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Production of Ag−ZnO powders by hot mechanochemical processing

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Abstract: Ag–CdO composites are still one of the most commonly used electrical contact materials in low-voltage applications owing to their excellent electrical and mechanical properties. Nevertheless, considering the restriction on using Cd due to its toxicity, it is necessary to find alternative materials that can replace these composites. In this study, the synthesis of Ag−ZnO alloys from Ag−Zn solid solutions was investigated by hot mechanochemical processing. The hot mechanochemical processing was conducted in a modified attritor mill at 138 °C under flowing O_2 at 1200 cm^3/min for 3.0 h. The microstructure and phase evolution were investigated using X-ray diffractometry, field emission gun scanning electron microscopy and transmission electron microscopy. The results suggest that it is possible to complete the oxidation of Ag−Zn solid solution by hot mechanochemical processing at a low temperature and short time. This novel synthesis route can produce Ag−ZnO composites with a homogeneous distribution of nanoscale ZnO precipitates, which is impossible to achieve using the conventional material processing methods. Considering the fact that the fundamental approach to improving electric contact material performance resides in obtaining uniform dispersion of the second-phase in the Ag matrix, this new processing route could open the possibility for Ag−ZnO composites to replace non-environmentally friendly Ag−CdO.

Key words: Ag−ZnO; nanocomposite; electrical contact material; powder synthesis; milling

1 Introduction

Ag−CdO composites are still one of the most used electrical contact materials in low-voltage applications [1]. These composites are characterized by high electrical and thermal conductivities and high resistance to arc erosion and welding [2]. Ag−CdO composites are principally obtained by internal oxidation of Ag−Cd cast alloys. Consequently, the homogeneous distribution of fine CdO precipitates in the Ag matrix is obtained [3].

Given the toxic nature of Cd and its compounds [4], the use of this element is expected to be minimized in the near future. In this context, Directive 2011/65/EU of the European Parliament (RoHS 2011/65/EU) has restricted the use of Cd in electrical and electronic equipment. However, the use of this element in electrical contact components has not been eliminated because no viable substitute for Ag−CdO composites has been developed.

In recent years, Ag−ZnO composites have attracted much attention as contact materials to replace Ag−CdO materials. However, when these composites are manufactured using internal oxidation processes, an oxide film is formed on their surface. Consequently, the internal oxidation of Zn is incomplete [5].

It has been reported that the electrical contact performance of Ag−ZnO composites is related to the uniformity of oxide dispersion in the Ag matrix [6]. Thus, Ag−ZnO composites produced by the internal

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oxidation cannot attain the high-grade functional properties of Ag−CdO composites.

To overcome the above problem, alternative processes have been reported. TALIJAN et al [7,8] studied the production of Ag–ZnO electrical contact material by a conventional powder metallurgy route using Ag and ZnO powders. They obtained a microscale distribution of ZnO in the Ag matrix. In this synthesis route, the dispersion scale of ZnO depends on the initial particle sizes of Ag and ZnO and their tendencies to agglomerate. WU et al [9] proposed a method to prepare Ag−ZnO electrical contact material by gas atomization internal oxidation forging technology (AIOF technology). They reported that the ZnO distribution obtained by this technique was not uniform. The microstructure was composed of a fine ZnO distributed inside the grains and large-sized ZnO precipitates at the grain boundary. Nevertheless, the microstructure of Ag−ZnO material prepared by AIOF technology is more homogeneous than that produced by casting and an internal oxidation route. YI et al [10] studied the effect of ball-milling pretreatment on the internal oxidation of Ag−Zn powders. They concluded that ball milling improved the dispersion of micrometric-sized ZnO precipitates during the internal oxidation process. GAVRILIU et al [11] and WEI et al [12] reported the synthesis of Ag−ZnO by a sequence of chemical precipitation and powder metallurgy techniques. GAVRILIU et al [11] used a Ag−ZnO powder mixture prepared through a wet way by Ag precipitation from an aqueous solution which contained a suspension of ZnO particles. On the other hand, WEI et al [12] used precipitates of Ag and ZnO obtained separately. Finally, IVANOV et al [13] and JAZI et al [14] studied the production of the Ag−ZnO alloy by a co-precipitation method. In this synthesis route, the Ag−ZnO powders are obtained by a sequence of chemical precipitation and heat-treatment processes. The results obtained indicate that by means of this method it is possible to produce nanoscale ZnO with a homogeneous distribution.

