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## EFFECT OF THE MILLING CONDITIONS ON THE DEGREE OF CRYSTALLIZATION OF AMORPHOUS SELENIUM BY MILLING IN A PLANETARY BALL MILL

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The effect of milling conditions (rotation speed of the milling device and duration of milling) on the phase composition of the products of milling of fully amorphous selenium has been investigated. The fully amorphous selenium was produced by quenching a stream of molten selenium into ice water. The milling was conducted using a planetary ball mill and the phase composition of the milling products was determined by differential thermal analysis. It has been found that the ball milling leads to the partial crystallization of the starting amorphous material. The phase composition of the milling products depends, in a rather complicated way, on the milling parameters. The dependence of the phase composition of the milling products is the result of competition of two processes: amorphization due to deformation and refinement of grains of crystalline material and crystallization of the already existing amorphous phase at the cost of heat evolved in the milling vial during the milling process.

*Key words:* selenium, ball milling, amorphization, crystallization.

Amorphous materials are the subject of permanent research effort, spurred by both the science and technology. The main reason for this research activity are the unusual properties of amorphous materials, unachievable in the crystalline state, offering a variety of already exploited and potential applications [1–3].

For many years amorphous materials were prepared by rapid quenching from the liquid state. Extremely high cooling rates (up to  $10^{10}$  K/s) are often required to avoid nucleation and growth of crystalline phase in order to produce a completely amorphous phase. This is a strong restriction in production and, consequently, in application of amorphous materials [1–5].

In the middle of the second half of last century a new technique emerged, enabling to synthesize various metastable materials. This technique, called mechanochemical synthesis or mechanical alloying, is a process of repeated fracturing, rewedding, and severe mechanical deformation of crystalline material. One of the ways the mechanical

alloying is realized is the intensive ball milling in vibrational or rotational mills [4, 5]. Amorphous phases of many metallic alloys have been already obtained by these techniques.

Already in the last decade of XX century we revealed [6–7] at least partial amorphization of crystalline selenium as well as the reverse effect – partial crystallization of amorphous selenium by milling in a planetary ball mill. Last year, at the XIII International Seminar on Physics and Chemistry of Solids held in Ustroń, we presented [8] the results of systematic studies of the effect of milling conditions on the amount

of amorphous phase in the products of milling of fully crystalline selenium. The purpose of the present study was to investigate the effect of milling conditions on the amount of amorphous phase in the products of milling of fully amorphous phase as well as the structural transformations occurring in the products of milling.

The starting material in all the experiments was the 99,5% pure, partly amorphous, selenium powder supplied by ALDRICH. The fully amorphous selenium was obtained by quenching a stream of molten selenium in water at room temperature.

The fully amorphous selenium was submitted to amorphization by intensive milling in a planetary ball mill Pulversette 7 produced by FRITSCH. Milling was carried out in two grinding vials of 25 ccm volume containing balls with diameter of 12 mm. Both the vials and balls were made of stainless CrNi steel. The milling conditions were changed by changing the milling time, the number of milling balls and/or the rotation speed of the milling device.

The amount of the amorphous phase in the milling product was determined by differential thermal analysis DTA performed using the NETZSCH DSC 404/3 differential scanning calorimeter with S-type Pt-PtRh measuring head and standard platinum sample pans. An empty pan was used as the reference.

All the milling procedures and DTA measurements were performed in atmospheric air under normal pressure.

A comparison of the DSC thermograms registered at a constant heating rate of 5 K/min for melt-quenched fully amorphous selenium and for products of milling it with 5 balls at the rotation speed of plate supporting the milling device amounting  $366 \text{ min}^{-1}$  is given on fig. 1. Two thermal effects are clearly visible on the DSC curve for amorphous selenium: weak endotherm at temperature of about 315 K and a distinct exotherm starting at  $\sim 390$  and peaking at 410 K. The endothermal effect is a signature of the retrification process (glass transition) and the exothermal effect corresponds to the crystallization of melt-quenched fully amorphous selenium. The shape of the DSC traces for the products of milling is very similar to that for starting material (fully amorphous selenium), but the positions of both the thermal effects on the temperature scale, as well as their intensities (areas and heights of the DSC peaks) differ markedly from those for melt-quenched selenium. The occurrence of these peaks on the DSC traces for the products of milling indicates that the products of milling contain some amount of amorphous phase. The retrification and crystallization temperatures of the amorphous phase present in the products of milling are distinctly lower than those for melt-quenched selenium. This means, that the amorphous phase in the milling products is thermodynamically less stable than that produced by melt quenching. The most probable reason for this difference is the presence of nuclei of crystallization, or crystalline regions in the grains of the milling products.

The area under the peaks on the DSC traces is proportional to the heat consumed or evolved during the observed phase transformation – in our case to the amount of amorphous phase in the investigated selenium sample. As it is seen on fig. 1, the amount of amorphous phase in the products of milling depends on the time of milling.

