Improved Ag-SnO_2 Electrical Contact Material Produced by Mechanical Alloying

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Abstract

Very pure electrical contact material Ag-SnO_2 composite powders have been produced by mechanical alloying (MA). The starting powders - the silver tin alloy Ag_3Sn and silver oxide Ag_2O - were mixed in a specific concentration ratio and then milled by the use of a Simoloyer® (horizontal rotary ball mill). During the milling process a chemical reaction takes place and simultaneously a mechanical alloying is carried out which leads to a high dispersed phase distribution of nanoscaled SnO_2-particles in a silver matrix. The influence of milling parameters on the milling process such as temperature, atmosphere, rotary velocity and ball/powder ratio were studied to optimize the process. It has been found that the temperature is the most significant factor to vary the milling time. The as-milled powders have been characterized by scanning electron microscope (SEM), transmission electron microscope TEM and X-ray diffraction (XRD).

1 Introduction

Silver contacts have been produced by different industrial methods to obtain a good and homogeneous oxide dispersion in a silver matrix in order to meet the requirement of following electrical properties:

- low erosion both in make and break operations,
- high extinction of the electrical arc,
- low welding force,
- preventing high temperature which leads to a superficial layer of oxide on the top of the contact.

Silver cadmium oxide used as a conventional material for electrical contacts and other electrical components during a couple of years because of a possession above mentioned properties [1]. However, especially concerning the problem of the toxicity of cadmium oxide, the application of this material will be reduced to a minimum in the near future and has to be replaced by a suitable material with similar but minor harmful properties. A very promising candidate for such an application is represented by the system silver tin oxide [2]. Tin oxide is most of the time preferred in terms of: very low welding force but unfortunately it presents large contact resistance because of a thick oxide layer formed on contact surface.

The aim of this work is to produce silver cadmium free electrical contacts with a new method of manufacturing powder on a nanoscale for low tension application. The obtained oxide dispersion should be much more effective in terms of

- welding or erosion (very local melting impact),
- on a mechanical point of view (strenghtening),
- on conductibility (less electrical loss in contact volume).

One of the ways to produce nanoscale particles is mechanical alloying. During MA two different powder particles are repeatedly deformed, fractured and rewelded. This process results in an extremely fine and dispersion of second phase particles in the matrix. If a chemical reaction takes place during the milling process, in other words two starting powders being converted into two different final powders by milling, this milling process is called as reactive milling (RM).

The development of a new process should be technologically superior and cost effective. Based on this reason the MA by means of high energy milling (HEM) is evaluated as an adequate technology for the processing of Ag-SnO_2 composite powder. Following this processing technique [3], the basic powder component Ag-SnO_2 was produced on the powder metallurgical route by RM. A preliminary study has shown that the life time of the contact can be considerably increased through an erosion rate divided by a factor of 3 to 10 while exposed to electrical arc [4].

Furthermore, the difficulty during RM is to avoid or reduce the contamination of the as-milled powder by Fe, Cr and Co which come from the grinding parts of the vessel and in particular the grinding media during the milling process. The longer the milling time, the higher the contamination, because the loss of material from grinding parts by wear increases with increasing of time. In the present work various ball mills, a gravity ball mill (Drummill) and a high energy ball mill (Simoloyer) were chosen and an investigation on influence of process parameters on the milling efficiency was carried out which is expressed in terms of the needed time to complete the reaction. Special emphasis is placed on the evaluation of the efficiency-determining parameters, such as milling temperature, atmosphere and rotary speed.

2 The processing

The processing of production of Ag-Sn_2O bulk materials can be described diagrammatically in Figure 1.

The starting materials are a powder mixture which consisted from silver tin alloy Ag_3Sn and silver oxide Ag_2O. Ag_2O is obtained by electrochemical deposition. Ag_3Sn is obtained after water atomization and sieving through different meshes. The powders were investigated by a scanning electron microscope