Mechanochemistry is the branch of chemistry that is concerned with the chemical and physicochemical transformations of substances in all states of aggregation owing to mechanical energy [15]. Mechanochemistry emerges as a highly promising and simple method to obtain materials which are very complicated to synthesize by other routes [16−18]. In this context, BALÁŽ et al [19] have published a review on recent developments in mechanochemistry, which provides a comprehensive overview of the advances achieved in this field, including both theoretical and practical aspects.

Generally, mechanochemical processes are performed at room temperature. There are very few reports on the synthesis of materials by mechanochemical processing at elevated temperatures. MILLET et al [20] firstly investigated the effect of temperature on the mechanochemical synthesis. They obtained a gallium nitride compound by hot milling of gallium under dry ammonia atmosphere in a modified uniball-mill. Recently, HUMPHRY−BAKER et al [21] studied the synthesis of Bi_2Te_3 between room temperature and 273 °C in a modified ball-drop reactor. They found that the activation energy of the reaction decreases when the temperature is increased, reducing the processing time significantly.

In a previous study, we reported that it is possible to obtain Ag−ZnO composites with uniform distribution of fine ZnO by conventional mechanochemical processing after 25 h [22]. Although these results are auspicious, it is necessary to reduce the processing time to make the Ag−ZnO composites a real alternative to commercial Ag−CdO composites. Therefore, the objective of this work was to study the production of an Ag−ZnO composite by hot mechanochemical processing.

2 Experimental

Three α-Ag−Zn solid solutions with nominal compositions of 5 at.%, 10 at.%, and 15 at.% Zn (3.1 wt.%, 6.3 wt.%, and 9.7 wt.% Zn), were produced by mechanical alloying of Ag (Sigma Aldrich, 99.9% purity, particle size >250 μm) and Zn (Merck, 99.9% purity, particle size between 590 and 149 μm ASTM) turnings in a SPEX 8000D mill. The millings were performed under Ar atmosphere (AGA Chile, 99.998% purity) for 3.0 h with a ball-to-powder mass ratio of 20:1. In order to prevent agglomeration during the process, stearic acid (0.040 g) was added. For further details about the Ag−Zn solid solution production, see reference [23].

The mechanically alloyed powders were hot-milled in a modified attritor (Fig. 1) for 0.5, 1.0, 1.5, 2.0 and 3.0 h at 138 °C under an oxygen flow of 1200 cm^3/min. The internal temperature was measured before and after

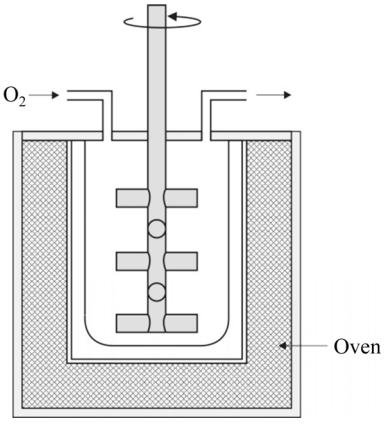

Fig. 1 Schematic diagram of modified attritor mill

each experiment. The mill was filled with 14 g of powder and 1400 g of balls. The rotation speed of the impeller was maintained at 400 r/min. An attritor mill was selected owing to its high processing capacity, which enables the hot mechanochemical process to potentially be scaled to the industrial level.

The evolution of the phases during hot mechanochemical processing was investigated by X-ray diffraction (XRD) using a Shimadzu XRD−6000 diffractometer with Cu K_α radiation. The α-Ag−Zn solid solution lattice parameter was obtained from Rietveld refinement of the X-ray diffraction data [24]. The crystallite size was calculated by means of the Scherrer equation [25]. The morphology of the powders was observed using a Zeiss EVO MA 10 thermionic scanning electron microscope (SEM), while its microstructure was examined by field emission gun scanning electron microscopy (FEGSEM) in a Zeiss Sigma 500 equipment and by transmission electron microscopy (TEM) using a FEI Tecnai F20 ST microscope. A schematic process flow chart is shown in Fig. 2.

