increasing milling time, the amounts of the amorphous phase increase whereas the amount of the

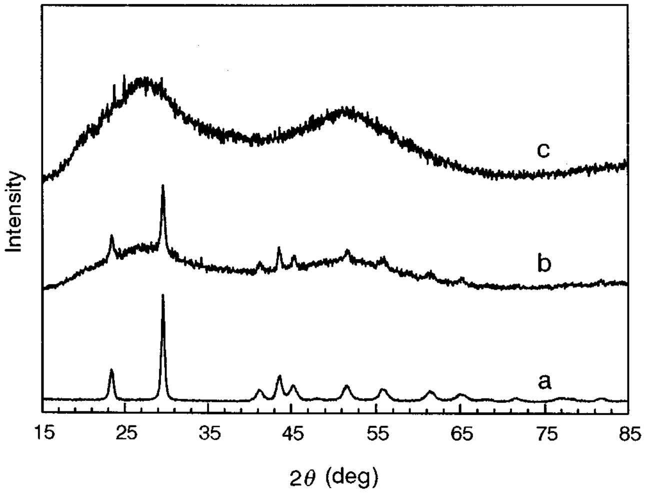

FIG. 1. XRD patterns for the element selenium after 0 h (a), 2 h (b), and 5 h (c) of ambient-temperature milling, respectively.

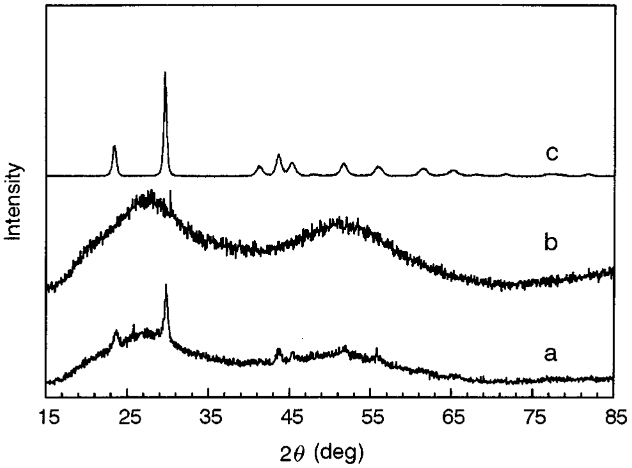

FIG. 2. XRD patterns for the element selenium after 1 h (a), 2 h (b) of cryogenic-temperature milling and after DSC for the 2 h milled sample (c), respectively.

crystalline phase decreases. The XRD after 5 h of milling shows a fully amorphous structure.

Since the melting temperature of Se is only 490 K, one may assume that the temperature in the impact spots during ball milling can even reach the melting temperature of Se and that the observed amorphization of Se may be due to rapid quenching of local melts produced by mechanical impacts. In fact, visual observations indicate that the milled samples consist of some plate-shaped pieces with a diameter around 0.5 mm. We are not sure whether the observed small pieces were formed from rapid quenching of local melts or the aggregation of the softened selenium upon mechanical milling. Indeed, the element selenium can be significantly softened during a thermal annealing above a temperature of 100 °C. In order to get a better understanding of the mechanism responsible for the amorphization of selenium upon high-energy ball milling, cryogenic-temperature milling experiments have been performed. Figure 2 displays the XRD patterns for the element Se after various milling times under a cryogenic temperature of -100 °C. It is clear that after 2 h of milling a fully amorphous structure can also be successfully obtained. In this case, no plate-shaped pieces were observed. SEM observations indicate that the milled samples are fine powders with a diameter around 30 μm. Raman spectrum measurements indicate that the melt-quenched amorphous Se consists of Se_8 rings and $[Se]_n$ chains, while the ball-milled amorphous Se contains only $[Se]_n$ chain molecules.[16] These results suggest that the observed amorphization of Se should not be attributed to a rapid quenching of local melts.

