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Synthesis of nanostructured SnO_2 materials by reactive ball-milling

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Abstract

Tin dioxide (SnO_2) is an important material in the field of solid-state gas sensors and the performances are strongly linked to the microstructure. Particularly, a decrease in the crystallite grain size leads to an increase in the sensing properties. Many chemical and physical techniques have been used to prepare nanosized SnO_2 particles, but few papers report the use of a ball-milling process that promote nanostructured grains. In this work, tetragonal phase SnO_2 powders were produced at room temperature (RT) by reactive milling of metallic tin (Sn) powder under pure oxygen atmosphere in a vertical planetary ball-mill. Powder samples were characterized by using X-ray diffraction (XRD), secondary electron microscopy (SEM), electron microprobe. Experimental results indicate that the formation of SnO_2 is a mechanically induced self-sustained reaction. Very short milling time is needed to complete the reaction and the obtained powder is made of aggregates of SnO_2 crystallites, the mean size of which is inferior to 10 nm according to XRD analyses. However, the strong agglomeration led to a decrease of the specific surface area. The reasons and the possible ways to overcome these phenomena are discussed.

Keywords: Mechanochemical synthesis; Nanostructured materials; Oxide materials; Powder metallurgy

1. Introduction

Tin dioxide (SnO_2) has many technological applications such as optoelectronic devices [1], photosensors [2], catalysis [3], negative electrode for lithium batteries [4]. Among these different applications, one of the most important is the use of SnO_2 as solid-state gas sensors [5]. In this case, the required performances are the gas selectivity and the gas sensitivity, which is strongly linked to the material microstructure. In particular, it has been shown that a reduction of the crystallite size to the nanometer scale leads to a significant increase of the gas sensitivity [6]. This result is related to the depth of the surface space charge region affected by gas adsorption in relation to the particle size. Consequently, nanosized SnO_2 have been prepared by different chemical and physical methods such as sol–gel [7], spray pyrolysis [8], pulsed laser ablation [9].

Besides the above techniques, high-energy ball-milling is an alternative cheap and simple method for the preparation of nanostructured materials [10,11]. Additionally, this technique can be used to induce chemical reaction, the process is then called reactive milling or mechanochemistry. In this case, the required reaction can occur between solid–solid or solid–gas reactants. Reactive milling of Ag_2O and Ag_3Sn powders have been used to elaborate nanocomposite materials consisting of nanosized SnO_2 particles embedded in a nanocrystalline silver matrix [12]. In addition, some papers report the production of nanostructured SnO_2 powders by mechanochemical reaction, $SnCl_2 + Na_2CO_3$ [13,14] or $SnCl_2 + Ca(OH)_2$ [15].

In the present work, we have investigated the synthesis of SnO_2 powders by the most simple mechanochemical process, that is the reactive milling of metallic tin (Sn) under oxygen atmosphere. The reaction mechanism and the microstructure of the obtained powders are presented.

2. Experimental procedure

Reactive ball-milling process was performed at room temperature (RT) in a vertical planetary ball-mill (Uni Ball Mill II). The stainless steel cell was loaded in a glove box under a purified argon atmosphere with 14 g of high purity metallic tin (99.9%, Goodfellow) together with six hardened steel balls with a diameter of 25.4 mm. The sealed cell was outgassed up to 10^{-5} mbar and then filled up with high purity oxygen gas at a pressure of about 4 bar. This value has been chosen in order to perform the experiment in excess of oxygen. The metallic tin powder was then ball-milled for different times. The ball to powder weight ratio and the rotation speed (100 rpm) were kept constant for all the experiments. In order to

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avoid a chaotic movement, the trajectories of the steel balls were controlled by a strong magnetic field generated by external magnets [12]. After milling, the powders were collected under air without excess scrapping and, whatever the milling times, the yield was close to 65%.

Ball-milled powders were analysed by X-ray powder diffractometry (XRD) using Cu Kα radiation ($\lambda = 0.15406$ nm) to identify the various phases and to estimate the crystallite sizes. The morphology and the microstructure of the obtained powders were examined by scanning electron microscopy (SEM) with a FEG Gemini 15-25 from LEO, while quantitative atomic analysis and X-ray cartographies were performed using a Cameca SX 50 electron microprobe. The specific surface area was measured using a Micromeritics Gemini 2370 BET surface area analyser, and the equivalent spherical diameter (D_{BET}, μm) was calculated from the formula: $D_{BET} = 6/\rho S$, where S is the specific surface area and ρ the density of the powder.

