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Particle properties and their modification in mechanically activated realgar As_4S_4

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In this work mechanical activation of realgar As_4S_4 was studied. The addition of sodium chloride NaCl as a solid diluent into the milling process substantially improved solid state properties of the obtained fines. However, the polymorphous transformation of α-As_4S_4 to β-As_4S_4 is reduced.

Key words: *Realgar, Mechanical activation, Sodium chloride*

Introduction

Over the years, arsenic compounds have found application in the manufacture of cosmetics, foods, glass, insecticides, medications, pigments, pyrotechnics as well as in metallurgy. Arsenic sulphides such as realgar As_4S_4 and orpigment As_2S_3 are of significant interest in mineral technologies because of their association with gold [1-2]. Recently interesting optical properties have been described for arsenic sulphides as a consequence of their sensitivity to light exposure [3-7]. This sensitivity is pronounced in disordered solids and found applications in optoelectronic materials [8].

Mechanical activation by high-energy milling is a suitable way to create disordered solids [9-10]. Among the different processes which are able to produce nanocrystalline powders the synthesis by means of mechanical activation is one of the most interesting from an industrial point of view. It exploits devices and processes that have many aspects in common with fine grinding and comminution of solids including nanoparticles [11-12], all frequent operations in minerals engineering.

The aim of this work was examine the changes in solid state properties of realgar As_4S_4 under influence of high-energy milling.

Experimental

The investigation of dry milling was carried out with realgar mineral α-As_4S_4 (Getchel Mine, Nevada, USA). Small amount of quartz SiO_2 (33-1161) was determined in this sample by XRD method.

High-energy milling

The high-energy milling of realgar samples was performed in a planetary mill Pulverisette 6 (Fritsch, Germany). The following milling conditions were used: dry milling - loading of the mill with 96 balls (10 mm diameter); material of milling chamber and balls: zirconia; ball charge 136 g; weight charge 3 g; rotational speed of the mill 400 rpm; milling time 2-20 min. Solid sodium chloride NaCl as milling diluent was added in various amounts into the milling chamber.

X-ray diffraction analysis

The X-ray diffraction patterns were recorded by an X-ray diffractometer Rigaku Model D/Max-2400 with Rini 2000 wide-angle goniometer (Rigaku, Japan). The following measuring conditions were applied 2θ range 10-90°, CuK_α radiation (λ=0.15406 nm), K_β filter, voltage 30 kV, current 40 mA, scan speed 3°/min, scan step 0.020°. The crystallite size of nanopowders was calculated from the Scherrer equation [13] as follows

$$d = \frac{Kr\lambda}{b\cos\Theta} \qquad (1)$$

where d - the average crystallite size, K=1.2 - the shape factor [14], r - radius of goniometer, λ=0.15406 nm, b-the angular line width, Θ–the Bragg´s angle. For the calculation of the particles crystallite size the peak at d=0.540 nm of α-As_4S_4 has been selected.

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Specific surface area

The specific surface area was determined by the low temperature nitrogen adsorption method. Gemini 2360 sorption apparatus (Micromeritics, USA) has been applied.

Particle size distribution

The particle size distribution of the realgar was measured by a laser beam scattering in a Helos and Rodos granulometer (Sympatec GmbH, Germany). The mean particle diameter was calculated as the first moment of the volume size distribution function.

SEM

The morphology of the samples was analyzed using FE-SEM LEO 1550 scanning microscope (Germany). The samples were not covered with any conductive material in order to avoid artifacts.

Results and discussion

X-ray diffraction patterns of the realgar particles milled for 1, 4, 15 and 20 minutes have been shown in Fig. 1. The patterns show many overlapping peaks with tendency of the gradual amorphization as a consequence of crystal structure disordering. The identified peaks belong to various arsenic sulphide phases (as analyzed further). Peak Q belongs to the admixtured quartz SiO_2 (33-1161). The whole process of realgar structure changes has been described in detail in [15]. The decrease of realgar nanosize particles from 60 to 16 nm has been registered. However, the addition of solid sodium chloride NaCl into the milling process was not applied in this paper.