The thermal stability of the element Se after various cryogenic-temperature milling times has been studied by DSC, as shown in Fig. 3. One exothermic peak was observed for all samples. In order to understand the origin of this exothermic phenomenon, samples after the exothermic signal were again examined by XRD. The results are demonstrated in Fig. 2(c) (for the sample after 2 h of cryogenic-temperature milling). By comparing Fig. 2(b) with Fig. 2(c), it is clear that the exothermic phenomenon in Fig. 3 can be attributed to crystallization of the amorphous phase. The amorphous phase has been completely restored into its original crystalline structure after DSC. From Fig. 3, one can also see that with increasing milling time the DSC curves become sharpened, indicating that the thermal behavior for the amorphous Se has been changed upon milling. It has been reported that the structure of amorphous Se phase is not well defined. Pang, Wang, and Ding have found that the cooling rate can strongly influence the structure of amorphous Se.[17] The crystallization temperature for the amorphous Se can vary in a broad temperature range, which depends on the cooling rate. This can be understood by the fact that the cooling rate can influence the local short-range order of amorphous Se, which will result in a variation of the crystallization temperature. With increasing milling time, the local structural fluctuations for the amorphous Se will be homogenized by extensive mechanical milling, which can therefore cause a sharpened DSC curve. The DSC curve for amorphous Se prepared by rapid quenching is included in Fig. 3(e). Notice that the peak temperature for the as-quenched amorphous Se is significantly higher than that of the one prepared by mechanical milling. The activation energy for crystallization of the amorphous selenium phase was measured using Kissinger's method by plotting,[18] for a number of heating rates b (5, 10, 20, 40, 60, and 80 K/min), $\ln(b/T_p^2)$ vs $(1/T_p)$, where T_p is the peak temperature of the transformation. The results reveal that the activation energy is 83.2 and 85.0 kJ/mol for the crystallization of amorphous selenium samples prepared by ambient-temperature milling and by cryogenic-temperature milling, respectively. It seems that the activation energy is not very sensitive to the milling temperature. However, the activation energy for crystallization of the amorphous selenium prepared by ball milling is different from that of the one prepared by rapid quenching. Pang, Wang, and Ding have reported that the crystallization of amorphous Se prepared by rapid quenching takes place in three separate stages and the activation energies of the crystallization processes are 52.9, 65.9, and 84.8 kJ/mol, respectively.[17] The higher the crystallization temperature, the larger the activation energy. Zhang, Hu, and Lu recently reported that the crystallization of amorphous selenium occurs in a single step and the corresponding activation energy is

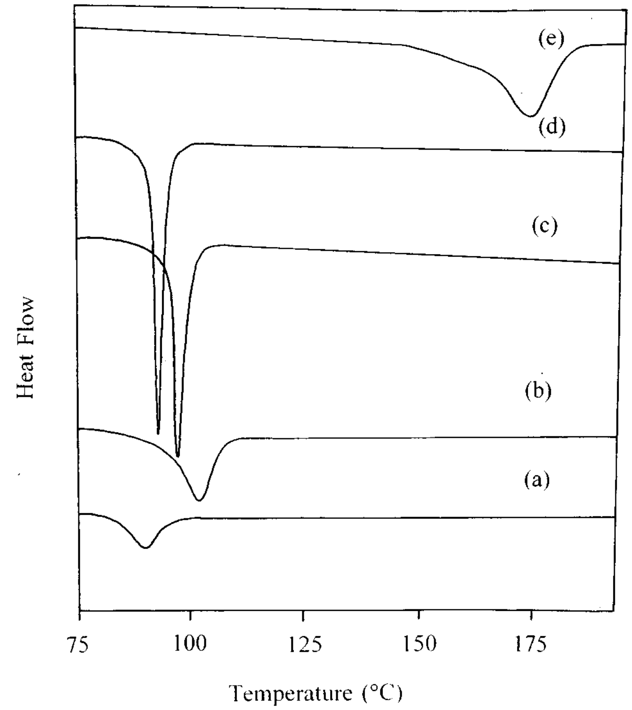

FIG. 3. DSC curves for the element selenium after 0.5 h (a), 1 h (b), 1.5 (c), 2 h (d) of cryogenic-temperature milling and for the as-quenched amorphous selenium (e), respectively.

54.5 kJ/mol.[19] It seems that the amorphous selenium prepared by ball milling exhibits a larger activation energy compared with the one prepared by rapid quenching, which is the same as the case of Si reported by Gaffet and Harmelin.[9] These results indicate that the activation energy for crystallization of amorphous selenium does not scale with the crystallization temperature, since the crystallization temperature for the amorphous selenium prepared by ball milling is much lower than that prepared by rapid quenching.