3 Results and discussion

Figure 3 shows the powder XRD patterns of Ag−15at.%Zn after 0, 0.5, 1.0, 1.5, 2.0 and 3.0 h of hot

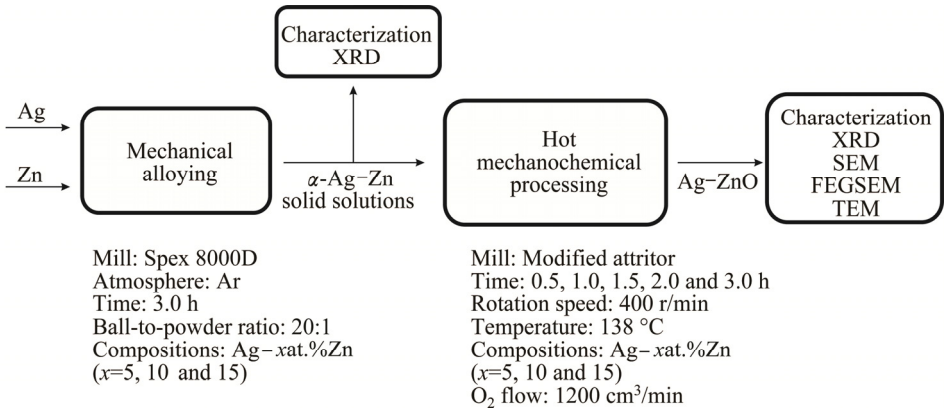

Fig. 2 Schematic process flow chart for synthesis of Ag−ZnO powders by hot mechanochemical processing

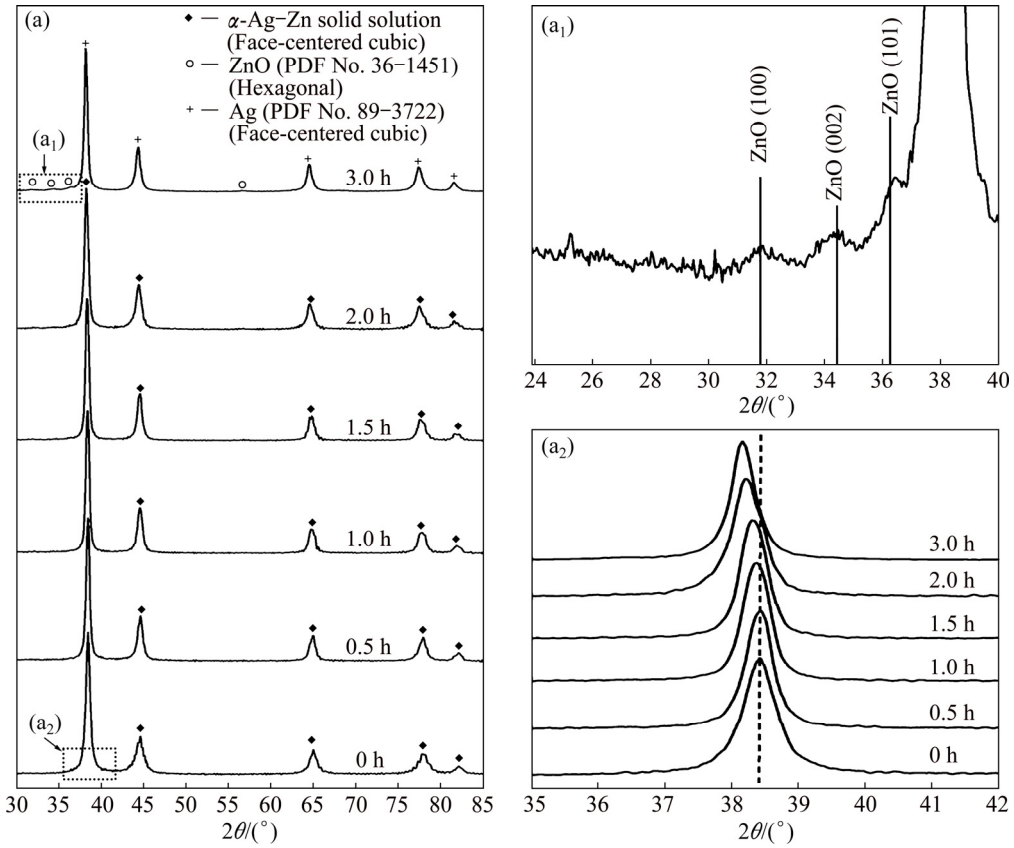

Fig. 3 XRD patterns of powders with nominal composition (Ag−15at.%Zn) after 0, 0.5, 1.0, 1.5, 2.0 and 3.0 h of hot mechanochemical processing and magnified zones of selected areas

mechanochemical processing. To compare the XRD patterns, they were normalized with respect to the maximum intensity. It is possible to detect the diffraction of ZnO after 3.0 h of hot mechanochemical treatment. Additionally, it is observed that the peaks of the α-Ag−Zn solid solution gradually shifted towards lower 2θ angles. This is related to the lattice parameter increase of the α-Ag−Zn solid solution owing to the loss of Zn because of oxidation during the hot mechanochemical processing. The increase in the lattice parameter continued until it reached a value close to the lattice parameter of Ag (Fig. 4). This behavior was reported by our group during the mechanochemical processing of α-Ag−Zn solid solution under air and with ethanol as the reaction agent [22]. It is important to note that the three samples in this study exhibited a similar behavior, after the hot mechanochemical processing it was only possible to detect the diffraction of ZnO and Ag (Fig. 5).