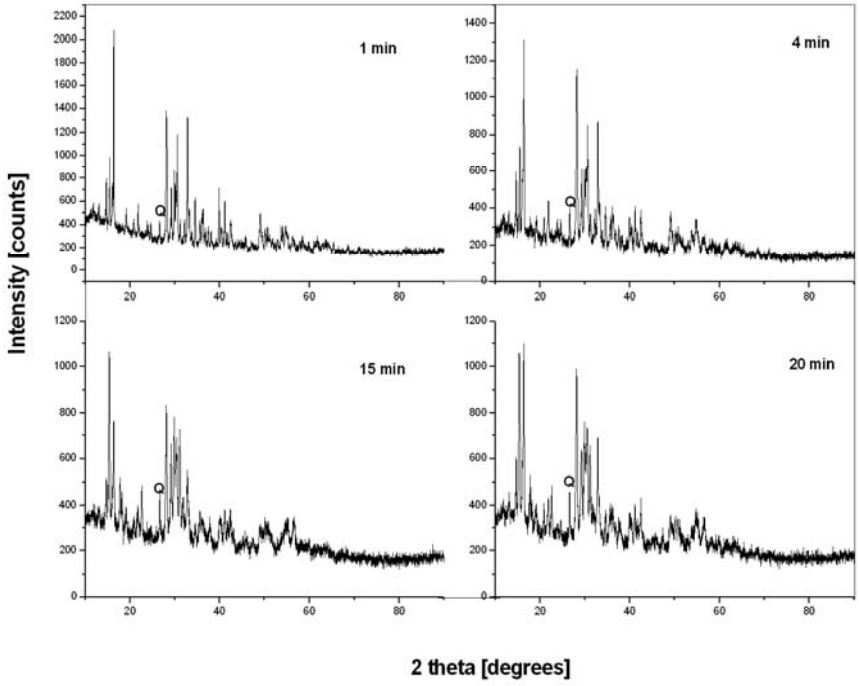

Fig. 1. XRD patterns of nanocrystalline realgar As_4S_4 milled at different times (milling time in patterns), Q-quartz SiO_2, 2θ = 10-90° [15].

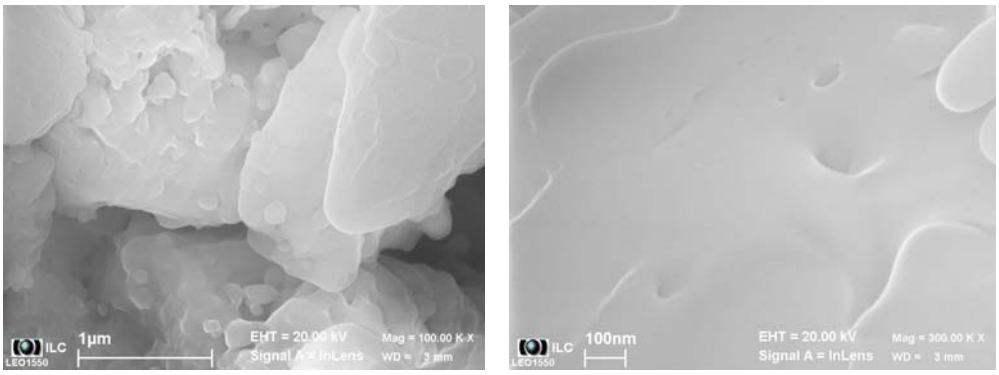

Fig. 2. SEM of realgar As_4S_4 milled at 20 min.

SEM microphotographs of milled As_4S_4 (Fig. 2) show glassy structures, which are characteristic for these types of compounds.

The dependence of new surface area, S_A on milling of realgar in a dry mode is given in Table 1. From the data one can conclude that the highest value of S_A was attained at $t_M = 7$ min. The prolonged milling is characterized by a decrease and stagnation of S_A values.

Tab. 1. Specific surface are, S_A of the milled realgar As_4S_4.

Milling time [min]	**S_A** [m^2g^{-1}]
0	0.3
2	0.9
4	1.6
7	2.0
10	1.3
15	1.1
20	1.3

There are several approaches to improve the milling behaviour of solids at higher energy input where agglomeration phenomena usually play decisive role [9-10, 16]. The application of a washable solid diluent sodium chloride NaCl directly into the milling process has been applied several times by mechanochemical synthesis of advanced nanocrystalline powders [17-21]. The use of the diluent reduces the volume fraction of nanoparticles and consequently prevents nanoparticles being agglomerated and control the particle size distribution.

