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Thermal behaviour of mechanochemically synthesized nanocrystalline CuS

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Abstract

Thermal behaviour of mechanochemically synthesized nanocrystalline CuS particles by high-energy milling in an industrial mill has been studied. Structure properties were characterized by X-ray powder diffraction that reveals the formation of copper sulphide CuS as well as of copper sulphate $CuSO_4 \cdot 5H_2O$. Thermal properties of the as-prepared products were studied by the differential scanning calorimetry together with X-ray inspection for detection by pass products formed. The decomposition of the as-prepared sample has been studied too. Thermal stability of the anhydrous $CuSO_4$ formed by the thermal decomposition is lower than the thermal stability of non-milled samples. The final product of the thermal decomposition is metallic copper instead of Cu_2O, which is stable up to 1100 °C. Differential scanning calorimetry (DSC) analysis proved that the percentage of chalcantite in the covellite mechanochemically synthesized by high-energy milling is 48–51%.

Keywords: Mechanochemistry; High-energy milling; Nanoparticles; CuS; Thermal properties

1. Introduction

Nanosized materials are polycrystalline materials, the crystal size of which is of the order of a few (typically 1–100) nanometers in at least one dimension. It has been proposed that as particles become smaller in size they may take on different chemical and physical properties. One of the most intriguing observations was that nanocrystals prepared by the altered “nano” approach exhibited higher surface chemical reactivity than more conventionally prepared samples [1–3]. The novel characteristics of these nanocrystalline materials as a result of particle dimension include surface area, quantum confinement, high diffusivities, increased solid solubility, high strength, sufficient formability and the other effects. Nanosized materials have been synthesized by a number of techniques starting from vapor phase (i.e., inert gas condensation), liquid phase (i.e., rapid solidification) and solid state (i.e., mechanical and/or mechanochemical treatment–mechanochemistry).

The approach starting from solid state applies high-energy ball milling and involves the production of high density of crystal defects (e.g., dislocations, grain boundaries, new surface structures, etc.).

The concept of high-energy milling has attracted considerable scientific and technical interest in recent years as a consequence of the unique nanostructures and properties developed by this process. The chemical reaction occurs at the interfaces of the nanometer sized grains that are continually regenerated during milling. As a consequence, reactions, that would normally require high temperatures to occur, due to separation of the reacting phases by the product phases, can occur at low temperatures in a ball mill. It was stated in [4] that many reactions for which the equilibrium thermodynamics does not afford favourable conditions can be realized by the effect of high-energy milling. An important feature of the process is the rapid refinement of the particle microstructure, i.e., grain size or crystallite size, during milling. While powder particle sizes generally decrease only to the micrometer level, a nanometer grain size is developed within each particle.

The main advantage of the mechanochemical approach to preparation of nanocrystalline materials via high-energy milling is that it is a “quantity” process permitting kilogram and tonnage quantities of nanomaterial to be produced in an ambient temperature in very short processing time. Moreover, the milling method is inexpensive and environment friendly, because it

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does not require large volumes of solutions and produces particles.

In nature, copper sulphide (CuS) usually exists in small quantities associated with other copper sulphides such as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4). It is found in the zone of secondary enrichment formed as a result of the alteration of primary sulphides. It can occur as thin crusts or as deep blue–black powdery or sooty masses, as well as grains in geothite, malachite and areas of gangue. During the last decades various technological applications of copper sulphides were discovered.

Recently, nanocrystalline copper sulphide has been used for manufacturing ion selective electrodes, hydrogen sulphide sensors, solar cells, photoelectric transformers and superconductors. Therefore, much research on CuS particles and their physicochemical properties has been carried out and several methods have been used for the preparation of this material [5,6]. Some nanoparticles were already synthesized by high-energy milling in the laboratory mills and very good results were achieved [7–11].

The thermal behaviour of natural sulphides has been published [12–14]. A few articles have been published on the thermal properties of synthesized sulphides [15–18]. However, thermal properties of the mechanochemically synthesized nanoparticles have not been studied so far.

The main aim of this paper was to point out the study of the thermal behaviour of mechanochemically synthesized nanocrystalline CuS nanoparticles applying high-energy milling in a vibratory mill.

2. Experimental

Nanocrystalline CuS particles were synthesized in an industrial eccentric vibratory mill ESM 654 (Siebtechnik, Germany). This mill has found implementation in a diversity of powder technology applications such as grinding of pigments, zirconia, carbides, poorly soluble ores, etc. [19,20]. In this work the following conditions were applied: time of milling in an air atmosphere, 6–48 min; loading of the mill with steel balls of 30 mm diameter in total amount of 17 kg; and rotation speed of the milling chamber 960 rpm.