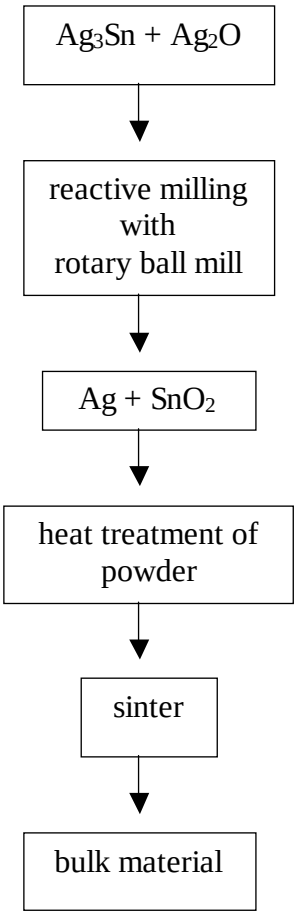


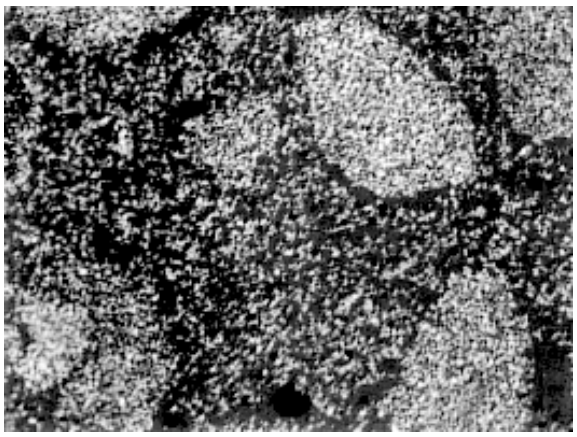
Figure 1: The processing to produce Ag and SnO_2 bulk material

CamScan CS2-9. Figure 2a and 2b show the micrographic particle shape of Ag_3Sn and Ag_2O starting powder.

During the milling process with a rotary ball mill a chemical reaction can take place. The corresponding equation will be described as follows:

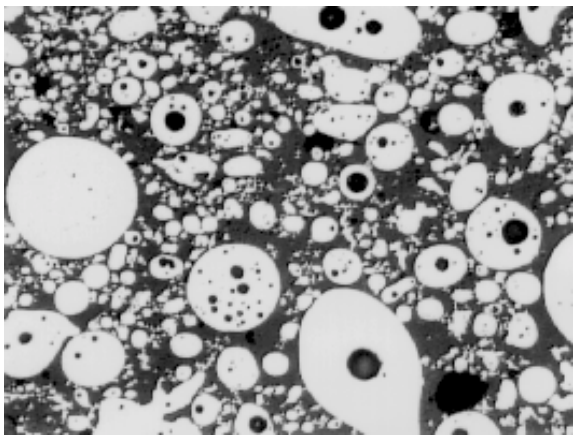
$$Ag_3Sn + 2Ag_2O \rightarrow 7Ag + SnO_2 \qquad (1)$$

Heat treatment at 100 °C was applied to improve the sintering ability. Then the powder was sintered with equipment from *Engelhard-CLAL*. The current paper focuses on the processing of powder manufacturing by reactive milling as well as the optimization of processing parameters. The following processing around sintering can not be discussed here due to confidentiality.



100 µm

Figure 2a: starting powder Ag_2O (SEM micrograph)



100 µm

Figure 2b: starting powder Ag_3Sn (SEM micrograph)

The contamination of Ag-SnO_2 composite by the elements such as Fe, Cr, Co and WC from the grinding tools which have a direct and close contact with ball milled powders can be dramatically detrimental to electrical properties. The possibility in order to minimize the contamination during the milling processes are reducing the milling time and increasing the wear resistance of the milling parts. The practical and realizable improvement methods are as follows:

- optimization of parameters to increase the process efficiency,
- structure improvement of the milling device,
- hard coatings on the surface of contact parts of the vessel to reduce the material loss through wear.

3 Milling device

In this investigation two milling devices were used to carry out the experiments. They are a high energy rotary ball mill, the Simoloyer, and a gravity ball mill, the Drummill. During the milling process the chemical reaction from starting powder Ag_3Sn-AgO_2 to Ag-SnO_2 should be completed. The object by means of the chemical reaction is to realize a mechanical

alloying with high dispersed tin oxide phase in the silver matrix. Details of experiments by the use of both milling systems are described below.

3.1 Drummill

A Drummill Comb 03/A03 (Volume 30 liters, alumina lining) with draingrating and grinding media (35 kg Al_2O_3, ZAL 292, ϕ 30 + 40 mm) has been applied (see Figure 3). The choice of this system based on the simple design and geometry of the chamber which can be respectively lined easily with wear resistant materials. A milling trial over a total time of about 30 h was carried out. Table 1 shows the parameter.

Table 1: milling parameter with Drummill Comb 03/A03

chamber temperature (°C)	room temperature
chamber capacity	30 liter
atmosphere	air
milling time (h)	6, 12, 18, 24 36, 48, 60, 72, 84, 90
ball mass (g)	35 000
powder mass (g)	350
rotational speed (rpm)	50
ball material	Al_2O_3, 26 kg/9 kg (ϕ = 30/ϕ = 40 mm)
lining at the inside of the drum	Al_2O_3

The principle of a drummill is showed in Figure 3b. After a mixing of ball and powder (in this case with a ratio of ball : powder = 100 : 1) the balls move together with the drum in a circle. If the drum moves with a critical rotational speed the balls fall down from the top of the drum, so the powder can be grinded. As the drummill works with gravity free fall principle, the rotational speed shall be kept at a critic value in order to guarantee the milling processing [5]. The critical velocity of drummill is calculated as:

$$n_k = \frac{42.3}{\sqrt{D_d}} \quad (1)$$

n_k is the critical velocity and D_d the diameter of the chamber. The maximum allowed rotational speed is given at 70 % n_k. The critical velocity of this drummill refers to about 50 rpm as it has a diameter of 0.35 m. The highest velocity of the balls by critic rotational speed of the drum could be described as follows:

$$H_{ff} = 55\% D_d \quad (2)$$

$$V = \sqrt{2gH_{ff}} \quad (3)$$

H_{ff} is the free fall path of a single ball in the chamber and V the maximum velocity of the collision.