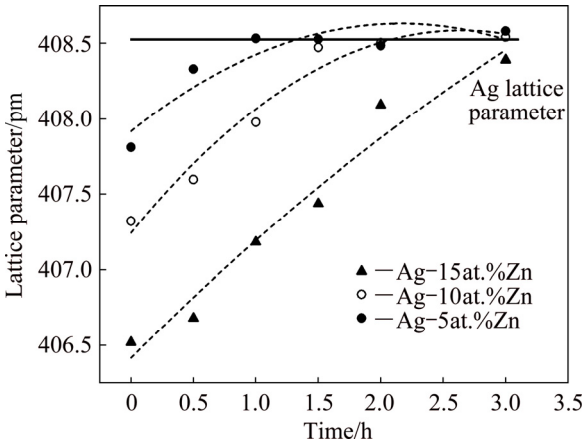

Fig. 4 Lattice parameters of α-Ag–Zn solid solution as function of hot mechanochemical processing time

Figure 6 shows the evolution of apparent crystallite size of α-Ag−Zn solid solutions during the hot mechanochemical processing. The apparent crystallite size increases for the samples Ag−5at.%Zn and Ag−10at.%Zn, and does not change significantly for the sample Ag−15at.%Zn. The increase in the apparent crystallite size can be understood considering that during the hot mechanochemical processing the Zn content of the α-Ag–Zn solid solutions decreases. The loss of Zn added to the accumulated energy during the milling produces a decrease in the activation energy for the recrystallization. The decrease in the activation energy, in addition to the local heating generated by the impact between the balls and the material produces dynamic recrystallization [26,27]. This effect is relevant if we consider that the recrystallization temperature of commercially pure Ag (99.99%) is between 100 and 200 °C [28,29]. Thus, the dynamic recrystallization is more evident in samples with less Zn contents, because

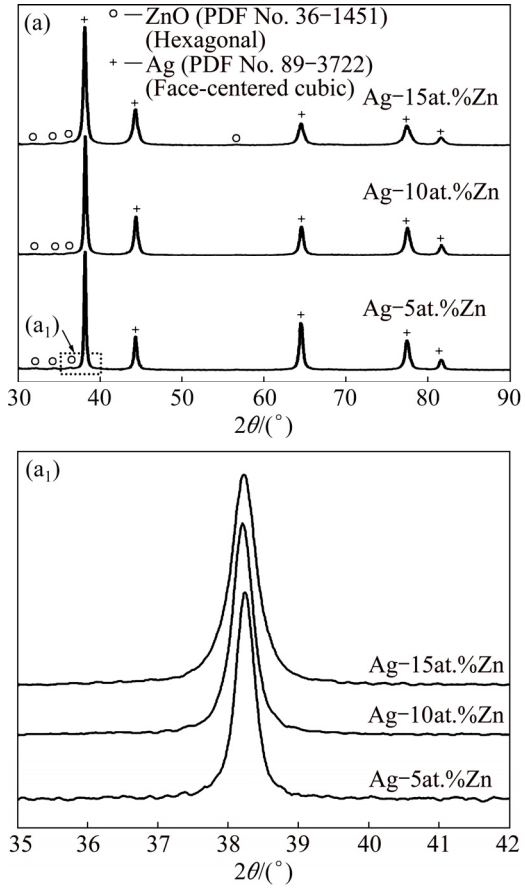

Fig. 5 XRD patterns of powders with nominal composition Ag−*x*at.%Zn (*x*=5, 10 and 15) after 3.0 h of hot mechanochemical processing and magnified zone of selected area

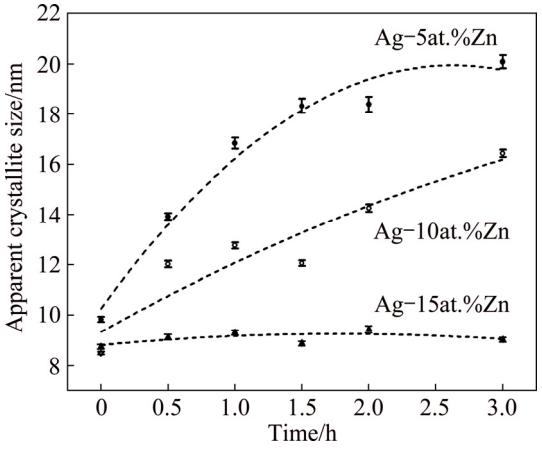

Fig. 6 Apparent crystallite size as function of hot mechanochemical processing time

in these samples the complete oxidation of Zn is reached in a short milling time.