MeS nanoparticles were prepared by high-energy milling of copper acetate and sodium sulphide according to the general equation:

$$(CH_3COO)_2Cu \cdot 4H_2O + Na_2S \rightarrow CuS + 2CH_3COONa + 4H_2O \qquad (1)$$

The reaction is thermodynamically feasible at ambient temperature, as the enthalpy change is negative. The value $\Delta H^{\circ}_{298} = -217 \mathrm{kJmol}^{-1}$ was calculated from thermodynamic data published in [21].

After the completion of reaction (1), the produced CuS nanoparticles have been washed, decanted and dried.

The X-ray diffraction measurements were carried out using a X'Pert diffractometer (Philips, Netherland) working in the 2θ geometry with Cu Kα radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards.

The differential scanning calorimetry (DSC) diagram was recorded at a heating rate of 10 °C/min under a helium flow of 80 ml/min using a DSC Setaram device, model 1 1 1.

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

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

3. Results and discussion

The formation of copper sulphide nanocrystalline particles is illustrated by the XRD pattern given in Fig. 1. The products of reaction (1) have been washed in order to remove water-soluble sodium acetate. Copper sulphide (CuS) (JCPDS-06-0464) and copper sulphate ($CuSO_4 \cdot 5H_2O$; JCPDS-11-0646) have been detected in products of washing. All mechanochemically synthesized CuS samples look quite similar. $CuSO_4 \cdot 5H_2O$ is probably coming from the oxidation of very reactive CuS nanoparticles that are very sensitive to mechanochemical oxidation, which is a general phenomena frequently described in the high-energy milling of sulphides [21]. The possible interpretation is a reaction of CuS generated during milling with water. As a source of water can serve both reaction precursors where it is bound in a crystalline form.

The dependence of specific surface area on milling time for mechanochemically synthesized CuS particles is given in Fig. 2(1). The specific surface area increases (13–15 $m^2 g^{-1}$) with the increasing time of milling. The results of the particle size analysis are displayed in Fig. 2(2). It can be observed that the percentages of every one of the fractions of analysed particles decrease very slowly after 24 min of milling, what is in a good agreement with observed small agglomeration effect of fine particles.

In order to obtain additional information concerning to the composition and the thermal stability of the sample obtained

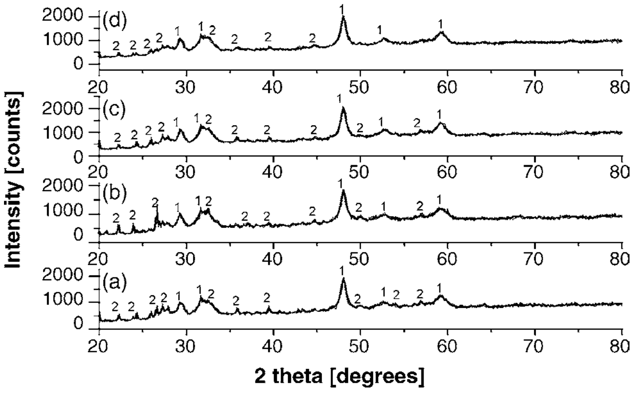

Fig. 1. XRD patterns of mechanochemically synthesized nanocrystalline CuS, milling time: (a) 6 min; (b) 12 min; (c) 24 min; (d) 48 min; (1) CuS-covellite; (2) $CuSO_4 \cdot 5H_2O$-chalcantite.

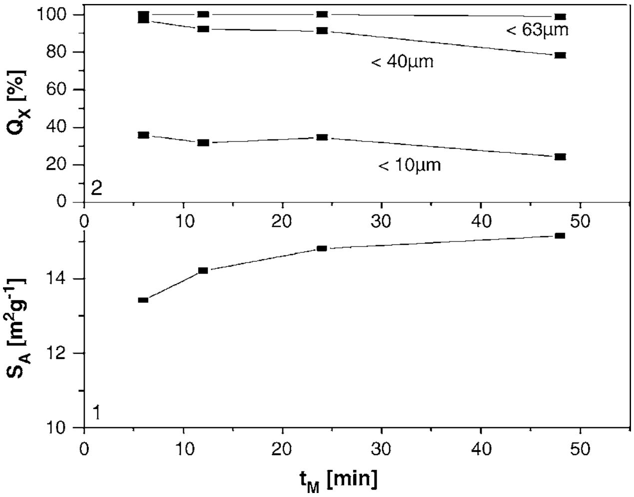

Fig. 2. Specific surface area, S_A (1) and fraction of particles less than x µm, Q_x (2) of mechanochemically synthesized CuS nanoparticles as a function of milling time, t_M ($x = 10$, 40 and 63 µm, respectively).

