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Synthesis of nanocrystalline SnO_2 powder from $SnCl_4$ by mechanochemical processing

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ABSTRACT

The rapid synthesis of nanocrystalline SnO_2 powder using a mechanochemical reaction of $SnCl_4$ (instead of the widely used tin (II) compounds) with $(NH_4)_2CO_3$ and the subsequent annealing of the product in air and under an H_2O/NH_3 atmosphere has been investigated using X-ray powder diffraction, TG and TEM. The reaction was complete within 5 min. Additional milling of the product at a higher milling intensity for 120 min led to the crystallisation of tetragonal SnO_2. The NH_4Cl salt matrix was removed by annealing at 300 °C. The average crystallite size of tetragonal SnO_2 was in the range of 2–48 nm and it can be controlled by variation heating temperatures and annealing atmospheres in the range of 300–700 °C.

1. Introduction

The mechanochemical synthesis of nanocrystalline powders with particles of less than 100 nm is currently widely studied [1]. This processing involves high-energy collisions of the grinding media and reactant, resulting in pulverisations, phase transformations and chemical reactions. As a consequence, chemical reactions which would normally require higher temperatures to occur due to separation of the reacting phase by the product phase, can occur at lower temperatures in a ball milling without any external heating [1]. By selecting proper conditions such as suitable chemical reaction paths, stoichiometry of starting reactants and milling conditions, mechanochemical processing can be used to synthesise nanocrystalline particles dispersed within a soluble salt matrix. Moreover, the crystallinity of the products can be improved by heat treatment prior to the removal of the solid matrix by washing [1]. A number of oxides, including ZrO_2, CeO_2, Fe_2O_3, Cr_2O_3, ZnO; sulphides such as ZnS, PbS, CdS and carbonates e.g. $CaCO_3$ have been synthesised in nanocrystalline form by mechanochemical processing [1]. In the above processes precursors such as $ZrOCl_2{\cdot}8H_2O$ [2], $ZrCl_4$ [3], $CeCl_3$ [4], $CaCl_2$ [5], and Zn, Pb, Cd-acetate [6] undergo reactions with CaO [3], NaOH [2,4], Na_2CO_3 [2,5] and $Na_2S{\cdot}9H_2O$ [6] during high-energy milling.

The mechanochemical approach in the SnO_2 area has been focused mainly on the preparation of nanocrystalline SnO_2 powder from tin (II) compounds by a reaction with Na_2CO_3, [7–9,13], K_2CO_3 and $Ca(OH)_2$ [10], reactive milling of metallic tin in oxygen [11] and by a reaction of solid $SnCl_4{\cdot}5H_2O$ with KOH [12]. Almost in all cases, subsequent annealing was necessary to complete the reaction [7–10,12,13]. The annealing of the product in air is necessary for the oxidation of SnO to SnO_2, on the other hand calcination temperatures above 500 °C result in a significant degree of nanocrystalline growth and to the presence of normal tetragonal phases and high pressure orthorhombic phases respectively [7,8,10]. One of the drawbacks associated with such syntheses is also a washing procedure of the salt matrix after annealing treatment.

Up until now, liquid $SnCl_4$ has not been used as a starting precursor in the mechanochemical synthesis, with the less reactive $SnCl_2$ used instead. The removal of the salt matrix by low temperature annealing, instead of the usual washing out, is also a new strategy, which until recently was used only in the case of nanocrystalline TiO_2 preparation [14]. In this paper, the mechanically accelerated synthesis of nanocrystalline SnO_2 with the rapid reaction of $SnCl_4$ and $(NH_4)_2CO_3$ is reported. The effect of milling time and annealing atmospheres on nanocrystalline grain growth is also discussed.