Following formulas 2 and 3 the highest velocity of the collision was calculated as 1.95 m/s which is the main parameter to describe the kinetic energy level by the use of the drummill. In this case the efficiency of the milling processing is low.

Figure 3a: Drummill Comb 03-A03

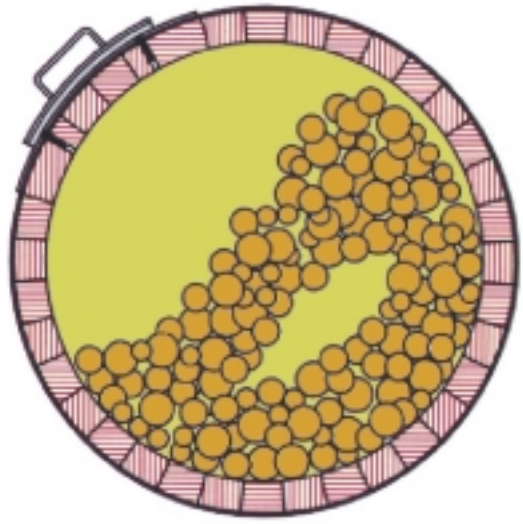


Figure 3b: cross-section of the chamber

3.2 High energy rotary ball mill (Simoloyer®)

A Simoloyer CM01-2l with 2 liter grinding chamber capacity was used for the reactive milling of Ag-Sn_2O composite. Figure 4a shows the milling device. The principle of the Simoloyer is based on a horizontally borne rotor in a strong design which allows the transfer of a high and homogeneous kinetic energy of ball impacts (Figure 4b). In comparison to vertical conventional attritors, the horizontal operating Simoloyer avoids dead zones mainly by gravity. Not only charging and operating, but also discharging can be performed under controlled atmosphere by means of an air lock. Furthermore, the temperature of the milling chamber unit and the processed powder can be controlled by an external cooling system. Different chamber volumes are available from 0.5 up to 400 l for laboratory respectively industrial applications. The special MALTOZ® – software offers to carry out the complete powder processing procedure under computer-controlled conditions. Table 2 shows the milling parameters by the use of Simoloyer which were selected to carry out the experiments.

Table 2: milling parameter with Simoloyer CM01-2l

chamber temperature (°C)	room temperature to 100 °C
chamber capacity	2 liter
atmosphere	air, vacuum, argon
milling time (min)	5, 10, 15, 20, 25, 30, 45, 60
ball mass (g)	2 000
ball/powder ratio	10 : 1, 25 : 1, 50 : 1
rotary speed (rpm)	operation cycle: 1300, 4 min/900, 1 min discharging cycle: 900 rpm, 4 min / 1300 rpm, 1min
ball material	100 Cr6, ϕ = 4.76 mm
material of vessel inside	1.4301

Usually the chamber of Simoloyer is designed with a double wall to flow cooling water. In order to meet the special demand of temperature variation during the milling proceeding the

Simoloyer was redesigned. A vessel without a cooling jacket has been designed and fitted with heating elements. An additionally thermocouple for the control of the heating elements has been installed to this device (Figure 4). Therefore the temperature could be varied from room temperature up to 200 °C

