Research Article

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Effects of NiO content on the microstructure and mechanical properties of AgSnO$_2$NiO composites

Abstract: The AgSnO$_2$NiO composites were prepared by internal oxidation method. The effects of different NiO content on the microstructure and mechanical properties of AgSnO$_2$NiO composites were studied. The phase structure and surface morphology of the prepared AgSnO$_2$NiO materials were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Metallographic Microscopy (MM). The results showed that the AgSnO$_2$NiO composites with different NiO content can be obtained by the process of preoxidation of AgSn alloy powder and internal oxidation of ingot containing Ni. The agglomeration phenomenon of Ni in the silver matrix was serious, which led to the agglomeration of in-situ generated NiO particles after internal oxidation. After the multi-pass drawing, the SnO$_2$ particles dispersedly distributed in the AgSnO$_2$NiO composites and the NiO particles gradually dispersed from the agglomerated state of the sintered ingot billet. The hardness of the prepared AgSnO$_2$NiO composites increased slightly with the increase of NiO content. The mechanical properties test showed that the introduction of NiO particles significantly improved the tensile strength and elongation of AgSnO$_2$ materials to a certain degree. Adding proper amount of NiO is beneficial to improve the overall performance of AgSnO$_2$ materials.

Keywords: Internal oxidation; AgSnO$_2$NiO composites; Microstructure and mechanical properties

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1 Introduction

Silver-metal oxide (AgMeO) electrical contact materials is widely used in the industrial production of control switches, relays, connectors and switch breakers for household appliances that are common in daily life [1–3]. Among them, Silver-cadmium oxide (AgCdO), which is known as "universal electrical contact material", has been firmly occupying the commanding height of the electrical contact material market for decades because of its low and stable contact resistance, small amounts of arc erosion and excellent resistance to welding [4, 5]. However, the Cd element in AgCdO is highly toxic, causing great pollution to the human body and the environment. Silver-tin oxide (AgSnO$_2$) is considered to be one of the most promising new environmentally friendly electrical contact materials to substitute AgCdO [6–8]. AgSnO$_2$ has the advantages of excellent anti-welding properties, arc erosion resistance and good resistance to mechanical wear, but it also has its shortcomings. The wettability between Ag and SnO$_2$ is poor and SnO$_2$ is a semiconductor. Under the multiple actions of the arc, the SnO$_2$ particles with lower density will be concentrated on the surface of the molten Ag, resulting in increased contact resistance and large temperature rise, which greatly reduces the electrical performance of the material [9, 10]. Moreover, the low interfacial bonding strength between the harder SnO$_2$ and the softer Ag leads to the poor plasticity and ductility of the AgSnO$_2$ electrical contact materials, and therefore, it is relatively difficult to processing and forming [11, 12].

Up to now, the preparation methods of AgSnO$_2$ electrical contact materials mainly include Internal Oxidation (I/O) and Powder Metallurgy (P/M) [13]. The particles produced by I/O are fine and distributed uniformly, while the materials produced by P/M have agglomeration phenomenon, the particle size is larger , and the distribution is uneven. Compared with the powder metallurgy method,

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Table 1: The amounts of raw materials to prepare 200g AgSnO$_2$NiO ingot

Preparation method	Sample number	Ingot billet (wt%)	Ag powder(g)	AgSn alloy powder(g)	Ni powder(g)
Internal oxidation and high-temperature sintering	1$^\#$ sample	AgSnO$_2$(5)NiO(0.5)	143.51	53.367	0.786
	2$^\#$ sample	AgSnO$_2$(5)NiO(1.0)	142.51	53.367	1.572
	3$^\#$ sample	AgSnO$_2$(5)NiO(1.5)	141.51	53.367	2.358
	4$^\#$ sample	AgSnO$_2$(5)NiO(2.0)	140.51	53.367	3.144

the AgSnO2 electrical contact material produced by the internal oxidation method has better processability and arc erosion resistance [14, 15]. Furthermore, the addition of different metal oxides such as CuO, In$_2$O$_3$, etc., and oxides of rare earth elements (La$_2$O$_3$, CeO$_2$, etc.) can effectively improve the wettability between Ag and SnO$_2$, thereby reducing the contact resistance and temperature rise during arcing [16–19]. Wang J *et al.* [20] found that CuO-doped AgSnO$_2$ material has denser microstructure, higher hardness, and better arc erosion resistance than AgSnO$_2$ materials. The arc erosion test indicated that the introduction of CuO can significantly inhibit the spatter loss of molten Ag during the welding process. Chen J *et al.* [21] studied the molten bridge phenomenon of the AgSnO$_2$In2O$_3$ electrical contact material and found that In$_2$O$_3$ can restrain the transfer of Ag, which plays a protective role for the material. Zhang L *et al.* [22] used powder metallurgy method to prepare AgSnO$_2$La$_2$O$_3$ electrical contact materials with excellent resistance to welding. The results showed that La$_2$O$_3$ can increase the viscosity of melt pool to and improve the wettability between Ag and SnO$_2$. However, there has been no report about the addition of NiO to AgSnO$_2$ composites. Interestingly, the AgNi electrical contact material has a lower contact resistance than AgSnO$_2$, but its mechanical strength and anti-welding performance are far inferior to AgSnO$_2$ [23, 24].