By integrating the DSC area, one can get the enthalpy release for the crystallization of the amorphous phase. These results are demonstrated in Fig. 4. Notice that the enthalpy releases for both the samples milled at the ambient temperature and at a cryogenic temperature increase with the milling time, and saturate to the same value of about 3.4 kJ/mol after certain times of milling. The enthalpy releases for crystallization of the amorphous phase actually scale with the relative amount of the amorphous phase formed during mechanical milling. From Fig. 4, it can be seen that only 2 h of cryogenic-temperature milling is required to obtain the fully amorphous selenium, whereas it needs about 5 h of ambient-temperature milling, suggesting a faster amorphization kinetics for the sample milled at a cryogenic temperature of −100 °C. This result is interesting since the amorphization kinetics show an inverse temperature dependence.

The mechanism responsible for amorphization of the element selenium induced by high-energy ball milling should be differentiated from those of mechanical alloying of elemental powder blends and mechanical milling of intermetallic compounds, since none of the suggested driving force can be responsible for amorphization of such an element. Cryogenic-temperature milling experiments suggest that the observed amorphization of selenium should not be attributed to rapid quenching of local melts produced by mechanical impacts. Chemical analysis indicate that the milled samples contain less that 0.6 at. %O and 0.1 at. %Fe, implying that the observed amorphization of Se cannot result from the impurity effects, e.g., formation of some oxides. Indeed, the amorphous selenium phase prepared by ball milling can completely return to its initial crystalline structure after a thermal process in DSC, as shown in Fig. 2(c). These arguments may stimulate one to find an alternative interpretation for amorphization of the element Se upon high-energy ball milling. For any amorphizing systems studied, the free energy of perfect crystalline solids, which has the lowest free energy, must be raised above that of an amorphous phase. Incorporating dissimilar atoms and chemical disorder can apparently raise the free energy of the system. However, the creation of defects (dislocations, grain boundaries) upon frequent actions of mechanical deformation is another kind of energy storage, which can raise the free energy of the element Se and drives the system to be amorphized. The energy stored in the pure metals associated with dislocations is typically less than 1–2 kJ/mol.[20] The grain-boundary energy in the nanocrystalline element Se was measured to be about 4.0 kJ/mol, which is dependent upon grain sizes.[21] It has been shown in Fig. 3 that the crystallization of the amorphous selenium phase formed by ball milling is 3.4 kJ/mol. The energy storage associated with dislocations and grain boundaries is therefore comparable with the energy difference between crystalline and amorphous selenium phases. In this case, defect-induced amorphization has been thermodynamically favored for the element selenium.

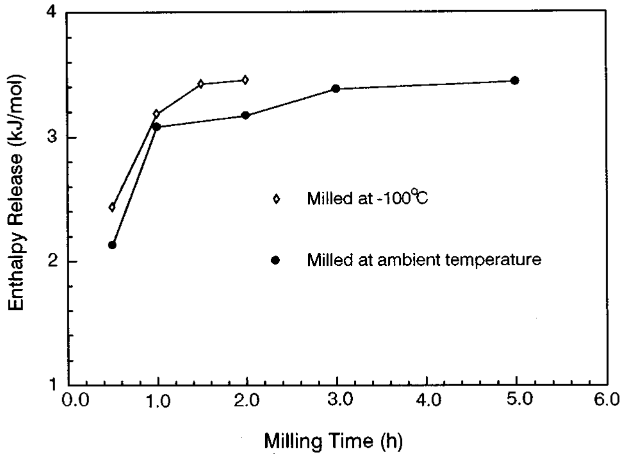

FIG. 4. Variation of the enthalpy releases for the crystallization of the amorphous selenium with the milling time.

Since partial recovery can take place during ball milling, it is expected that two parallel effects may occur upon mechanical deformation, i.e., the creating of defects due to actions of mechanical deformation and the annihilating of defects due to a thermal recovery.[22] The defect level in the milled powders is thus limited by the rate of recovery during milling, which depends on the milling temperature. In this case, it would be understandable that cryogenic-temperature milling can cause a faster amorphization kinetics, as shown in Fig. 4. At a higher milling temperature, the rate of defect recovery is higher, which will decrease the steady-state level of defects and in turn slow down the rate of amorphization.

In summary, we have prepared the fully amorphous selenium by high-energy ball milling. A simple estimate indicates that the creation of defects (dislocations, grain boundaries) during ball milling can be responsible for the amorphization of such a crystalline element. Combined with previous findings of amorphization of Si and Ge by high-energy ball milling, we suggested that high-energy ball milling can induce amorphization in some covalently bonded systems, which is in analogy with other nonequilibrium processing methods, such as irradiation.

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