Additionally, in the samples with a higher Zn content, the ZnO precipitates produced during hot milling probably have a pinning effect on grain boundary movement during the recrystallization process [30]. It is important to note that milling time above 3.0 h was

initially employed, but due to dynamic recrystallization of Ag during the hot-milling procedure and its subsequent softening, a large amount of powders were stuck onto the surfaces of the milling chamber and the balls. This behavior was more pronounced in the samples with less Zn content.

Figure 7 shows the morphologies of the Ag−*x* at.% Zn (*x*=5, 10 and 15) samples before and after 3.0 h of hot mechanochemical processing. It can be seen that Ag−5at.%Zn sample after hot milling is formed by flat and irregular agglomerates in comparison with Ag−10at.%Zn and Ag−15at.%Zn samples, which are formed by roughly spherical agglomerates. In relation to the size distribution, the average size of the agglomerates decreases from (85.9±9.7) to (28.4±2.5) μm when the Zn content in the alloy increases from 5 at.% to 15 at.%. The above observations can be explained considering the fact that during the hot mechanochemical processing the dynamic recrystallization of the samples with less Zn contents is verified. This recrystallization produces an increase in the ductility of the powders, which promotes the generation of flat, irregular and large agglomerates due to the plastic deformation and welding of the particles. On the contrary, because the samples with higher Zn contents do not experience dynamic recrystallization during the hot mechanochemical processing, these powders have a brittle behavior, which promotes the fracture events and the subsequent reduction of agglomerate size.

The quantity of ZnO produced during the hot mechanochemical processing was calculated indirectly by using an equation previously proposed by our group in Ref. [31],

$$x\text{at.\% Zn}=(732.91\pm7.47)-(42867.25\pm297.94)\Omega \quad (1)$$

which relates the atomic volume of the α-Ag−Zn solid solution Ω, nm^3, with its Zn concentration (at.% Zn) with a prediction error less than 12%. This equation was obtained as a result of a statistical fit between the composition and the atomic volume of α-Ag−Zn solid solutions for compositions between 3.87 at.% Zn and 17.56 at.% Zn [31]. The atomic volume (Ω) of a metal or solid solution alloy is defined as the mean volume per atom. It is calculated by dividing the volume of the unit cell by the number of atoms in the cell.

The obtained results are shown in Fig. 8. The initial rate of the ZnO oxidation is very similar to the three compositions in this study (Ag−5at.%Zn: (3.08±0.72) wt.% ZnO/h; Ag−10at.%Zn: (3.17±0.72) wt.% ZnO/h; Ag−15at.%Zn: (3.26±0.35) wt.% ZnO/h). To explain this, it is necessary to conduct a complete kinetic study of the process, which is beyond the scope of this work.

As evident from Table 1, the experimental ZnO contents after the hot mechanochemical processing are similar to the theoretically predicted values considering the total Zn oxidation. The above results suggest that it is possible to complete the α-Ag−Zn oxidation by hot mechanochemical processing at a lower temperature