In order to combine the advantages of both AgSnO$_2$ and AgNi electrical contact materials and to obtain a uniform microstructure of fine particles, AgSnO$_2$NiO composites were prepared by internal oxidation combined with high temperature sintering. NiO particles were formed in situ on the surface of the Ag matrix during the sintering process. In this paper, the effects of NiO content on the microstructure and mechanical properties of AgSnO$_2$NiO composites were studied. The result can provide a useful reference for the compound modification method between different silver-metal oxide electrical contact materials.

2 Experimental procedures

2.1 Raw materials and composition proportion

The raw materials used in this experiment and the requirement of purity and particle size are as follows: Ag powder (purity ≥ 99.99%, particle size of 40-50 μm), Ni powder (purity ≥ 99.5%, particle size of 40-50 μm), AgSn alloy powder (purity ≥ 99.99%, particle size of 40-50 μm). The required raw materials and amounts were given in Table 1.

2.2 Preparation of AgSnO$_2$NiO composites

2.2.1 Pre-oxidation treatment of AgSn alloy powder

The AgSn alloy powder was tiled on corundum. The pre-oxidation temperature was gradually raised from room temperature to 373 K for 1 h, 473 K for 1 h, 673K for 2 h, and 1073 K for 4 h.

2.2.2 Internal oxidation of ingot billet containing Ni and processing of AgSnO$_2$NiO composites

First of all, the Ag, AgSnO$_2$ and Ni powders were put into a planetary ball mill (QM-ISP2) for ball milling and mixing at 1000 rad/min for 5 h. Then, the uniformly mixed alloy powder was placed in a cold press mold and pressed into an alloy biscuit under the pressure of 20 MPa for 2 min. The obtained biscuit with a diameter of 27 mm was placed in a box furnace and sintered in an oxygen-containing atmosphere. The sintering process was similar to pre-oxidation treatment. Maintain a sufficiently long sintering time, so that Ni was completely oxidized to obtain in-situ NiO particles. The prepared AgSnO$_2$NiO composites were repressed under the pressure of 50 MPa for 5 min and re-sintered at 1093 K. Finally, the wire was obtained by extrusion and drawing.

2.3 Characterization

The phase structure of the prepared AgSnO$_2$NiO composites was analyzed by a Bruker D8 advanced X-ray Diffraction (XRD). The surface morphology, element distributions and fracture morphology of the AgSnO$_2$NiO composites were characterized by a Tescan VEGA-3SBH tungsten filament Scanning Electron Microscope (SEM) coupled with Energy Dispersion Spectrometer (EDS). The microstructures of AgSnO$_2$NiO ingot billets and wires were observed and investigated by a ZEISS Scope.A1 Metallographic Microscope (MM). The hardness at different processing stage was tested on a MC010 series microhardness tester under the load of 50 g for 15 s. Hardness value was the average of the measured values at the 5 test points of the sample. After the drawn wire was annealed, a tensile test was performed using an AG-IS type 10KN universal testing machine at a tensile speed of 0.5 mm/min to obtain tensile strength and elongation results.

3 Results and discussion

3.1 Effects of NiO content on the microstructure of AgSnO$_2$NiO composites

Figure 1 shows the XRD pattern of the AgSnO$_2$NiO composites with NiO content of 2% prepared by internal oxidation. It can be seen that only Ag, SnO$_2$ and NiO phases were contained in the composite after internal oxidation, indicating that the AgSnO$_2$NiO composite can be successfully prepared by the internal oxidation method.
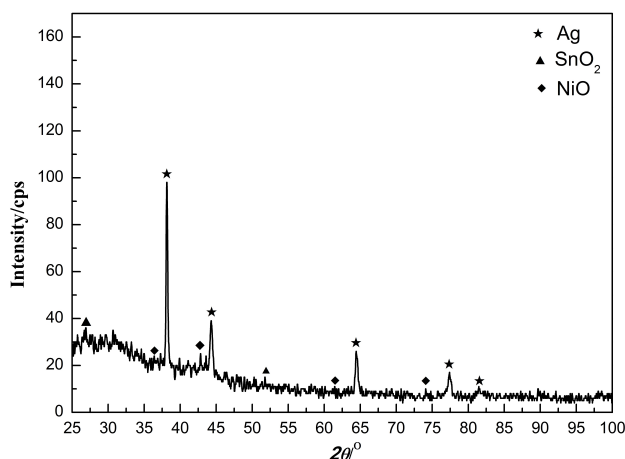