Sodium chloride NaCl has been applied in our study as a solid diluent in realgar milling in order to modify the properties of fines. After milling, water soluble NaCl was washed out with de-ionized water using ultrasonic bath. In Figure 3 the values of specific surface area for selected milling times and various $NaCl/As_4S_4$ ratio are given.

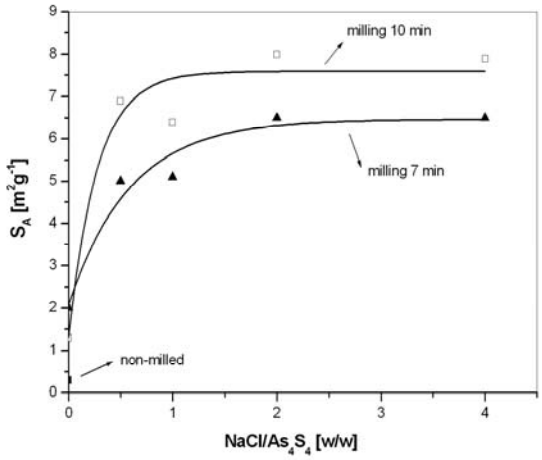

Fig. 3. Specific surface area of realgar As_4S_4 in dependence of $NaCl/As_4S_4$ ratio (w/w).

The addition of NaCl had positive influence on surface area of milled realgar particles which increased several times in comparison with realgar milled without diluent. However, the effect of NaCl addition is limited by the value $NaCl/As_4$ S_4=2.0. The further increase of NaCl amount has no effect. The dilution of milled realgar with sodium chloride over this critical value is so large that realgar particles loose contact and the milling energy is preferentially transferred to NaCl particles. As consequence, the particle size of realgar nanoparticles is practically constant (Fig. 3).

It has been shown in our previous work that the transition of the low temperature α-As_4S_4 to the high-temperature β-As_4S_4 as well as the formation of nanosize realgar particles in the range 16-48 nm is possible [15].

However, the dilution effect of NaCl addition has detrimental influence on $\alpha \rightarrow \beta$ transformation of realgar (Fig. 4).

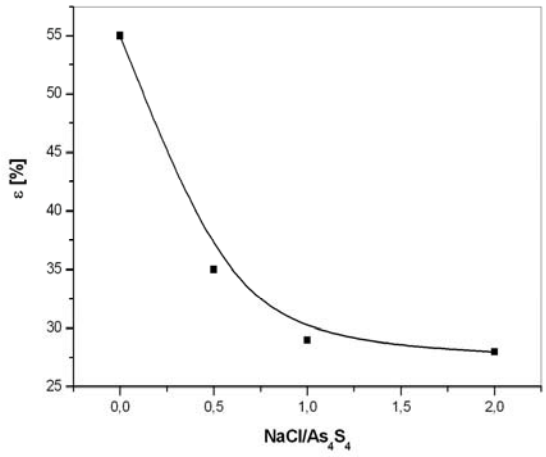

Fig. 4. Dependence of realgar As_4S_4 $\alpha \rightarrow \beta$ conversion degree, ε on dilution by NaCl, NaCl/As_4S_4 (milling time 7 min).

The value ε=28 % has been obtained for sample milled for 7 min which is substantially lower as the value ε=55 % obtained for the same sample but without addition of NaCl. The sodium chloride matrix phase effectively separated the milled powder thus allowing the nanocrystalline grain structure that was developed during milling. However, from the point of mechanochemical polymorphous transformation this effect has retarding influence on realgar $\alpha \rightarrow \beta$ conversion degree as a consequence of reducing the diffusion phenomena, which are predisposing for the reaction procedure.

Conclusions

1. Increase in specific surface area of realgar As_4S_4 particles when using sodium chloride NaCl as a solid diluent during milling has been detected.
2. Application of sodium chloride NaCl by milling has a detrimental effect on $\alpha \rightarrow \beta$ conversion of As_4S_4.

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