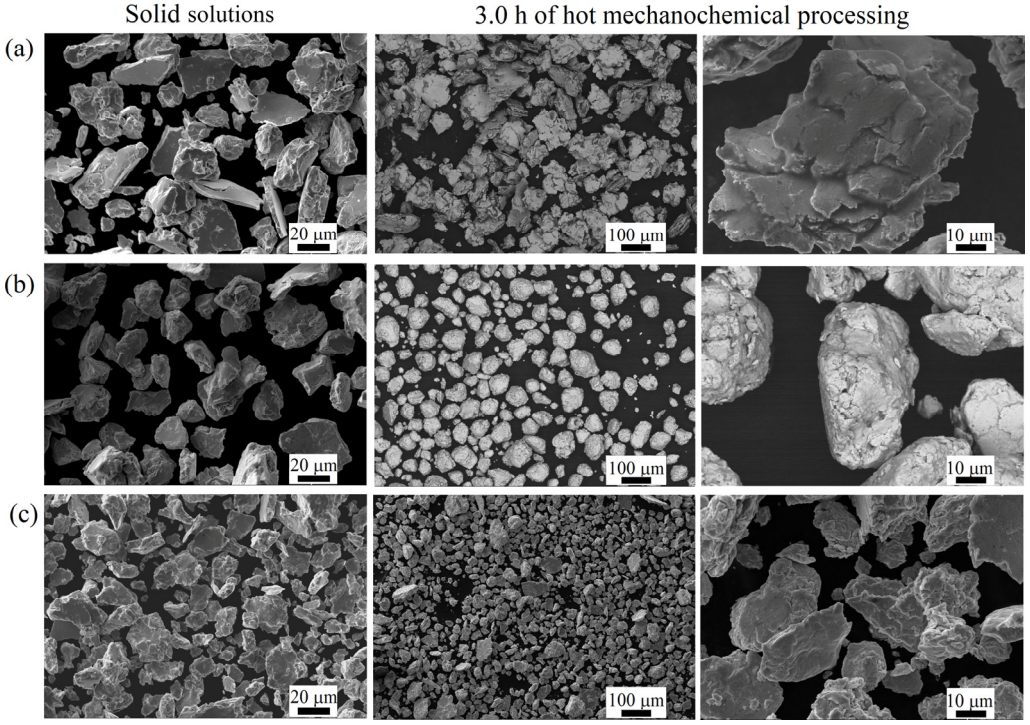

Fig. 7 SEM micrographs of Ag−5at.%Zn (a), Ag−10at.%Zn (b) and Ag−15at.%Zn (c) samples before and after 3.0 h of hot mechanochemical processing

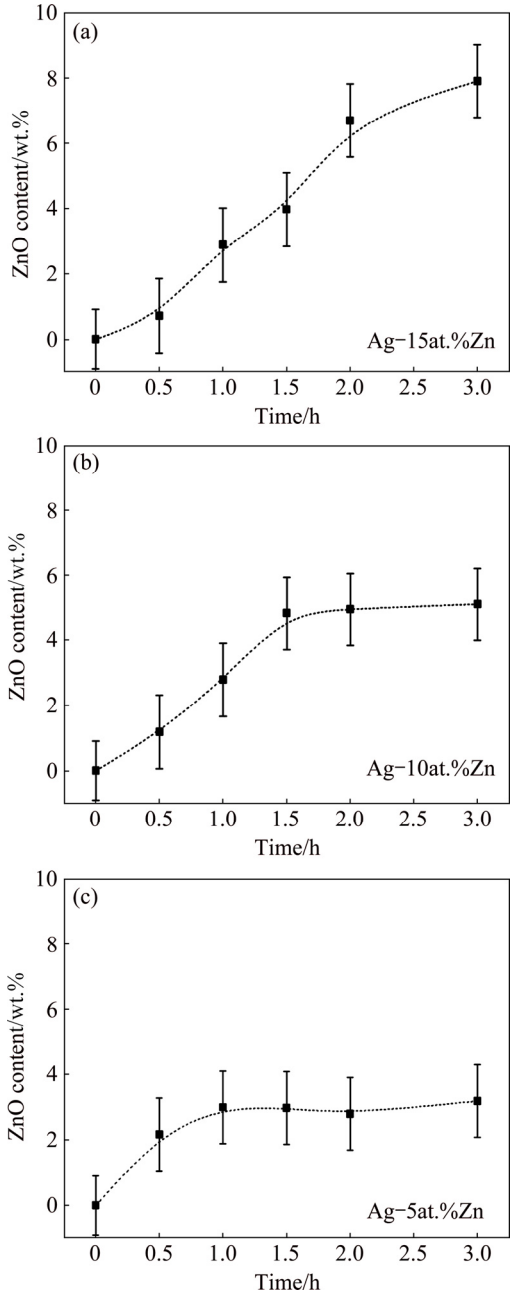

Fig. 8 ZnO content as function of hot mechanochemical processing time

Table 1 Theoretical and experimental ZnO compositions after hot mechanochemical processing

Initial Zn content/at.%		Final ZnO content/wt.%	
Nominal	Calculated	Theoretical	Experimental
15	12.95±2.45	8.41±1.88	7.91±1.11
10	8.68±2.44	4.93±1.86	4.95±1.11
5	6.07±2.42	2.85±1.84	3.00±1.11

(130 °C) in comparison with the internal oxidation route (600−860 [9], 650 °C [10], 800 °C [32]) and in a shorter time (3.0 h) compared with the conventional mechano-chemical process (25 h [22] and 8 h [6]).

To determine the size and distribution of the ZnO precipitates, a powder sample with a nominal composition Ag−15at.%Zn after 3.0 h of hot mechano-chemical processing was metallographically prepared and observed by FEGSEM using backscattered electron. Figure 9 reveals that nanoscale ZnO precipitates (dark grey points) are uniformly distributed in the Ag matrix (light grey zone).