Figure 1: XRD pattern of AgSnO$_2$NiO composites with NiO content of 2%

Figure 2 shows the surface morphology of the AgSnO$_2$NiO composites with NiO content of 2% and the corresponding energy spectrum analysis of region A, B, C and D. It can be seen that agglomeration of NiO particles occurred in the prepared composites. Figure 2b shows the morphology of the four marked regions more intuitively. The energy spectrum analysis of region A and B showed that there were a small amount of Ag and SnO$_2$ among NiO particles. It is noteworthy that only SnO$_2$ and NiO exist in region D, indicating that the black material in the wrapping layer outside the agglomerated NiO is SnO$_2$.

Figure 3 shows the metallographic structure of the AgSnO$_2$NiO biscuit and the sintered ingot billet after internal oxidation with NiO content of 2%. There was a clear difference between the biscuit and the sintered ingot billet in area A. The area A in Figure 3a was a light gray round spot (pure Ni powder particles), while it was dark gray and there was a circle of black structure around it (a mixture of SnO$_2$ and NiO particles) in Figure 3b. The result indicated that the internal oxidation of Ni generated NiO through high-temperature sintering. Comparing Figure 3a with Figure 3b, it was shown that the agglomerated Ni in the biscuit hardly diffused during the internal-oxidation sintering, and the NiO was basically generated in-situ, which is caused by the immiscibility of Ag and Ni. Therefore, with the increase of Ni content, the agglomeration of Ni in the silver matrix will be more serious, eventually leading to serious agglomeration of NiO particles after internal oxidation, and the size of NiO particles generated is larger. In addition, the areas B in Figure 3a and Figure 3b were both ring structures in which SnO$_2$ particles surround the Ag matrix. It can be deduced that the Sn diffused to the surface of AgSn particle and reacted with oxygen to generate SnO$_2$ particles during the pre-oxidation of the AgSn alloy powder.
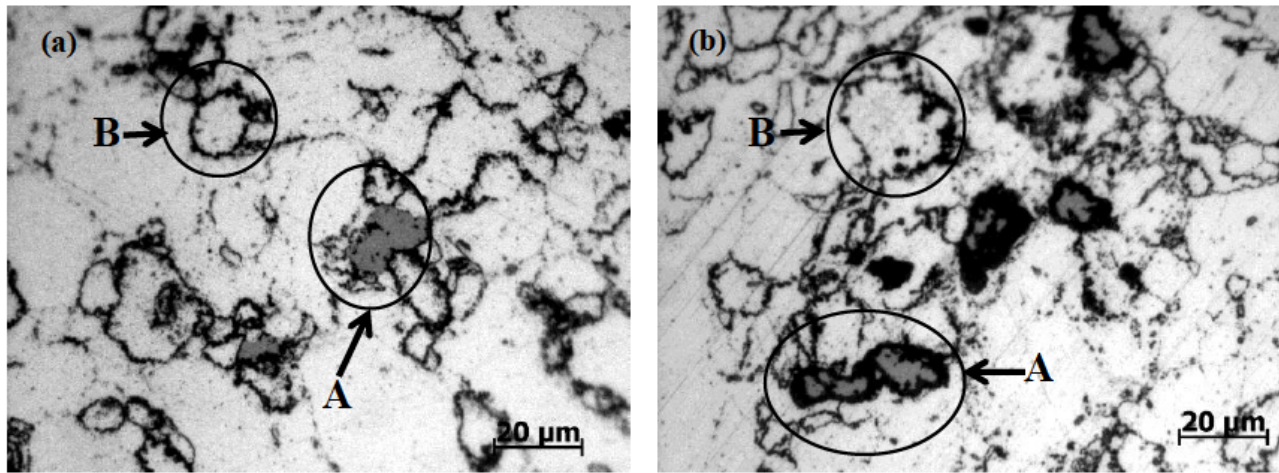
Figure 4 shows the horizontal microstructure metallography diagram of the wire after extrusion and drawing of the AgSnO$_2$NiO composites with NiO content of 2%. It was found that the smaller SnO$_2$ particles dispersedly distributed in Ag matrix and the larger NiO particles were present in the Ag matrix mainly in the state of particle agglomeration. With the increase of plastic deformation, it was not obvious that the agglomerated NiO particles were completely dispersed.