In a series of additional experiments it has been proved that the intensity of milling, changed by changing the number of milling balls and/or by changing the rotation speed of the milling device, also effects the amount of amorphous phase in the milling products.

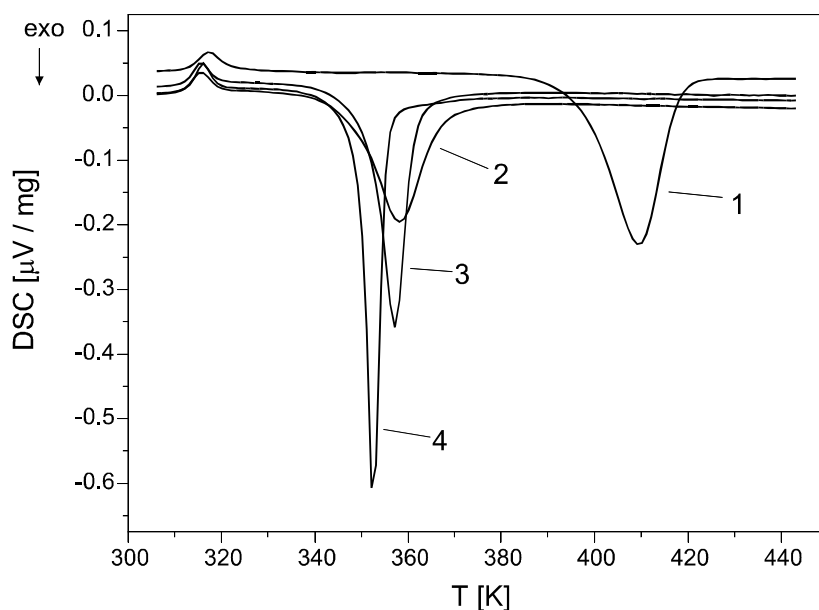


Fig. 1. DSC traces registered at the same heating rate of 5 K/min for unmilled fully amorphous selenium (1) and for products of milling it at the rotation speed of  $366 \text{ min}^{-1}$  for: 15 min (2), 1 hour (3) and 3 hours (4)

The results of more detailed analysis of the milling conditions (rotation speed of the plate supporting the milling device and milling time) on the retrification and crystallization temperature of the amorphous phase present in the milling products are shown on fig. 2. As it is seen on the left part of fig. 2, in the initial stage of milling process the temperature of retrification slightly decreases, and then oscillates around the level something lower than the retrification temperature for melt-quenched selenium. The amplitude of these oscillations is, however, comparable with the accuracy of determinations of the retrification temperature. The right side of fig. 2 represents the dependence of the crystallization temperature on the time of milling realized at two rotation speeds of the milling device. Independent of the rotation speed, the crystallization temperature initially abruptly decreases reaching a minimum value after 0,5 h milling, then slightly increases, and for prolonged milling ( $t > 1\text{h}$ ) achieves a saturation value of about 350 K ( $\sim 20 \text{ K}$  lower than that for melt-quenched selenium).

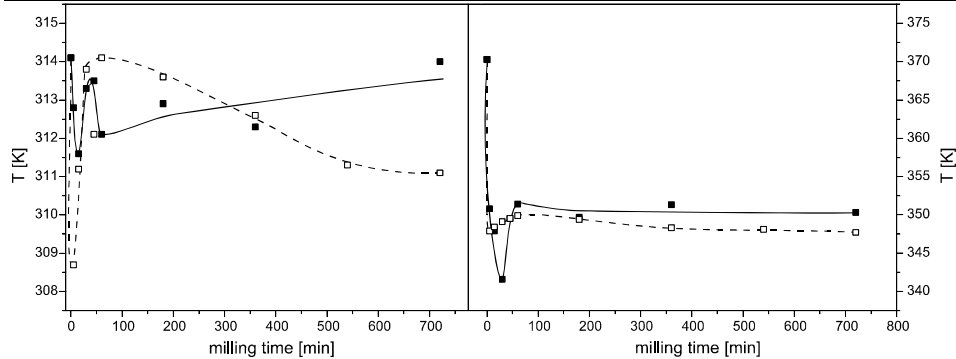


Fig. 2. Effect of milling time on the glass transition (left) and on the crystallization temperature (right) of the products of milling of amorphous selenium at two rotation speeds ( $\blacksquare$   $366 \text{ min}^{-1}$ ,  $\square$   $506 \text{ min}^{-1}$ )

