SOLID STATE REACTION DURING MECHANICAL ALLOYING AND HEATING OF MECHANICALLY ALLOYED NICKEL-TIN POWDERS

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Abstract

Ni-Sn intermetallic compounds (IMCs) can be formed during mechanical alloying of blended Ni and Sn powders. However, with mechanical alloying times of up to 25 hours, formation of the intermetallic compounds was not governed by the blended Ni and Sn powder compositions but influenced by Ni/Sn interfacial reactions. Heating of the Ni-Sn powders mechanically-alloyed for 25 hours resulted in formation of intermetallic compounds having compositions with respect to nominal blended Ni and Sn powders compositions. By adjusting heating temperatures, porous Ni-Sn intermetallic compounds could be obtained. In addition, electrical conductivity of the Ni-Sn intermetallic compounds increased with increasing heating temperature.

Keywords: porous Ni-Sn IMCs, solid state reaction, Ni/Sn interfacial reaction, electrical conductivity

Introduction

Mechanical alloying is one of various methods employed for producing Ni-Sn IMCs structures having lithium storage properties suitable for applications in lithium ion battery. Examples of Ni-Sn IMCs include nickel-rich Ni_3Sn IMC (Hou et al. 2008), the Ni_3Sn_2 IMC (Kim et al. 2003; Kosho et al. 2007) and Ni_3Sn_4 IMC (Lee et al. 2002; Amadei et al. 2005; Cheng and Shi 2005). Formation of porous Ni_3Sn IMC was previously reported to occur after heating of Ni-32.5 wt. % Sn powders mechanically alloyed for 25 hours (Tongsri and Tosangthum 2011). Employing only mechanical alloying to form Ni-Sn IMCs takes a long period (Amadei et al. 2005; Cheng and Shi 2005; Gerbaldi et al. 2008; Mulus et al. 2009). With a long period of mechanical alloying, production cost of Ni-Sn IMCs may be high. According to the previous work (Tongsri and Tosangthum 2011), the process consisting of short-term mechanical alloying followed by heating of the mechanically alloyed powders is possible to produce other Ni-Sn IMCs. In this works, Ni and Sn powder blends with nominal compositions with respect to Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 IMCs (predicted by the binary Ni-Sn phase diagram in Figure 1) were mechanically alloyed with an interrupted manner (the milling was stopped every hour for 10 minutes to allow cooling of the milled powders in the milling chambers) for accumulative milling times of up to 25 hours. IMC phase evolution during mechanical alloying and after heating of the mechanical alloyed powders was examined.

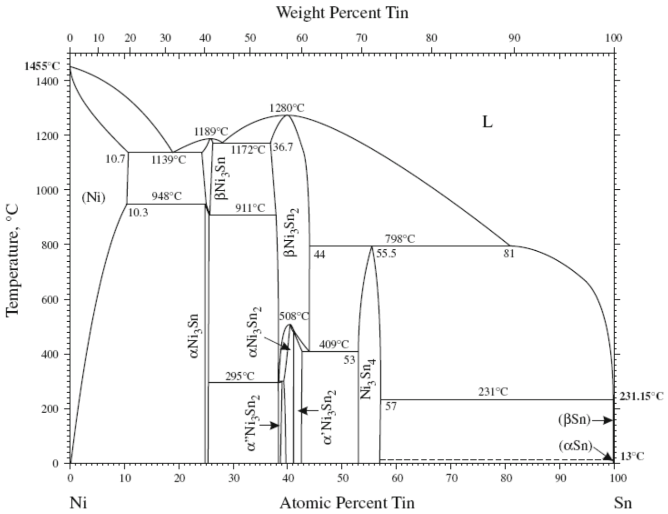


Figure 1 Binary Ni-Sn phase diagram (Okamoto 2008)

Methodology

Milling and characterization

Mechanical alloying was performed with blended elemental Ni and Sn powders with varied Sn powder contents, such as 41.0, 58.0 and 73.0 wt.%. The blended powders were mechanically alloyed in an attritor under milling conditions including ball to powder ratio (BPR) of 5:1 and milling speed of 300 rpm. Milling was conducted continuously for 1 hour and interrupted by stopping milling for 10 minutes for allowing the alloyed material to be cooled down. The mechanically alloyed powders with accumulated milling times of 5, 15 and 25 hours, were characterized by using X-ray diffraction (XRD) technique and scanning electron microscopy (SEM) equipped with backscatter electron (BSE) mode and energy dispersive X-ray spectroscopy (EDS).