2. Experimental

The starting materials were $SnCl_4$ (Lachema) and $(NH_4)_2CO_3$ powders (Lachema). The mechanochemical synthesis was performed in a high-energy TB-1 planetary mill developed by Kadaň Ltd., Slovakia with two milling jars, having a power input of 1.7 kW, and in which, the jars were continuously cooled with water. These mill jars

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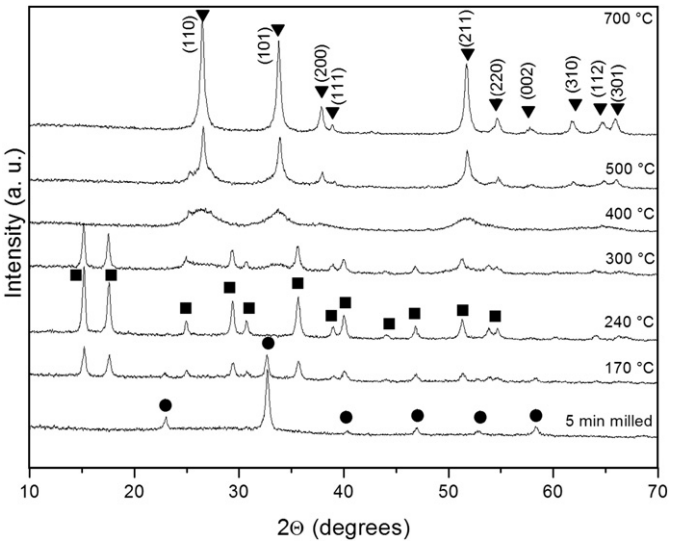

Fig. 1. XRD patterns of the $SnCl_4$+3 $(NH_4)_2CO_3$ mixture milled for 5 min and heated in the temperature range of 170–700 °C in air (▼): tetragonal SnO_2, (●): NH_4Cl, (■): $(NH_4)_2SnCl_6$.

have an inner radius of 32 mm. The distance from the mill axes to the jar centre is 58 mm. The milling rotation frequency of the central axes was 890 rpm. The ball speed under these conditions was calculated according to Eq. (7) and (15) of Ref. [15] at 8.3 m s^{-1}. Corundum 10 mm balls with a weight of 100 g and corundum jars with a 0.3 dm^3 inner volume were used as the milling media. The first powder series was prepared by the reaction of 5.25 g $(NH_4)_2CO_3$ with 2.2 ml of $SnCl_4$. Liquid $SnCl_4$ was carefully added to the jars containing the $(NH_4)_2CO_3$ powder, which were then promptly closed. The milling time was 5 min. The ball to powder mass ratio was 10:1. Annealing of the as-milled powder was carried out in an air atmosphere with a temperature range of 170–700 °C for 1 h. The second powder series was prepared under the same conditions as the first one, but the annealing of the as-milled powder was performed under an H_2O/NH_3 atmosphere. The third powder series was prepared with an additional milling of 3.3 g of powder from first series, for 5 and 120 min and the ball to powder mass ratio was 30:1. The prepared samples were annealed in the range of 300–700 °C for 1 h in air. The structure of the prepared powder was examined via X-ray diffractometry with a Philips PW 1050 diffractometer using Cu-K_α radiation. The average crystallite size (D) was calculated according to Scherrer's equation:

$$D = 0.9\lambda/[(B_s - B_m)\cdot\cos\theta], \quad (1)$$

where D is the crystallite size, λ the wavelength of the X-ray radiation (0.15418 nm), B_s and B_m are the full widths at half-maximum height of the most intensive peak of the sample and of the standard and θ is the diffraction peak position of the sample. Polycrystalline α-Al_2O_3 standard was used for the correction of the instrumental peak-broadening B_m. The particle size, phase composition and crystallinity of the product were examined by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) on a Jeol JEM 2000 FX device working at an acceleration voltage of 160 kV. The samples for TEM investigation were dispersed using ultrasound. A small amount of powder was mixed with ethanol and subjected to vigorous ultrasound stirring for 10 min. Subsequently a drop of strongly diluted ethanol suspension was deposited onto the TEM Cu-grid, which had been covered with a holey carbon film. After air drying, the samples were examined by TEM. Thermal analysis-thermogravimetry (TG) was performed with a Derivatograph Q-1500 D, (MOM, Budapest, Hungary) under the following conditions: weight of the sample: 100 mg; heating rate: 10 °C/min; reference material: α-Al_2O_3, atmosphere: air, static.