Figure 5 shows the vertical microstructure metallographic diagram of the wire after extrusion and drawing of AgSnO$_2$NiO composites with NiO content of 2%. It was known that dark grey and larger agglomerates in the area A was NiO particles, and the area B are linearly-arranged SnO$_2$ particles which are gradually dispersed along the extrusion and drawing directions, as is shown in Figure 5a,
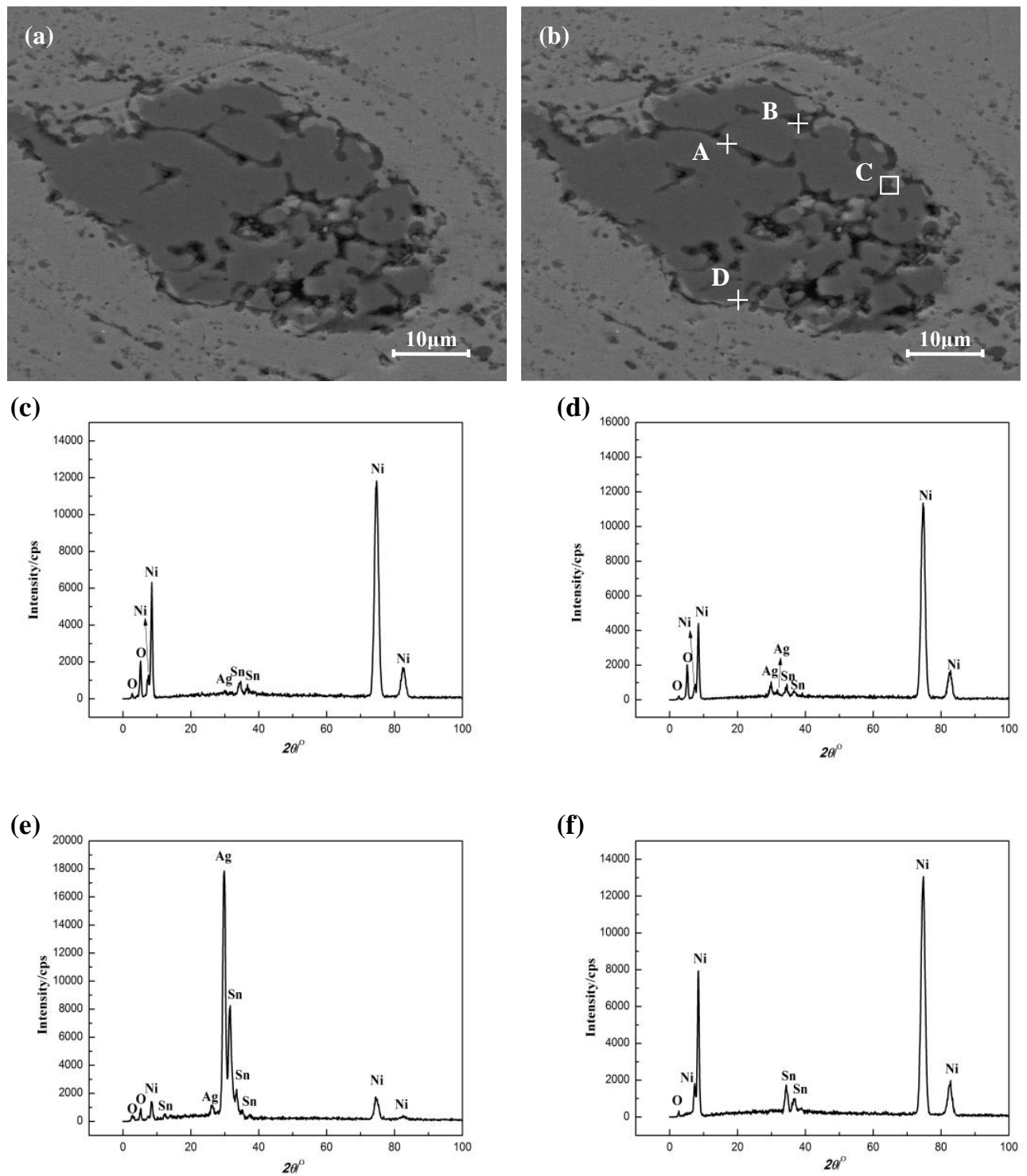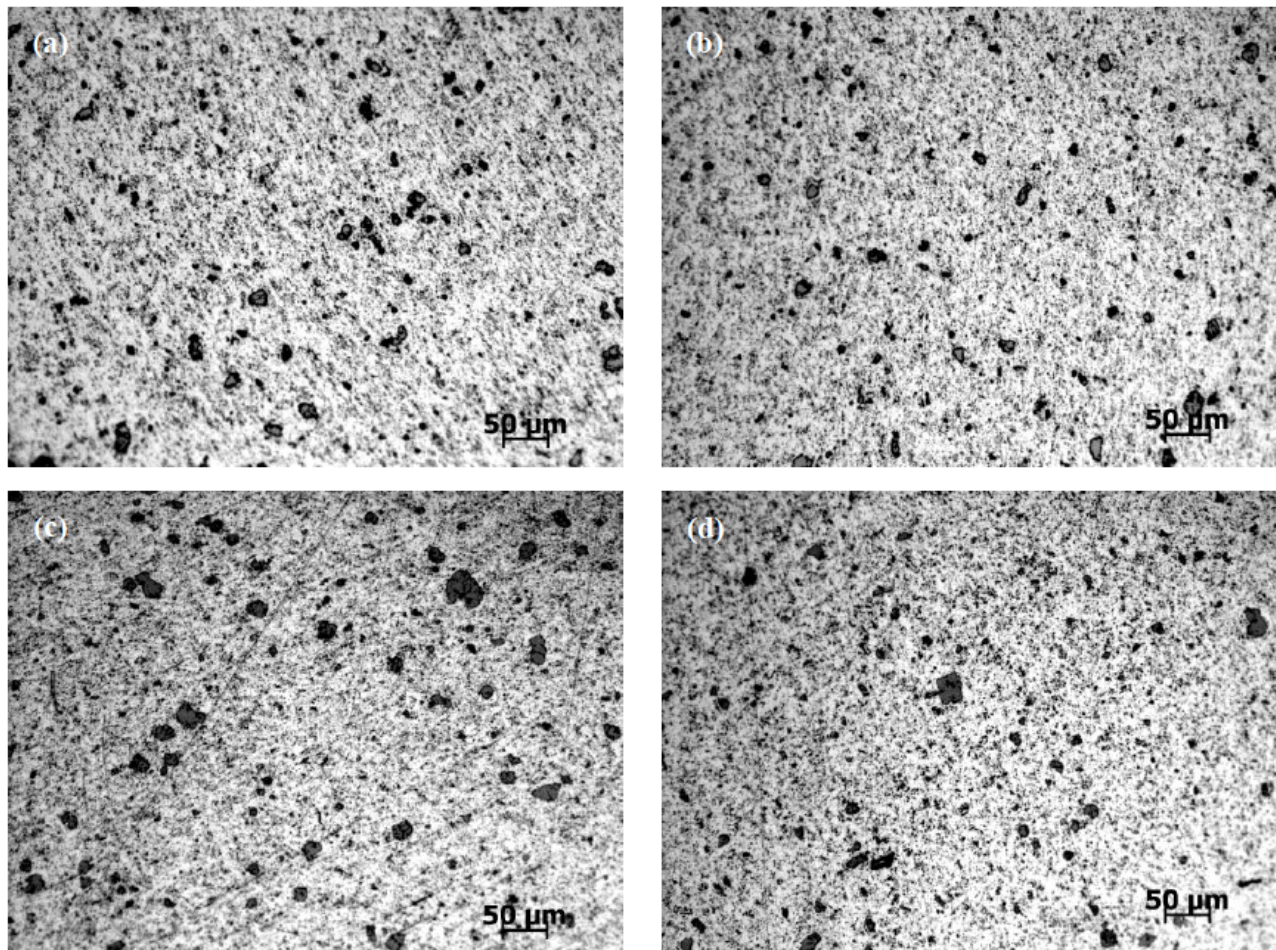
Figure 2: Surface morphology of the AgSnO$_2$NiO composites and corresponding energy spectra: (c) region A; (d) region B; (e) region C; (f) region D;
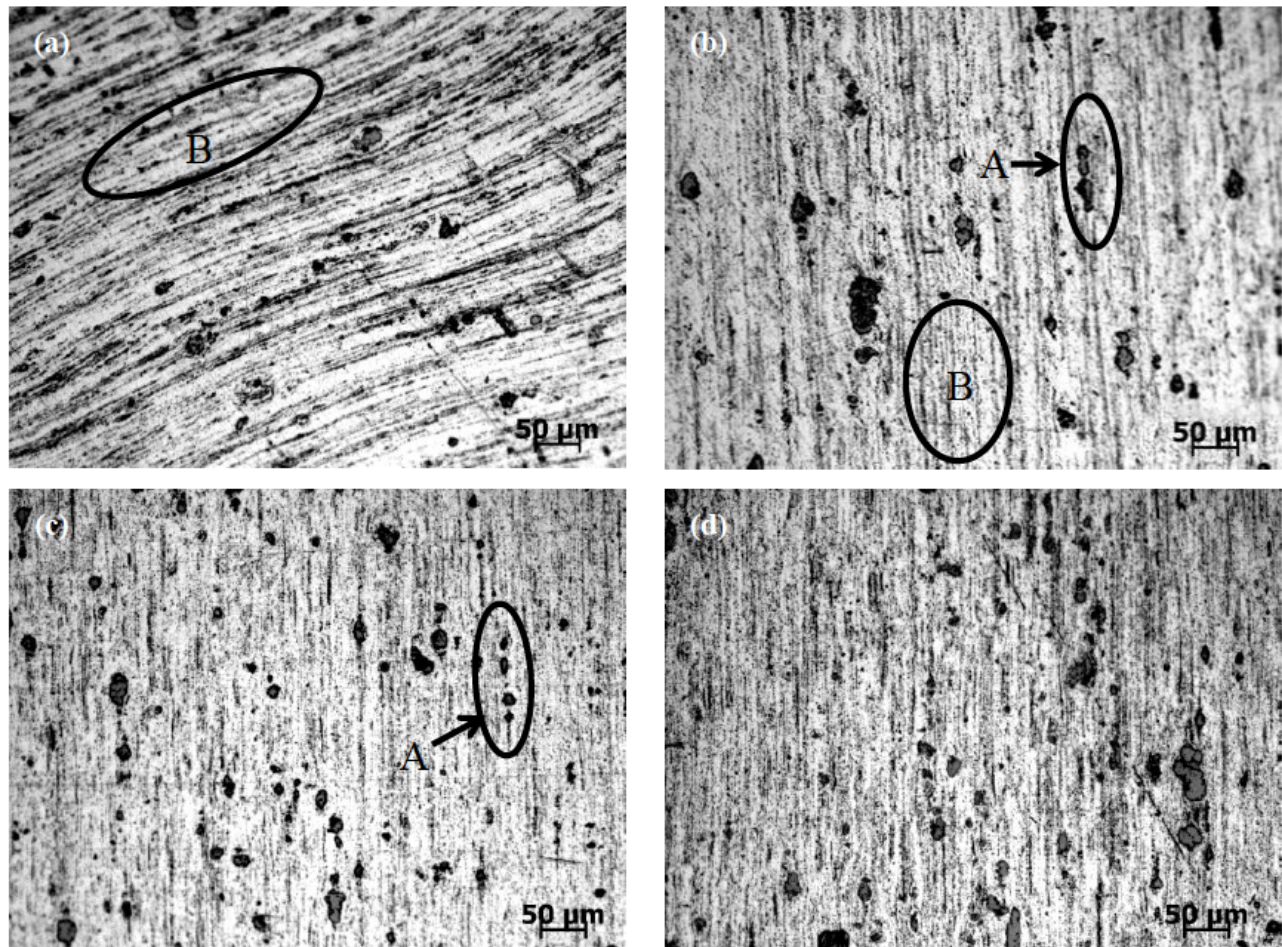
Figure 3: Microstructure of AgSnO$_2$NiO ingot billet × 500; (a) biscuit; (b) sintered ingot billet;