Heating of the mechanically alloyed Ni-Sn powders

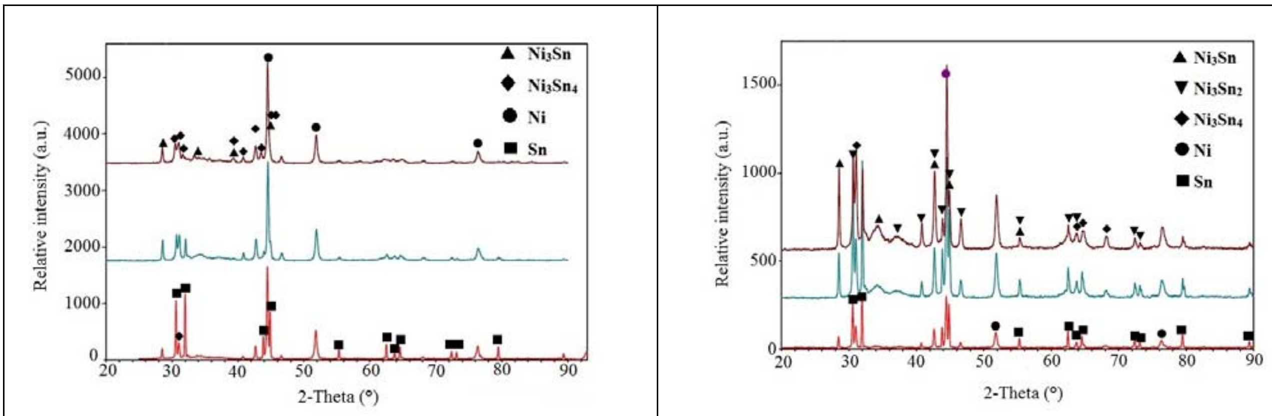
The mechanically alloyed Ni-Sn powders were heated under Ar atmosphere in a temperature range between 300-1200°C with holding time of 10 minutes. The heated materials were characterized by using XRD technique, SEM equipped with BSE. The heated Ni-Sn samples were prepared into a square shape having 1.5 x 1.5 mm dimensions for testing electrical conductivity using an electrical conductivity measuring instrument (SIGMATEST 2.069).

Results and Discussion

Mechanically alloyed powders.

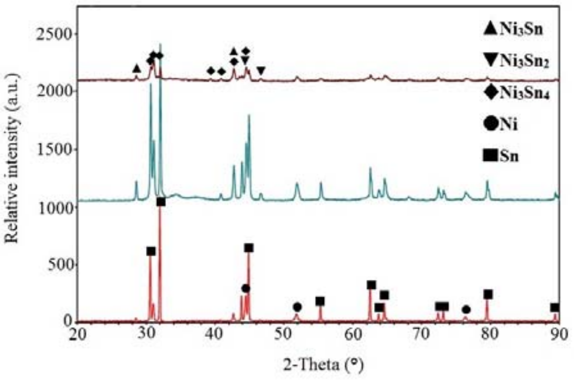
The mechanically alloyed Ni-Sn powders, with different milling times and different Sn contents, showed formation of Ni-Sn IMCs indicated by XRD patterns (Figure 2). The XRD peaks of the mechanical alloying of Ni-41.0 wt. % Sn powders revealed formation of Ni_3Sn, Ni_3Sn_4, Ni and Sn phases (Figure 2(a)). The mechanical alloyed Ni-58.0 wt. % Sn powders (Figure 2(b)) and Ni-73.0 wt. % Sn powders (Figure 2(c)) showed XRD patterns corresponding to Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4, Ni and Sn phases. XRD intensities of metal (Ni, Sn) phases decreased with increasing milling times whereas those of IMCs (Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4) increased with increasing milling times.