3. Results and discussion

The XRD patterns of the $SnCl_4$+3$(NH_4)_2CO_3$ mixtures after milling for 5 min and subsequent annealing at different temperatures are shown in Fig. 1.

According to XRD patterns, the reaction between $SnCl_4$ and $(NH_4)_2CO_3$ is completed after 5 min of high-energy milling and milling is accompanied by the decomposition of the excessive $(NH_4)_2CO_3$ as well, which was coupled with a strong ammonium odour after opening the jar. Since we have not observed any diffractions corresponding to either tetragonal SnO_2 or orthorhombic SnO_2 and only peaks associated with NH_4Cl were present, we assume, that a non-crystalline network of hydrated SnO_2 was formed during milling. In this case, the following reaction can be suggested for the process:

$$SnCl_4 + 3(NH_4)_2CO_3 \rightarrow SnO_2\cdot(1-x)H_2O + xH_2O + 4NH_4Cl + 3CO_2 + 2NH_3$$
$$\Delta H^\circ = -150\,kJ/mol \quad (2)$$

It should be noted that $(NH_4)_2CO_3$ is insoluble in the liquid $SnCl_4$ and the potential formation of $SnO_2{\cdot}xH_2O$ can hinder the fluent reaction flow. The application of the high energy milling, mainly due to the re-generation of the reaction surface can overcome this problem effectively. The short reaction time can be explained by milling induced hydrolysis of $SnCl_4$ and $(NH_4)_2CO_3$ and consequently by the strong acid–base interaction between $SnCl_4$ and $(NH_4)_2CO_3$ hydrolytic products. As can be seen from the XRD measurements in Fig. 1, the annealing of the samples in the range of 170–300 °C resulted in the formation of an unexpected $(NH_4)_2SnCl_6$ intermediate product and the diffractions corresponding to NH_4Cl gradually disappeared.

Heating at temperatures above 300 °C leads to the evaporation and decomposition of $(NH_4)_2SnCl_6$. The crystallisation process of SnO_2 started at temperature 300 °C as can be seen from the XRD measurement given in Fig. 1. The presence of the broadened reflections in the XRD pattern is related to the most intense diffractions of the tetragonal SnO_2 phase (JCPDS 41-1445). Annealing of the precursor at 400 °C for 1 h resulted in the formation of nanocrystalline tetragonal SnO_2 with a crystallite size calculated from Eq.(1) to be about 3 nm. The crystallite size increases from 3 nm at 400 °C to 48 nm at 700 °C. The effect of the annealing temperature, atmosphere and milling time on the average crystallite size of SnO_2 is summarised in Table 1. In order to obtain more detailed information on the size of generated crystallites, the product was further studied using TEM and SAED methods. Fig. 2(a) shows the bright-field (BF) TEM image with SAED pattern in the inset of the samples annealed at 300 °C, and the related image recorded in dark-field (DF) is in Fig. 2(b). TEM and SAED examinations show that the powder consists of very fine tetragonal SnO_2 nanocrystallites with a size around 2 nm and therefore SAED rings (inset in Fig. 2(a)) are narrower than those of the halo circles typical for amorphous material. The occurrence of nanosized crystallites in the sample upon annealing at 300 °C is also clearly shown in

Table 1
Influence of the annealing temperature, annealing atmosphere and milling time on the mean crystallite size of SnO_2

	Annealing temperature [°C] / As-milled	300	400	500	600	700	Milling time [min]	Annealing atmosphere
Crystallite size D [nm]	–[a]	~2	3	17	29	48	5	air
	–[a]	4	5	8	18	35	5	H_2O/NH_3
	~2	~2	3	5	25	40	120	air

[a] Since product was amorphous, the crystallite size was not calculated.