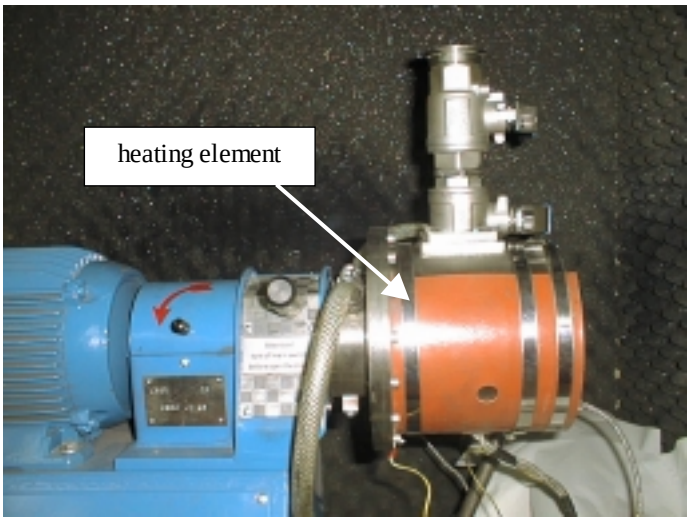


Figure 4a: Simoloyer CM01-2l with heat element

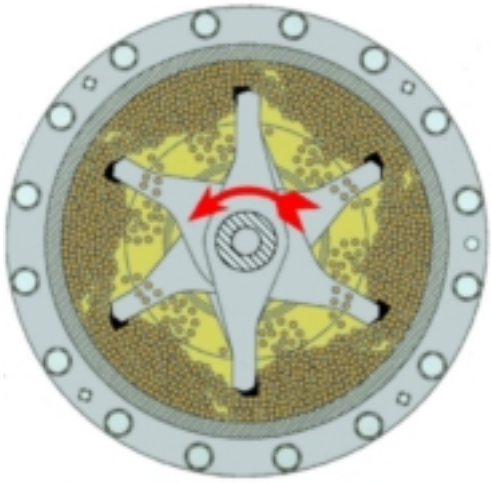


Figure 4b: cross-section of the chamber

4 Optimization of processing

4.1 Choice of milling devices

The experiments of RM were at first carried out with the drummill. 35 kg Al_2O_3 balls and 350 g powder mixture of Ag_3Sn and Ag_2O was filled into the 30 l chamber. The drum rotates with a rotational speed of 50 rpm under air (see Table 1). The powder samples were extracted regularly. It was observed that after long milling time up to 30 h the alumina balls were strongly damaged (Figure 5). The X-ray diffraction patterns of the powders after different milling time were showed in Figure 6 which were resolved by a *Seifert C-3000* using monochromatic CuK_α radiation.

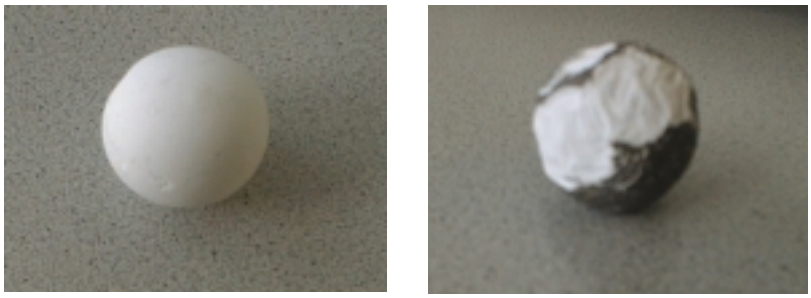


Figure 5: alumina balls before (left) and after 30 h (right) milling test

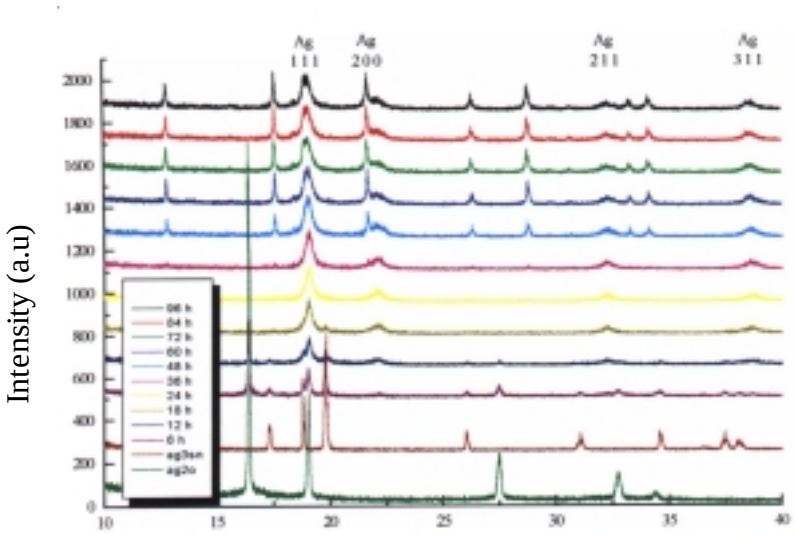


Fig. 6: X-ray diffraction patterns of starting and as-milled powder by using of Drummill at room temperature in air

From these results it can be seen that the proceeding duration is very long duo to low kinetical energy impact. After 36 h the reaction is not completed. Furthermore, a high contamination of as-milled powder caused by damage of the alumina balls is not able to be avoided as the alumina is very brittle. Based on these results further experiments with drummill was terminated.

As followings a high energy rotary ball mill, the Simoloyer, was chosen for the advanced experiments of process optimization. As the completeness of the reaction during the milling process, the contamination and the microstructure of the as-milled powder depend directly on the milling parameter, hence a optimization of the process parameter is necessary. The considerable parameters which influence strongly above mentioned terms are temperature, atmosphere and milling intensity.