Decrease of Ni and Sn peak intensities may relate to diffusion of Sn atoms into Ni powder particle surfaces and followed by formation of interfacial IMCs. In mechanical alloying, dissolution of Sn atoms into Ni powder particle surfaces to form a Ni-Sn solid solution is possible whereas dissolution of Ni atoms into Sn powder particles is impossible. Although extension of terminal solid solubility and dissolution of immiscible metal systems can achieved by mechanical alloying (Suryanarayana 2001), dissolution of Ni into Sn cannot be achieved by mechanical alloying of Sn-rich Sn and Ni powder blends (Buarod et al. 2011). For the Ni-rich Ni-Sn alloy, extension of terminal solid solubility can be prepared by mechanochemical synthesis (Grigorieva et al. 1997).



(a) Ni-41 wt. % Sn

(b) Ni-58 wt. % Sn



(c) Ni-73 wt. % Sn

Figure 2 XRD patterns of the Ni-Sn powders mechanically alloyed for 5, 15 and 25 hours (from bottom to top)

The large volume fraction of grain boundaries presenting in the nanocrystalline state is expected to enhance the solid solubility in these materials. Diffusivity at grain boundary is enhanced by 1,000 times or even greater as the size of the crystalline reaching to a few nanometers (Schumacher et al. 1989). With a high energy milling, powder particle disintegration generates heat, which promotes formation of Ni-Sn IMCs. Because mechanical alloying with a short period of milling cannot dissolve all Sn atoms throughout the whole Ni powder particles, the reactions to form Ni-Sn IMCs occur only at Ni/Sn interfaces.

Figure 3 shows microstructures of the mechanically alloyed Ni-Sn materials milled for 25 hours. The images taken by using SEM equipped with BSE mode reveal that there are large gray areas, identified as Ni particles and fine gray areas, identified as particles of Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 IMCs embedded in lighter areas background, identified as Sn particles. EDS was carried out for chemical analysis of the mechanically alloyed Ni-Sn materials. The EDS results confirmed the existence of Ni, Ni-Sn IMCs and Sn phases as indicated by spectra 1, 2 and 3, respectively, as given in Figure 3(b), 3(d) and 3(f). Schematic diagram, representing microstructures of the mechanically alloyed Ni-Sn powders, is given in Figure 4. The diagram shows that formation of interfacial Ni-Sn IMCs occurs along Ni particle peripheries. Formation of Ni-Sn IMCs using a high energy ball mill was reported by (Lee et al. 2002; Amadei et al. 2005; Cheng and Shi 2005). Co-existence of the Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 was reported in the Ni-40 wt. % Sn, Ni-60 wt. % Sn and Ni-73 wt. % Sn materials continuously milled for 25 hours (Buarod et al. 2011).

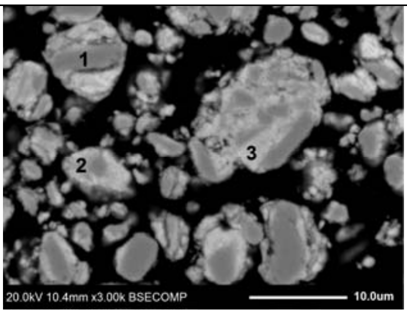
The formation of IMCs from two different element powders may be explained by using the mechanism of ball-powder-ball collision (Gilman and Benjamin 1983). In a system involving two different ductile components, the initial collision of metal powders causes flattening and work-hardening. Then they are cold welded and heavily deformed. The flattened powders are brought into intimate contact leading to formation of layered composite powder particles. With continued milling, the cold welding and deformation of layered particles result in refined microstructure. With increasing milling time, the lamellar spacing of the agglomerated particles is quickly reduced. Interfacial reactions take place at the clean or fresh surfaces of the intimate layers in the powder particles to form IMCs.

The formation of Ni-Sn IMCs by short period mechanical alloying cannot be totally predicted by the binary Ni-Sn phase diagram (Figure 1). In this experiment, it was found that nominal composition control is difficult to be achieved probably due to dominant Ni/Sn interfacial conditions. The reasons for formation of IMCs with compositions different from the nominal powder blend compositions include solid state reaction nature of mechanical alloying, slow diffusion of constituent atoms in solid state of materials and interfacial reaction.