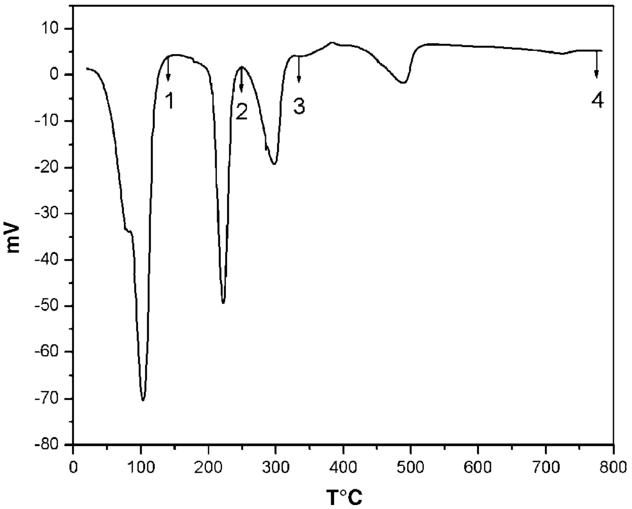

Fig. 3. DSC diagram of the mechanochemically synthesized CuS during 48 min. The marked points refer at the temperatures at which samples were taken for XRD inspection.

by milling, it has been considered of interest to carry out a DSC analysis together with an X-ray inspection for trying to detect the by pass products formed after the different DSC peak recorded.

Fig. 3 shows the DSC diagram obtained for the CuS mechanochemically synthesized by milling for 48 min.

The XRD patterns recorded at room temperature after the sample reached the points marked as 1, 2, 3 and 4, respectively, on the DSC diagram are shown in Fig. 3. A set of different DSC experiments were stopped at the temperatures of 150 °C (point 1), 250 °C (point 2), 345 °C (point 3) and 800 °C (point 4), respectively, and, after cooling, the samples were removed and weighed for determining the weight loss percentages that are reported in Table 1 (Fig. 4).