Figure 4: Horizontal microstructure metallography of AgSnO$_2$NiO after extrusion and drawing × 200 (a) extrusion rod diameter of 6.0 mm; (b) wire drawing diameter of 5.2 mm; (c) wire drawing diameter of 3.4 mm; (d) wire drawing diameter of 1.5 mm

Figure 5: Vertical microstructure metallography of AgSnO$_2$NiO after extrusion and drawing × 200 (a) extrusion rod diameter of 6.0 mm (b) wire drawing diameter of 5.2 mm (c) wire drawing diameter of 3.4 mm (d) wire drawing diameter of 1.5 mm

b and c. With the increase of drawing passes, the distribution of SnO$_2$ particles became more uniform, as shown in Figure 5d, and the NiO particles were partially dispersed, as shown in areas A in Figure 5b and c. On the whole, since the size of NiO particles was much larger than that of SnO$_2$ particles, it is difficult to be completely dispersed, resulting in its uneven distribution in the Ag matrix.

Figure 6 shows the fracture surface of the wire (diameter of 1.3 mm) after extrusion and drawing. It can be seen that dimples of different sizes were formed in the fracture center of the four kinds of AgSnO$_2$NiO wires, and there is no obvious large granular structure in the dimples, indicating that the agglomerated NiO particles were gradually dispersed during the plastic deformation process. Moreover, it also indicates that the fracture mode of the samples was ductile fracture, which means that the prepared composites have good processing properties.