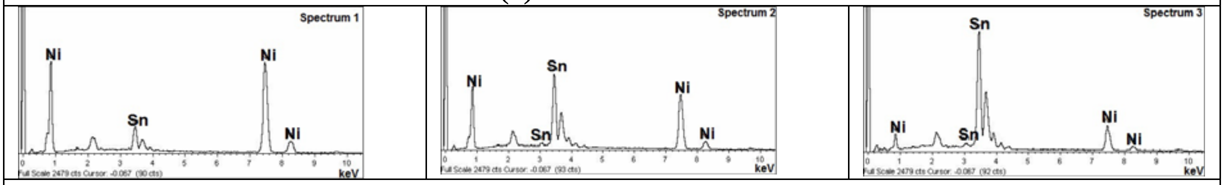
Heating of the milled Ni-Sn alloyed powders.

XRD patterns of the Ni-Sn materials, mechanically alloyed for 25 hours and heated at varied temperatures with a holding time of 10 minutes, are shown in Figure 5. In general, XRD peaks of Ni and Sn phases decreased whereas those of the IMCs increased with increasing temperatures. The XRD peaks show predominant Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 IMCs in the Ni-41 wt. % Sn, Ni-58 wt. % Sn and Ni-73 wt. % Sn materials mechanically alloyed for 25 hours and heated to high temperatures.

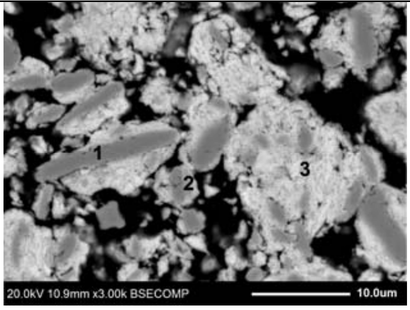
SEM images of the Ni-Sn materials mechanically alloyed for 25 hours and heated for 10 minutes at different temperatures are shown in Figure 6 with microstructural features were observed to vary with heating temperatures. In general, with increasing heating temperatures the IMCs are formed at the periphery of Ni powder particle and grow to its center (Figure 6 (b)). The gray coarse Ni particles gradually disappeared when the heating temperatures were increased. Increase of heating temperatures promoted formation of Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 IMCs according to the nominal powder blend compositions. This is attributed to the rapid diffusion of Sn atoms into Ni particles in a solid state. In addition to formation of Ni-Sn IMCs, with increasing temperatures bonding by sintering between powder particles was also observed. Sintered necks were observed to increase with increasing heating temperatures. With combination of heating temperature and time, porous Ni-Sn IMCs could be tailored.



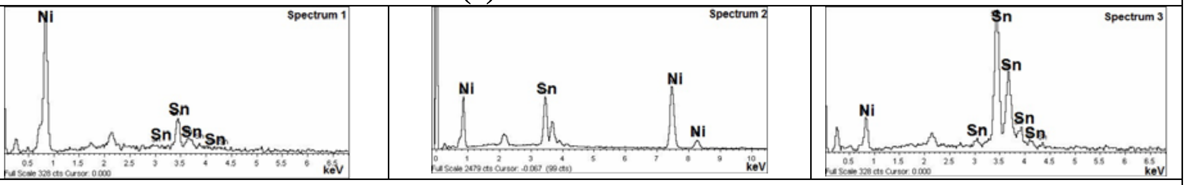
(a) Ni-41wt.% Sn



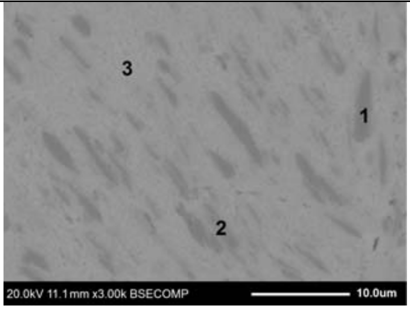
(b)