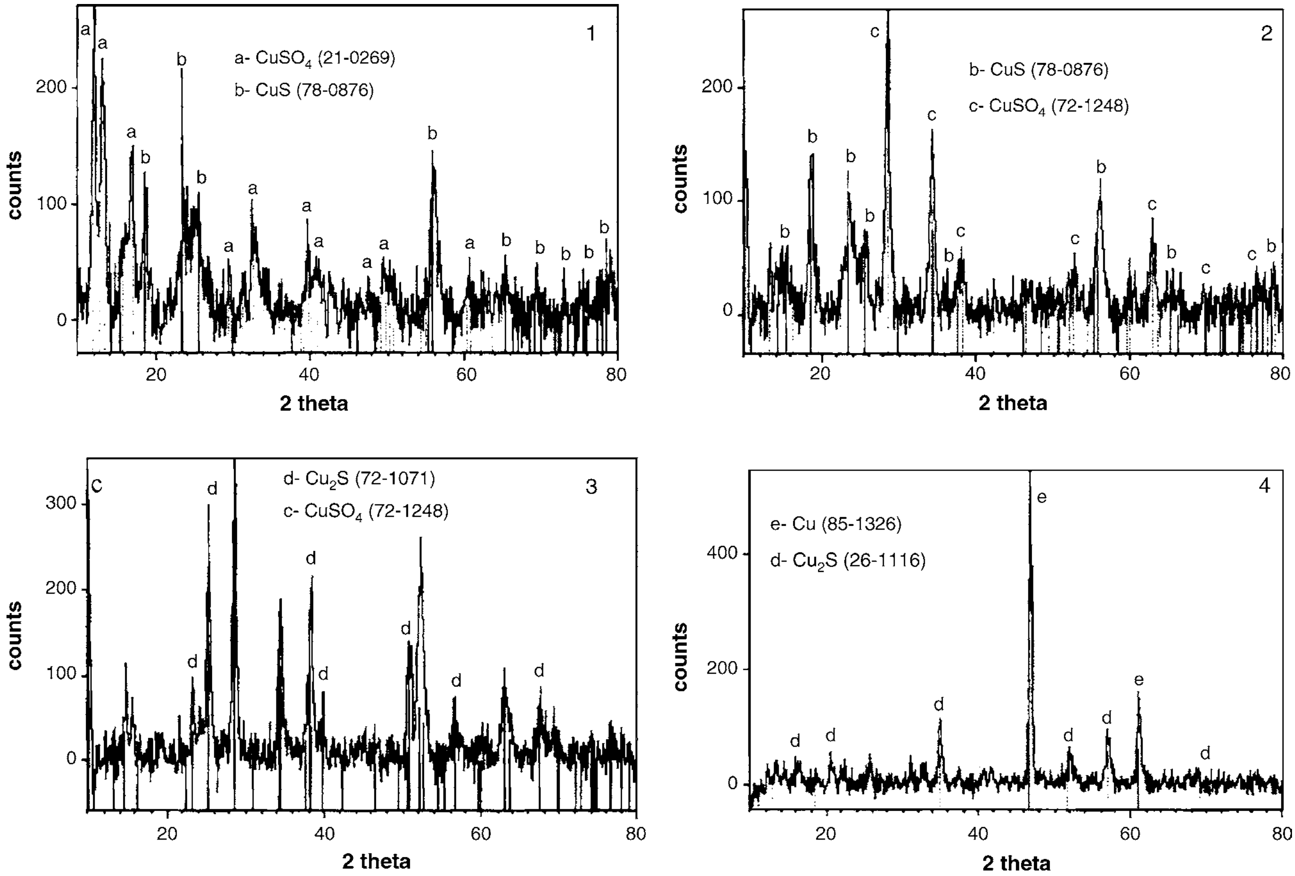

Fig. 4. XRD patterns after DSC until the points marked at Fig. 3: (1) 150 °C; (2) 250 °C; (3) 345 °C; and (4) 800 °C.

Table 1
DSC and subsequent XRD analysis of mechanochemically synthesized CuS (milling time 48 min)

XRD analysis	DSC analysis	
	Temperature (°C)	Weight loss (%)
CuS	150	
$CuSO_4{\cdot}H_2O$		14.1
CuS	250	
$CuSO_4$		21.6
Cu_2S	345	
$CuSO_4$		31.0
Cu_2S	800	
Cu		51.2

The above results confirm that the starting sample is constituted of a mixture of CuS and $CuSO_4{\cdot}5H_2O$ that decomposes according to the following steps associated with each of the peaks observed at the DSC diagram:

$$CuSO_4.5H_2O \xrightarrow{150^\circ C} CuSO_4.H_2O + 4H_2O \quad (2)$$

$$CuSO_4.H_2O \xrightarrow{250^\circ C} CuSO_4 + H_2O \quad (3)$$

$$2CuS \xrightarrow{345^\circ C} Cu_2S + S \quad (4)$$

$$CuSO_4 \xrightarrow{800^\circ C} Cu + SO_3 + \tfrac{1}{2}O_2. \quad (5)$$

In summary, the DSC data show that the CuS constituting the starting sample loss sulphur leading to the formation of Cu_2S associated to the endothermic peak observed at 300 °C. The Cu_2S formed remains stable under inert atmosphere up to 800 °C that is the highest temperature here investigated. The $CuSO_4{\cdot}5H_2O$ decomposes as expected in successive steps. The endothermic peaks observed at 110 and 220 °C correspond to the dehydration of this compound to the monohydrate and the anhydrous salt, respectively, in good agreement with the very well-known data for the dehydration of chalcantite, provided that $CuSO_4{\cdot}5H_2O$ is very often used as standard by the manufacturers of TG, DTA and DSC devices [22]. However, it is noteworthy to point out that the thermal stability of the anhydrous $CuSO_4$ formed is considerably lower than the thermal stability of unmilled samples. The broadened endothermic peak observed at 500 °C (associated with the thermal decomposition of the anhydrous copper sulphate), occurs at a temperature of about 200 °C lower than that previously reported [22]. Moreover, the final product of the thermal decomposition is metallic copper instead of Cu_2O that according to reference [22] is stable up to 1100 °C.

Finally, the analysis of the above results together with the percentage of weight loss shown in Table 1 suggest that the percentage of $CuSO_4{\cdot}5H_2O$ in the CuS mechanochemically synthesized by milling a stoichiometric mixture of copper acetate tetrahydrate and sodium sulphide for 48 min is about 48–51%.

4. Conclusions

The presented paper describes the structure and thermal properties of the copper sulphide CuS nanoparticles synthesized from copper acetate and sodium sulphide in the industrial eccentric vibratory mill. It has been proved by combining XRD and DSC techniques that thermal decomposition is a multistep process, which includes formation of different copper forms as $CuSO_4{\cdot}H_20$, $CuSO_4$, Cu_2S and Cu. The variety of products is a consequence of the fact that during high-energy milling besides CuS also $CuSO_4{\cdot}5H_20$ is formed. Milling decreases all reaction temperatures, the decomposition temperatures of CuS are decreased by approximately 200 °C compared with that in the phase diagram. The *x* presence of $CuSO_4{\cdot}5H_20$ in future research would be necessary.

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