4.1 Influence of temperature

A investigation of a interrelationship within temperature, milling time and completeness of the reaction was carried out from company *SRMP* by use of a vibrating frame grinder. Figure 7 reports the results of this prime experience [4]. This diagram allows to explain that heating higher than 100 °C is not suitable from a kinetic point of view.

Based on this study the temperature has been varied from 25 to 100 °C (see Table 2) during the milling process. The milling trials have been performed under air and under argon by Simoloyer with a grinding chamber volume of 2 liters. The dependency of the reaction efficiency on the milling time was observed. A optimized temperature should be so determined and selected that at which the reaction from powder mixture of Ag_3Sn and Ag_2O to final powder mixture of Ag and SnO_2 could be completed with the shortest time needed and highest yield of ball milling. In other hand in consideration of an industrial scale application as well as a continuous process a temperature below 100 °C is expected. In any case a good and static temperature route is necessary for the reproducibility of milling process.

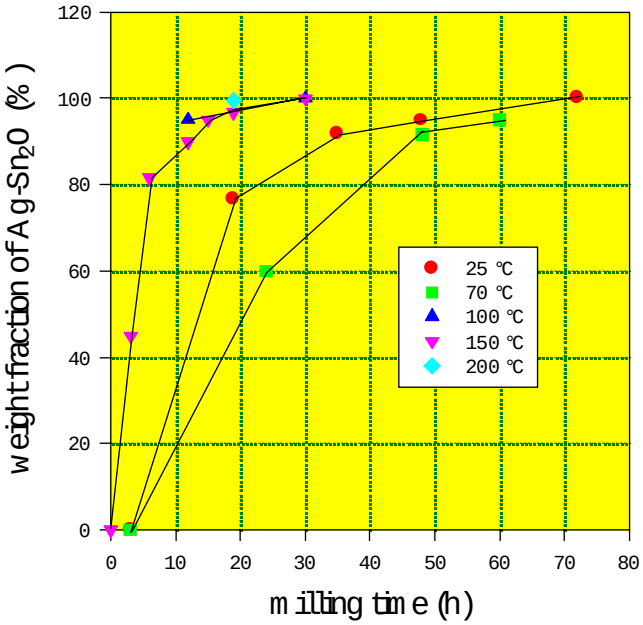


Figure 7: relation of weight fraction of Ag-Sn_2O, temperature and milling time

The further experiments show up to now that the optimum milling temperature to perform a quick process (about 25-30 min) is 100 °C. Figure 8 shows the results of the quick process.

A connection between the milling temperature and the crystallite size was observed by means of scanning electron microscopy that increasing the milling temperature the crystallite size increases. According to these results we can estimate that the milling temperature has a significant effect on the size of particles at 100 °C and thus it is a decisive parameter for the quality of the as-milled powder.

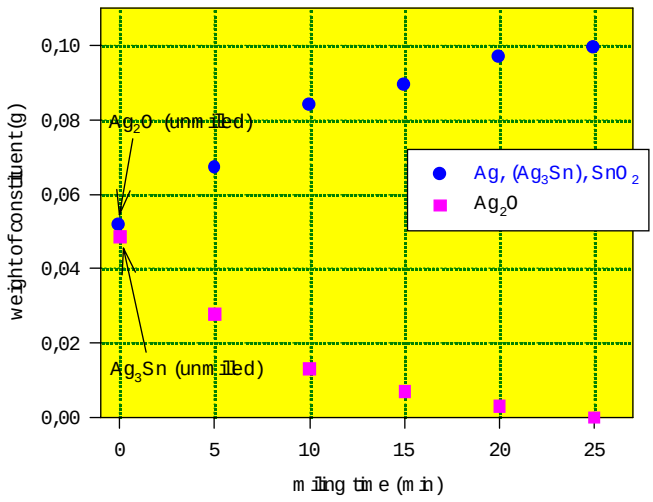


Figure 8: chemical analysis of silver oxide in addition to the milling time

4.2 Influence of atmosphere

It was supposed that oxidizing atmosphere avoids sticking and agglomeration of powder whereas reducing oxygen content increases the transformation kinetics [3]. Figure 9 shows the influence of atmosphere on the efficiency reaction before the optimization of milling temperature with the vibrating frame grinder [4].