3. Results and discussion

The variation of the oxygen pressure in the cell over an extended milling period is represented in Fig. 1. The oxygen pressure starts to drop quickly during the first hour of ball-milling, keeps on decreasing slowly up to 6 h before becoming stable. The difference between the initial pressure (4.2 bar) and the steady value of $P(O_2)$ (0.4 bar) is equal to the oxygen pressure calculated from the following reaction with an initial Sn weight of 14 g and by assuming a complete reaction:

$$Sn + O_2 = SnO_2 \quad (1)$$

This first result indicates that the reaction kinetic is extremely fast and the reaction is complete before 10 h of ball-milling.

Fig. 2 shows the XRD patterns of the starting material and ball-milled powders for times between 1 and 66 h. For the unmilled powder, only the peaks corresponding to FCC metallic tin are seen. The XRD pattern of the powder after 1 h of ball-milling confirms the fast variation of the oxygen pressure in the mill chamber described above. Indeed, even if the Sn peaks are still present, the major phase is already tetragonal SnO_2. After 3.5 h, the reflections corresponding to Sn phase are hardly seen and after a milling time of 7 h, the reaction is complete and the unique phase is SnO_2. An extension of the milling time leads to a broadening of the SnO_2 peaks while no other phases are observed. In particular, no trace of iron under metallic or oxide state has been detected even after a milling time of 66 h.

Even if a more accurate determination should be attempted, average crystallite sizes of the different powder have been estimated from the full width at half maximum of the (1 1 0) tetragonal peak by using Scherrer method. Fig. 3 represents the variation of the XRD crystallite size versus the milling time.

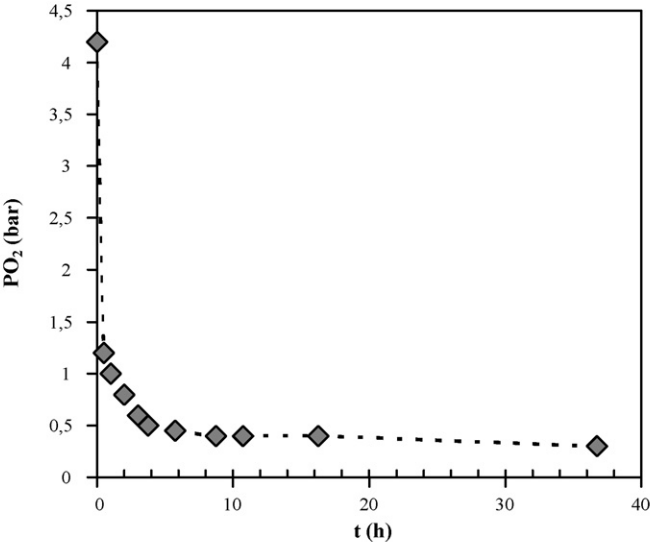

Fig. 1. Evolution of the cell oxygen pressure vs. the milling time.