3.2 Effects of NiO content on the mechanical properties of AgSnO$_2$NiO composites

Figure 7 shows the change trends of the microhardness of the AgSnO$_2$NiO composites during the processing. It can be seen that the microhardness values of AgSnO$_2$NiO drawn wire were all higher than 105 HV and the NiO content has little effect on the microhardness. When the AgSnO$_2$NiO composites with NiO content of 2% was drawn into a wire with a diameter of 1.5mm, the microhardness reached a maximum of 125.03 HV. The reason is that the SnO$_2$ particles are completely dispersed, and the agglomerated NiO particles are partially dispersed, which together play a dispersion strengthening role.

Figure 8 shows the change trends of elongation and tensile strength when the AgSnO$_2$NiO composites with different NiO content were drawn into a wire with a diameter of 1.30 mm. It can be seen that the NiO content has no significant effect on the tensile strength of AgSnO$_2$NiO (main-
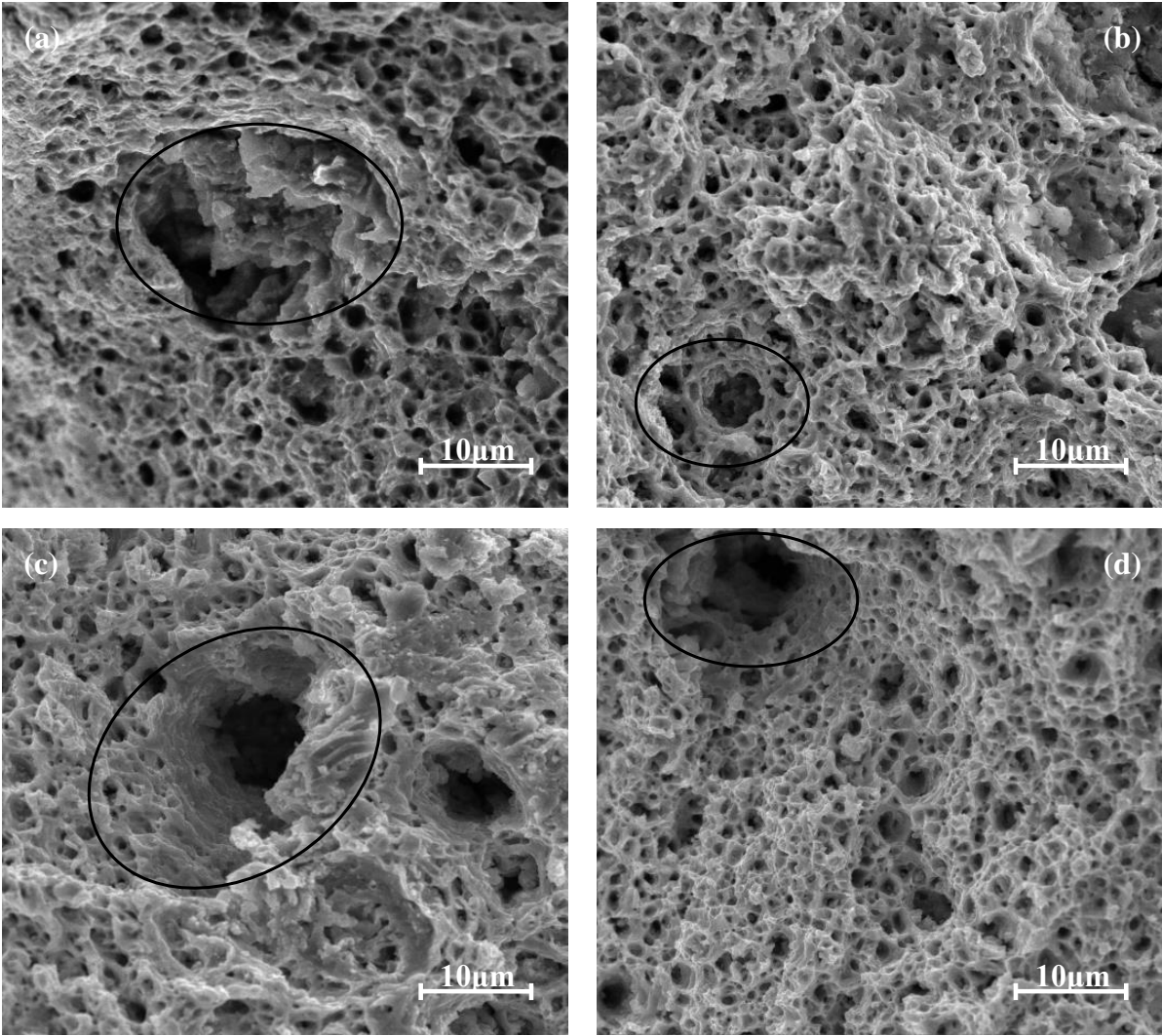
Figure 6: Fracture morphology of AgSnO$_2$NiO after extrusion and drawing × 5000 (a) 1[#] sample AgSnO$_2$(5)NiO(0.5); (b) 2[#] sample AgSnO$_2$(5)NiO(1.0); (c) 3[#] sample AgSnO$_2$(5)NiO(1.5); (d) 4[#] sample AgSnO$_2$(5)NiO(2.0)
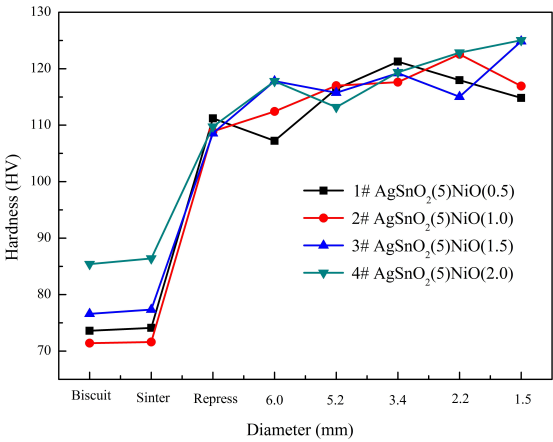
Figure 7: Change trends of microhardness after processing
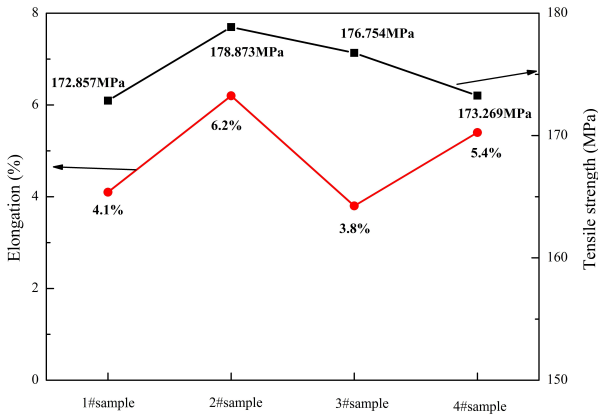
Figure 8: The chart of AgSnO$_2$NiO samples' elongation and tensile strength