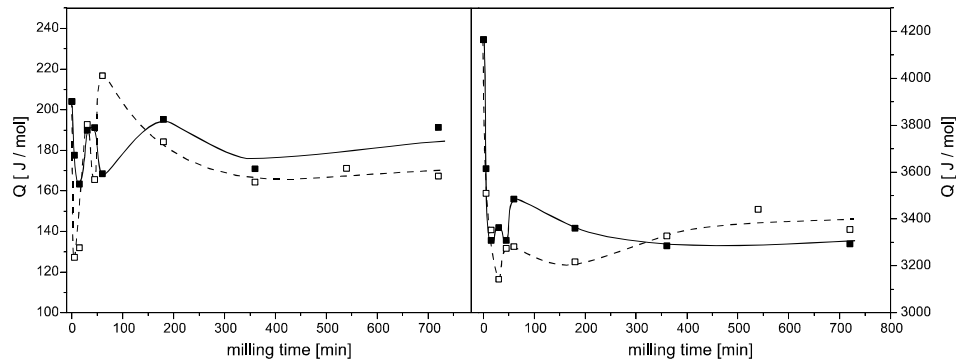


Fig. 3. Effect of milling time on the heat consumed during the glass transition (left) and evolved during the crystallization (right) of the products of milling of amorphous selenium at two rotation speeds ( $\blacksquare$   $366 \text{ min}^{-1}$ ,  $\square$   $506 \text{ min}^{-1}$ )

The heat effects of retrification and crystallization of the products of milling were determined basing on the proportionality of the area of the DSC peak to the heat evolved or consumed during the observed transformation, and making use of the calibration experiment in which the endotherm corresponding to the melting of high purity indium was registered. The dependencies of the retrification and recrystallization heat on the milling time are presented on fig. 3. As it seen on the left part of this figure, the heat consumed during the retrification process decreases in the first few minutes of milling and then oscillates at a level of about 10% lower than the retrification heat for melt-quenched selenium. The shape of the dependence of the heat evolved during the crystallization (right side of fig. 3) on the milling time is very similar to that for the crystallization temperature shown the right side of fig. 2. The value of the crystallization heat abruptly decreases in the first few minutes of milling and after passing through the minimum value (0,5 hour milling) tends to stabilize at the level of about 3300 J/g, distinctly lower than the crystallization heat for melt-quenched selenium, ( $\sim 4150 \text{ J/g}$ ). This permits to estimate the amount of the crystalline phase in the products of milling lasting more than  $\sim 1,5 \text{ h}$  ( $\sim 80 \text{ mass\%}$ ).

The results of the present study clearly indicate that the continuous ball milling of amorphous melt-quenched selenium causes its partial crystallization. Under the milling conditions applied in the presented series of experiments, the milling product was never fully amorphous, nor fully crystalline (their crystallization heat was always distinctly lower than that for fully amorphous selenium, but never equal to zero). The crystallization degree and the crystallization temperature (thermal stability) of the amorphous component of the milling products depend on the milling condition. It seems, that this dependence results from competition of two processes. One of them is the crystallization of the metastable amorphous phase due to heat evolved in the milling vials during the collisions of milling balls. On the other hand, the crystalline component of milled material is amorphized due to generation of defects and destruction of crystalline phase resulting from the delivery of mechanical (kinetic) energy from colliding balls.

Full description of the kinetics of phase transformations induced by intensive ball milling deserves further studies. Among others, the effect of milling conditions on the activation energy for both the reformation and crystallization processes in the milling products must be systematically investigated. The investigations of the milling products obtained under more mild milling conditions (rotation speeds of the milling device and number of balls lower than those applied in the present work) should be also performed. The efforts in this direction will be continued.

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**ВПЛИВ УМОВ РОЗМЕЛЮВАННЯ НА СТУПІНЬ КРИСТАЛІЗАЦІЇ  
АМОРФНОГО СЕЛЕНУ, ПОДРІБНЕНОГО В ПЛАНЕТАРНОМУ  
КУЛЬОВОМУ МЛИНІ**

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Досліджено вплив умов розмелювання (швидкість обертання млина і тривалість розмелювання) на фазовий склад аморфного селену. З'ясовано, що кульове розмелювання спричинює часткову кристалізацію початкового аморфного матеріалу. Залежність фазового складу продуктів розмелювання – результат двох процесів: перехід в аморфний стан завдяки деформації і кристалізація аморфної фази під час процесу розмелювання.

*Ключові слова:* селен, кульове розмелювання, перехід в аморфний стан, кристалізація.

**ВЛИЯНИЕ УСЛОВИЙ РАЗМАЛЫВАНИЯ НА СТЕПЕНЬ  
КРИСТАЛЛИЗАЦИИ АМОРФНОГО СЕЛЕНА, ИЗМЕЛЬЧЕННОГО В  
ПЛАНЕТАРНОЙ ШАРОВОЙ МЕЛЬНИЦЕ**

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Исследовано влияние условий размалывания (скорость вращения мельницы и длительность размалывания) на фазовый состав аморфного селена. Установлено, что шаровое размалывание вызывает частичную кристаллизацию исходного аморфного материала. Зависимость фазового состава продуктов размалывания – результат двух процессов: переход в аморфное состояние благодаря деформации и кристаллизация аморфной фазы во время процесса размалывания.

*Ключевые слова:* селен, шаровое размалывание, переход в аморфное состояние, кристаллизация.

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