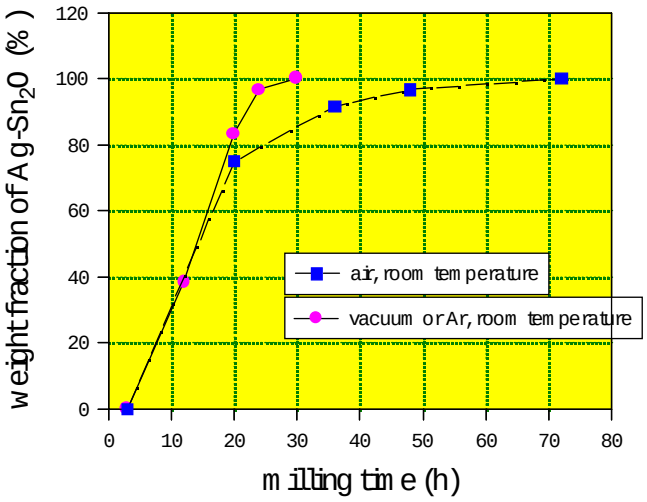


Fig. 9: milling results in vacuum and in air

The sticking and agglomeration were occurred at the beginning of the experiments by the use of Simoloyer. This appears expectedly due to a steady motion of the balls in the process. By cyclic varied rotary speed this state could be eliminated, thus a unchanging process of deformation, fracture and welding can be broken through cyclic operating. An operation cycle has been chosen with a time interval of 4 min at 1300 min^{-1} followed by 1 min at 900 min^{-1}. A discharging cycle was composed by an interval of 4 min at a rotary speed of 900 min^{-1} and an interval of 1 min at 1300 min^{-1}. The results were showed in Figure 10.

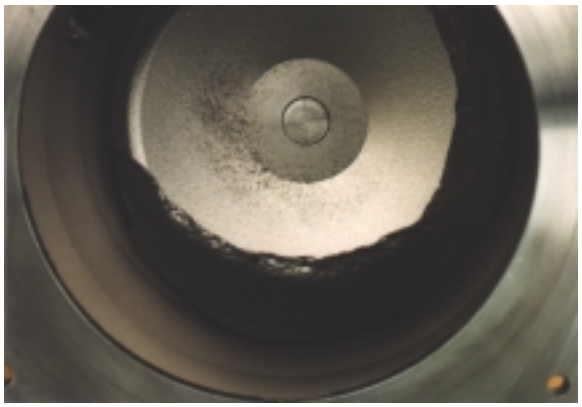


Figure 10a grinding chamber after constant operation

Figure 10b: grinding chamber after cycle operation

By use of the Simoloyer the kinetic energy is strongly increased which leads to an increasing of transformation kinetic. Consequently, the difference of the influence by selecting the atmosphere under air or argon on the milling process could be reduced. Milling experiments

show that the similar results at least regarding the transformation kinetic can be achieved under air as well as under inert gas (Argon).

4.3 Influence of milling intensity

It is known by experience that the higher the milling intensity, the shorter the milling time [3]. Consequently the contamination of the as-milled could be reduced with the increasing of the milling intensity. As a comparative basis the definition of the milling intensity of the vibrating frame grinder is displayed as follows [3]:

$$I = \frac{M_B V_{\max} f}{M_p} \tag{3}$$

I (m/s^2) is the milling intensity, M_B (kg) the mass of the ball, V_{max} (m/s) the velocity of collision, f (Hz) the impact frequency and M_p (kg) the mass of powder. It could be seen clearly from this formula that the milling intensity is enhanced with the increasing of M_B, V_{max} and f, but inversely proportional to M_p.

There is not yet a concrete definition of the milling intensity of Simoloyer. Nevertheless, according to various experiments it is known that the milling intensity is directly proportional to velocity of the ball and the mass of the ball. Furthermore it is connected with the ratio of ball/powder. Therefore the milling intensity could be described:

$$I = f(k, m, V, P) \tag{4}$$

k is a experimental coefficient, m the mass of the ball, V the velocity of the balls and P the ratio of ball/powder.

The process of high energy milling of Simoloyer is realized by increasing the velocity of rotor, which leads to a much higher velocity of the milling balls than drummill and the vibrating frame grinder [4]. As the velocity of the milling balls is a important factor, it was determined that a minimum velocity of 8 m/s is needed in order to reach a highly energetic ball collision[6]. A much higher velocity of the collision (up to 14 m/s) can be achieved by the Simoloyer. Additionally, the total-energy-supply must be approximately 0.55 kW per liter volume of the milling device and this value is linear up to the scaled industrial device.

5 Powder characterization

5.1 Microscopic studies

The milled powder was characterized by scanning electron microscope with a *CamScan CS2-9*. Figure 11 shows two example SEM-photos of as-milled Ag-SnO_2 composite after 5 and 30 min milling time. The observed powder has a size distribution from 100 to 300 µm. Increasing the milling time the powder size becomes homogeneous and fine. Further investigation of the microstructure of as-milled powder was carried out by means of transmission electron microscope by a *Hitachi H-8100*. A very fine dispersive distributed SnO_2 in a Ag matrix with a grain size of about 25 nm was observed (see Figure 12a). Figure 12b indicates the two crystalline phases of the powder components by a TEM diffraction micrograph. By means of a JCPDS-data base using the Miller indication the radius and location of the dark dots can be related to Ag and SnO_2 after 45 min milling time by 100 °C. This indicates a complete implementation of the chemical reaction from starting powder

Ag_3Sn-Ag_2O to final powder Ag-SnO_2 and a satisfied mechanical alloying of the two phases Ag and SnO_2.