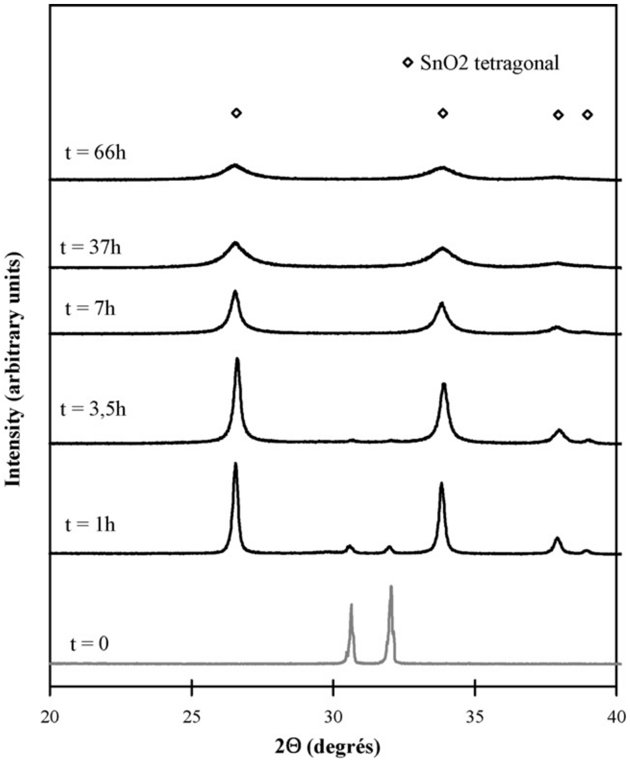

Fig. 2. XRD patterns of Sn powders milled under oxygen for 0, 1, 3.5, 7, 37 and 66 h.

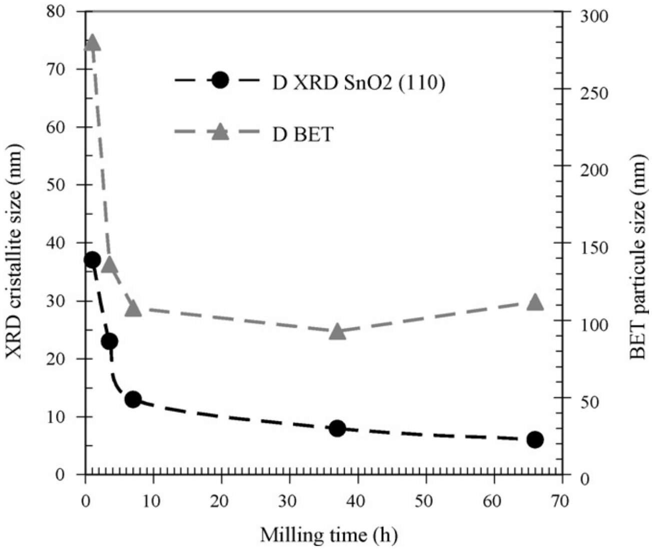

Fig. 3. XRD crystallite sizes and BET particle sizes of the powder as a function of milling time. The crystallite size of the initial tin powder is also indicated.