tained at about 175 MPa), but it has a significant effect on the elongation.When the content of NiO was 1%, the tensile strength of the wire is the highest (178.873MPa), and the elongation r is also the best (6.2%).

4 Conclusions

(1) The microstructure characteristics of $AgSnO_2NiO$ composites prepared by internal oxidation method were as follows: SnO_2 distributed in an annular shape around the Ag matrix, and the NiO was in agglomerated distribution. The agglomeration of NiO is related to the agglomeration of Ni before internal oxidation.

(2) After extrusion and multi-pass drawing process, the oxide particles dispersedly distributed in the Ag matrix. The SnO_2 particles are linearly arranged in the Ag matrix in a like-fibrous shape along the extrusion and drawing direction. However, with the increase of plastic deformation, agglomerated NiO particles can be partially dispersed. But it is difficult to completely disperse the NiO particles.

(3) NiO content has no significant effect on the tensile strength of $AgSnO_2NiO$ composites, but it has an important influence on the elongation. When the content of NiO was 1%, the tensile strength and elongation of the $AgSnO_2NiO$ composites reached a maximum of 178.873MPa and 6.2%.

(4) The preparation process has a significant effect on the microhardness of $AgSnO_2NiO$ composites. When the $AgSnO_2NiO$ composites with NiO content of 2% was drawn into a wire with a diameter of 1.5mm, the microhardness reached a maximum of 125.03 HV. The reason is that defects such as pits and holes inside the material gradually decreased with the process of repressing-resintering, drawing, and extrusion. In addition, with the increase of drawing passes, SnO_2 and NiO particles are gradually dispersed and uniformly distribute in the Ag matrix, which play a role in dispersion strengthening.

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