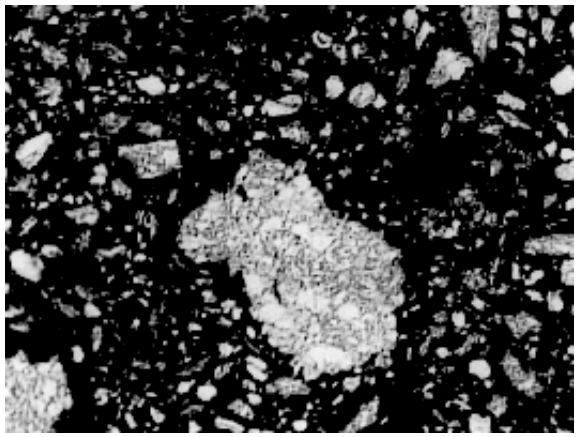


Fig. 11a: as-milled powder after 5 min in air (SEM micrograph)

Fig. 11b: as-milled powder after 30 min in air (SEM micrograph)

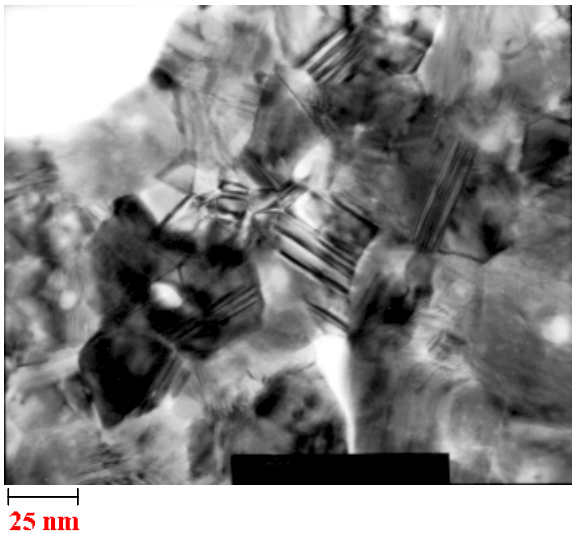


Fig. 12: TEM micrograph of SnO_2 grains in silver matrix after 45 min in air

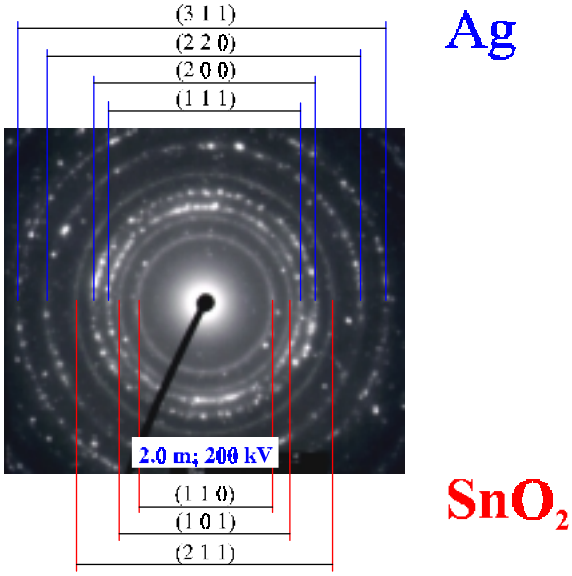


Fig. 12b: TEM electron diffraction patterns of silver and tin oxide after 45 min in air

5.2 X-ray analysis (XRD)

Several measured XRD patterns of the as-milled powder after different milling time by the use of Simoloyer are represented in Figures 13 and 14.

It can be seen that after a short time (5 min) the diffraction peaks of silver oxide and silver tin decrease and they disappear at 20-25 min. Pure silver peaks were perfected after 40 min. By comparison between both pattern groups of 60 °C and 100 °C it could observed that a clearer silver patterns after 25 min could be achieved by the experiments by 100 °C than that by 60 °C. This indicated that the reaction by 100 °C is quicker than that by 60 °C because a increasing of the temperature favored the kinetic of chemical reaction.