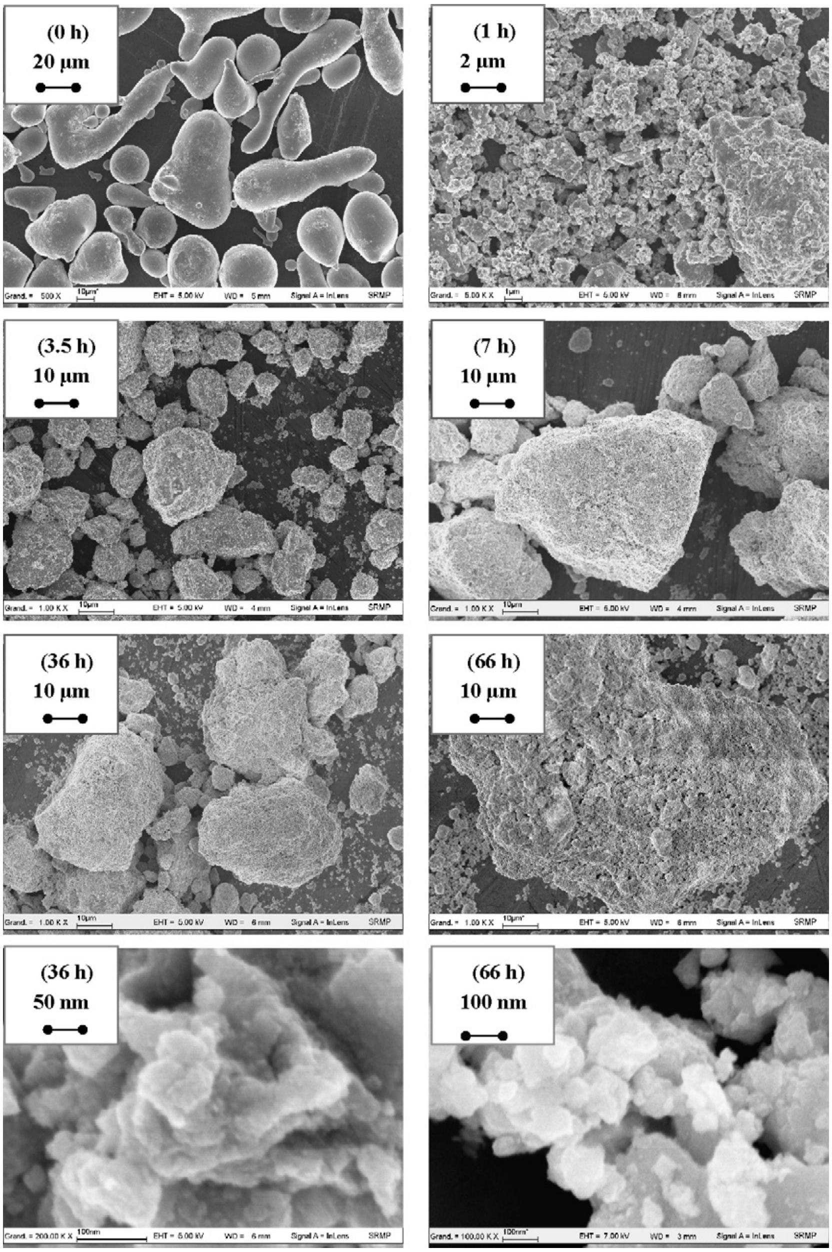

Fig. 4. SEM micrographs (secondary electron mode) of tin powder (0 h) and ball-milled powders after different milling times.

XRD crystallite size decreases for milling times up to 7 h before reaching a quasi steady-state with a final value close to 6 nm after a milling time of 66 h. Then, we have reported the evolution of the BET particle size, estimated from the surface area analyser by assuming spherical particles. The BET particle size, which represents the average diameter of spheres within the particle, follows a similar trend as the XRD crystallite size but the values are higher. This result indicates the apparition of some dense aggregates.

Fig. 4 displays the SEM micrographs of the starting tin material and of the powders obtained after different milling times. The starting powder consists of atomized coarse regular Sn particles with smooth surfaces. Their apparent diameter is comprised between 20 and 70 μm. After 1 h of ball-milling, the powder morphology changes dramatically with the apparition of small aggregates. For milling times longer than 1 h, the size and the shape of the particles change hardly. Indeed, the SnO_2 powders are mainly constituted of coarse particle agglomerates of irregular morphology with a wide size distribution. As revealed by the higher scale micrograph of the 36 and 66 h of the ball-milled powders, these large agglomerates, which can exceed 10 μm in diameter, are built of fine particles with sizes well inferior to 100 nm.

It is well known that contamination from milling media could be important during high-energy ball-milling [11]. Fig. 5 represents the iron contamination content in the ball-milled powder as a function of the milling time. The iron content in the SnO_2 powder increases with the milling time and quantitative analyses

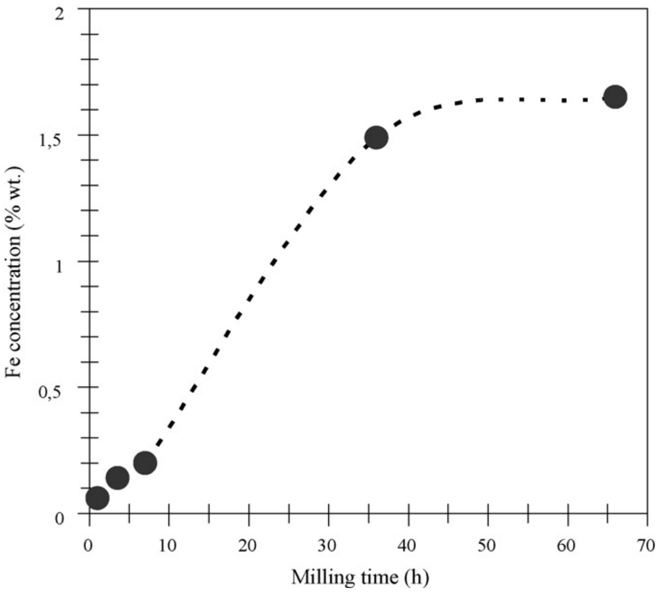

Fig. 5. Iron content in the ball-milled SnO_2 powders vs. the milling time.

performed by electron microprobe have revealed that the iron level in the powder milled for 66 h is inferior to 2% (wt.). The microprobe image of Fig. 6 shows the presence of fine particles containing iron in the ball-milled powder. To perform this analysis, the milled powder has been compacted at room temperature before being polished.