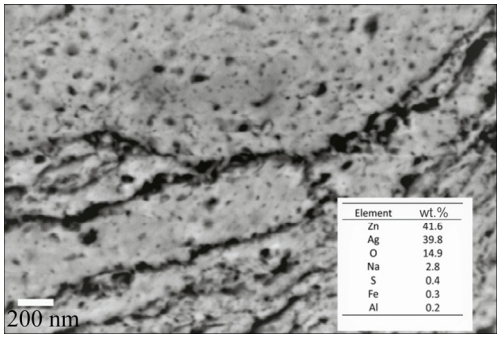

Fig. 9 FEGSEM micrograph of metallographically prepared sample of Ag−15at.%Zn powders after 3 h of hot mechano-chemical processing (The table lists the average of eight EDS analyses carried out to determine the composition of the dark grey points)

Figure 10 shows TEM analysis results of the powders after hot mechanochemical processing. The selected area electron diffraction (SAED) pattern (Fig. 10(a)) shows the presence of ZnO, which confirms the powder XRD results. Figures 10(b−d) shows the bright and dark images obtained using ZnO reflections in two different sectors. It can be seen that the powder microstructure consists of nanoscale ZnO precipitates embedded in the Ag matrix. The occurrence of this microstructure can be explained principally considering two factors: (1) the high density of the crystalline defects generated during milling, which act as preferential sites for ZnO nucleation and (2) the fracturing and cold welding of the powder particles during the hot mechannochemical processing which improve the ZnO dispersion. Because the electrical performance of the Ag−ZnO composites depends on the distribution and size of the oxide phase, it is expected that the obtained microstructure will improve the electrical contact properties of the Ag−ZnO composites. Figure 10(e) shows the EDS (energy-dispersive X-ray spectroscopy) analysis results for the powders with a nominal composition of Ag−15at.%Zn after 3.0 h of hot mechanochemical processing. The Cu and C in the EDS spectrum were originated from the TEM grid support. If all oxygen detected (1.90 wt.%) is assumed to be combined with the Zn to form ZnO, the calculated ZnO content in the powders reaches 7.68 wt.%. This value is similar to that previously calculated using Eq. (1) (Table 1).