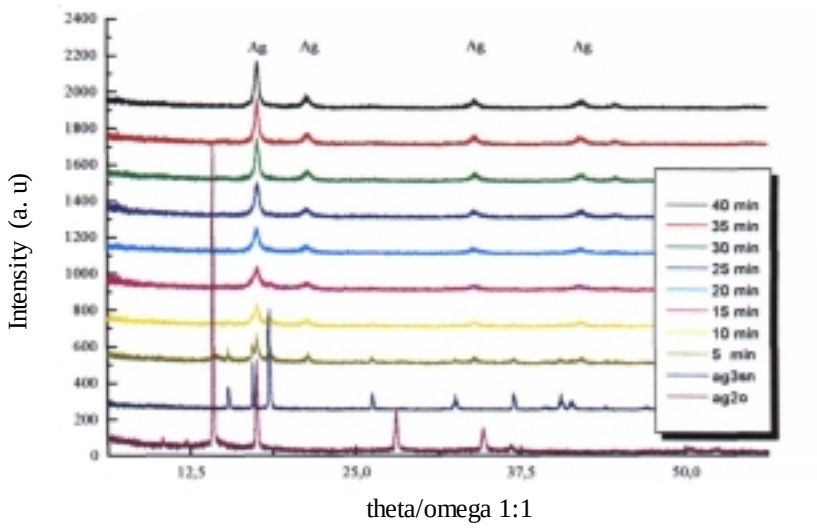


Fig. 13: X-ray diffraction patterns of starting and as-milled powder by using of Simoloyer at 60 °C in air

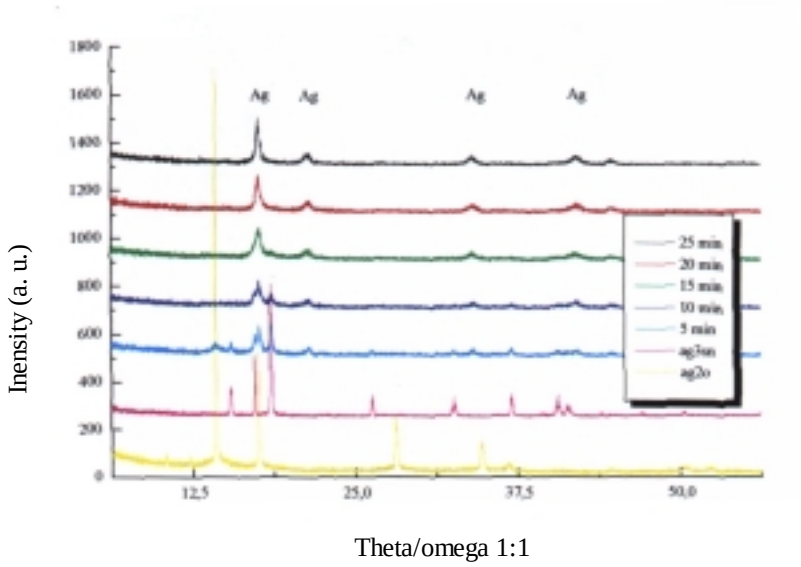


Fig. 14: X-ray diffraction patterns of starting and as-milled powder by using of Simoloyer at 100 °C in air

5.3 Hardness

The hardness of the Ag-SnO_2 composite was measured and showed in Figure 15. The hardness increases with the increasing of milling time within 35 min.

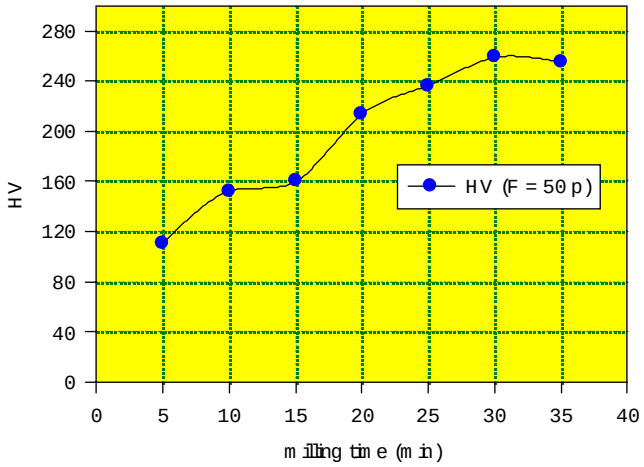


Figure 15: Hardness of as-milled Ag-SnO_2 composite

5.4 Chemical analysis

Chemical analysis of the Ag-SnO_2 composite was carried out by means of energy dispersive analysis (EDX). Very low contents of Fe and Cr , both < 0,3 wt % , were detected after 45 min milling time. Shorting the milling time to 30 min the contents of Fe and Cr could be reduced to about 0.1 wt %. It indicates that the contamination of powder is very low.

6 Conclusions

- High energy ball mill, the Simoloyer, offers a very high efficiency for the reactive milling.
- Mechanical alloying leads to a fine dispersion of the tin oxide phase in the silver matrix.
- The temperature is the significantest factor to influence the milling time. By 100 °C the milling process could be finished within 35 min.
- The influence of both atmosphere, air or argon, on the milling process is slight.
- The contamination of the final powder Ag-SnO_2 is reduced by shorting the milling time.
- Drummill is not suitable for the RM, because the milling efficiency is too low.
- Further investigations on the energetic balance during the process should be carried out for a better understanding of milling mechanisms.

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