In our study, X-ray diffraction results show that the tin oxidation does not occur gradually with milling time but happens abruptly during a very short milling period. Moreover, we observe a drop of the gas pressure inside the milling vial. These two results suggest that SnO_2 forms through a self-sustaining reaction of the self-propagating high temperature synthesis (SHS) type. As observed for Ti or Zr in similar conditions [16], tin oxidation during milling pure metallic tin under oxygen is an example of mechanically induced self-sustaining reaction. As described in [17], the reaction consisted of three steps: (1) a very short activation period during which size reduction and mixing take place but very little product is formed; (2) an instantaneous period, during which ignition occurs between the balls and the milling vial and a combustion front propagates through the powder charge; and (3) the extension of the milling in order to complete the reaction. Even if we have no data during the first seconds of our milling, we observe these different steps in our study. It is important to underline that, in contrary to solid–solid systems, there are relatively few papers which report the investigation of mechanically induced self-sustaining reaction in the case of solid–gas systems. Garcia-Pacheco et al. have studied reactive milling of nickel and cobalt under air [18]. However, under their milling conditions, they have not observed a SHS reaction type. Indeed, the production of nanocrystalline CoO and NiO powders increase slowly with the milling time and the reaction is not complete after milling times exceeding 100 h.

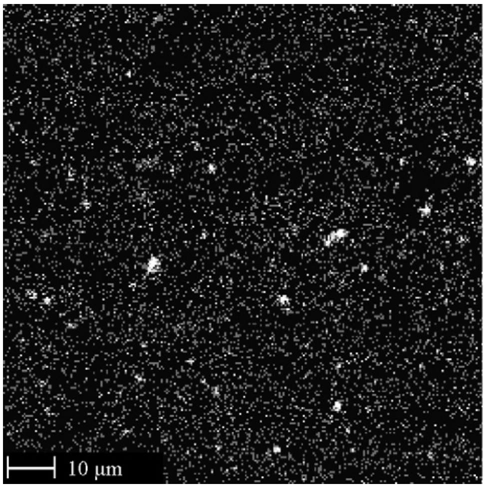

Fig. 6. Microprobe image of the surface sample showing the iron distribution in the powder after a milling of 7 h.

During the SHS reaction, the product undergoes a rapid heating and this temperature increase leads to the formation of coarse grains. Indeed, in our case, even if we have seen that the milling permits to decrease strongly the SnO_2 crystallite sizes up to values inferior to 10 nm, the ball-milled powders are made of large agglomerates several times larger than the crystallite size. This effect reduces the benefits of the crystallite size decrease and results in an increase of the specific surface area. So, before validating the reactive ball-milling as an alternative process of the elaboration of SnO_2 gas sensor, it would be better to overcome this phenomenon. According to Tousimi et al. [19], the introduction of a partial pressure of oxygen in argon gas that just corresponds to the number of oxygen atoms needed to oxidise the metal in the mill permits to refine the grain size of the ball-milled powder. Moreover, the addition of a process control agent (PCA) in the mill could prevent excessive cold welding amongst the powder particles and then reduce the agglomeration level [11]. Some PCA commonly used are benzene, stearic acid or methanol. The investigation of these two ways (change of the oxygen pressure and/or introduction of PCA) might allow to reduce the agglomeration phenomena and to refine the grain size of the ball-milled powder. Nevertheless, the role of these milling conditions on the mechanically induced self-sustaining reaction and so on the reaction kinetic should certainly have to be considered.

4. Conclusion

Nanostructured tetragonal tin dioxide powders have been successfully synthesized by milling metallic tin at room temperature under oxygen in a vertical planetary ball-mill. In the used conditions, the tin oxidation is a mechanically induced self-sustaining reaction, in which the phase transformation from Sn to SnO_2 is complete after a short milling time. The estimated XRD crystallite size of the milled powder is inferior to 10 nm. However, the significant agglomeration level of the powder attenuates the benefits of the decrease of the crystallite size. Further studies will concentrate on increasing the specific surface area by reducing this agglomeration phenomenon and on testing the material with various gas agents.

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