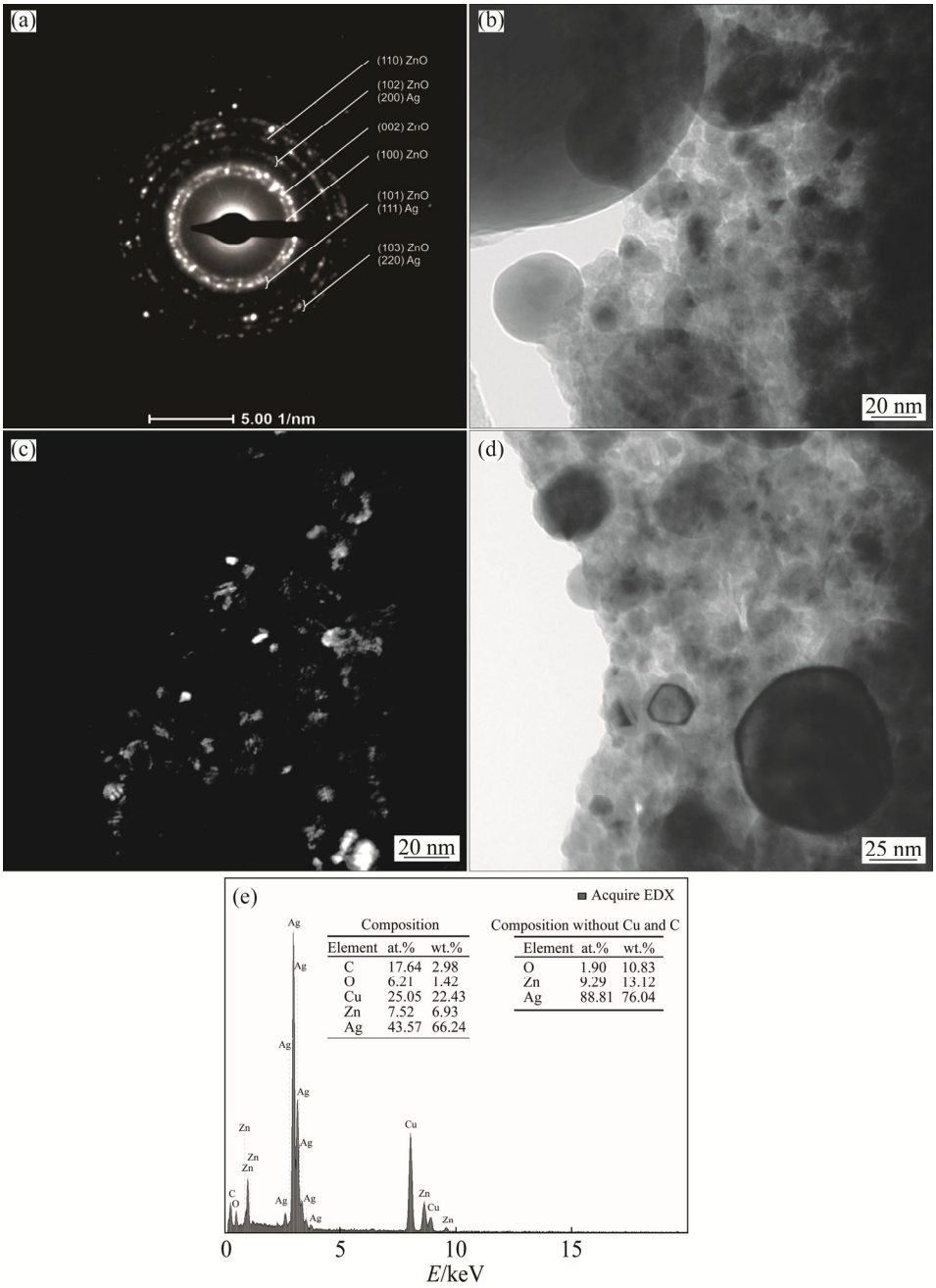

Fig. 10 Selected area electron diffraction pattern of powders with nominal composition Ag−15at.%Zn after 3.0 h of hot mechanochemical processing (a), bright and dark images obtained using (100) ZnO reflections in two different sectors (b−d) and EDS spectrum of powders and corresponding elemental analysis results (e)

In comparison to the synthesis methods reported in literatures, the ZnO distribution produced by hot mechanochemical processing is finer and more homogeneous than those obtained by powder metallurgy [7,8], AIOF technology [9], or chemical precipitation processes [11,12], while comparable to the co-precipitation method [13,14].

4 Conclusions

Hot mechanochemical processing of Ag−x at.% Zn (x=5, 10 and 15) solid solution powders has been investigated. XRD analyses showed that it is possible to complete the Zn oxidation at a low temperature and a short time in comparison with the conventional methods. During the hot mechanochemical processing, the dynamic recrystallization of the samples with less Zn contents was observed. The final morphology of the hot milled powders changed from large and flat to small and spherical agglomerates with increasing Zn content in the initial solid solution. This fact was attributed to the greater plasticity of the samples with less Zn content due

to the effect of dynamic recrystallization. TEM analyses of the processed powders showed the presence of nanoscale ZnO precipitates uniformly distributed in the Ag matrix. Based on the above results it can be concluded that Ag−ZnO composites with a uniform distribution of nanoscale ZnO precipitates can be obtained by applying hot mechanochemical processing. This new processing route could open the possibility for Ag−ZnO composites to replace the non-environmentally friendly Ag−CdO composites used in low-voltage electrical contact materials.

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热机械化学法制备 Ag−ZnO 粉末

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摘　要：Ag−CdO 复合材料由于其优异的电气和力学性能，仍然是低压应用中最常用的电触头材料之一。然而，考虑到由于镉的毒性而对其应用的限制，有必要寻找可取代这种复合材料的替代材料。本研究以 Ag−Zn 固溶体为原料，采用热机械化学工艺制备 Ag−ZnO 合金。在 138 °C、1200 cm^3/min 的氧气流下，在改进的球磨机中对合金样品进行热机械化学处理 3 h，利用 X 射线衍射技术、场发射扫描电镜和透射电镜对合成材料的显微组织和相演变进行研究。结果表明，低温下的热机械化学处理可使 Ag−Zn 固溶体在短时间内完全氧化。这种新的合成方法可以制备出纳米 ZnO 相均匀分布的 Ag−ZnO 复合材料，而这是用传统的材料加工方法无法实现的。考虑到改善电触头材料性能的根本途径在于实现 Ag 基体中第二相的均匀分散，这一新工艺为 Ag−ZnO 复合材料取代非环境友好的 Ag−CdO 提供了可能。

关键词：Ag−ZnO；纳米复合材料；电触头材料；粉末合成；球磨

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