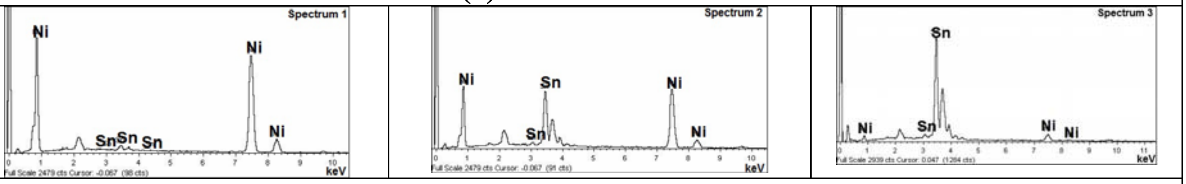
(c) Ni-58wt.% Sn



(d)



(e) Ni-73wt.% Sn



(f)

Figure 3 SEM images for the Ni-Sn powders mechanically alloyed for 25 hours (a, c and e) and EDS patterns of Ni-41wt.% Sn (b), Ni-58wt.% Sn (d) and Ni-73wt.% Sn (f)

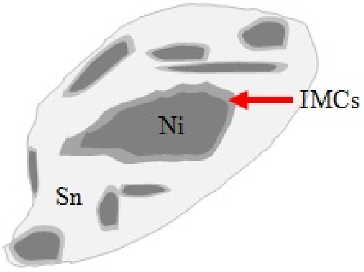
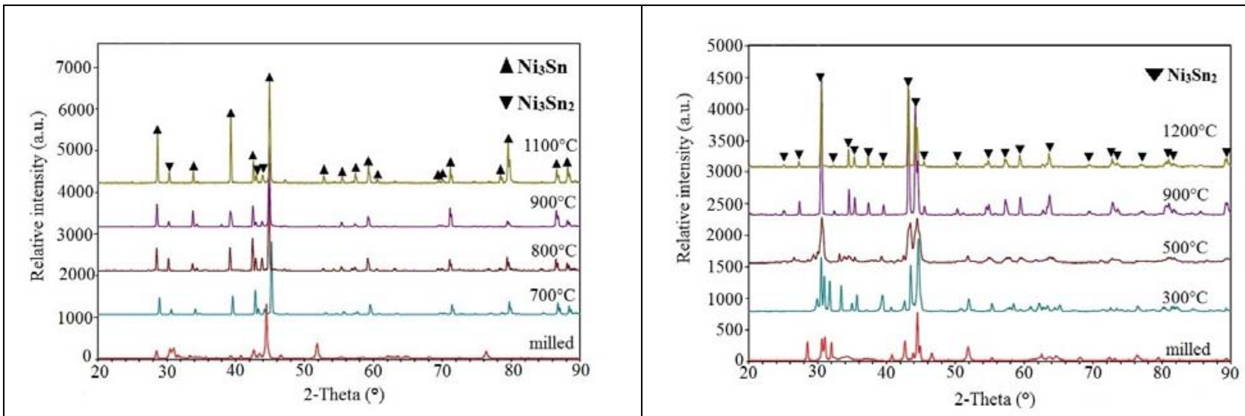
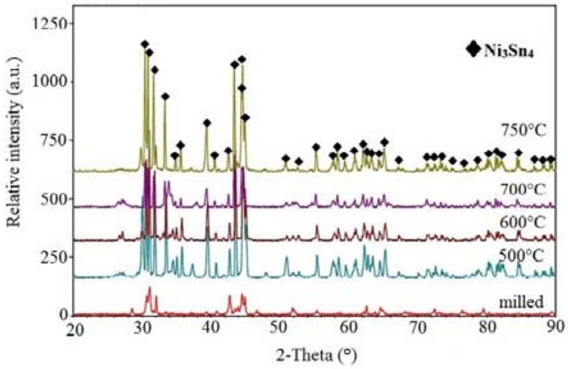


Figure 4 Schematic diagram of the mechanically alloyed Ni-Sn powder



(a) Ni-41 wt. % Sn

(b) Ni-58 wt. % Sn

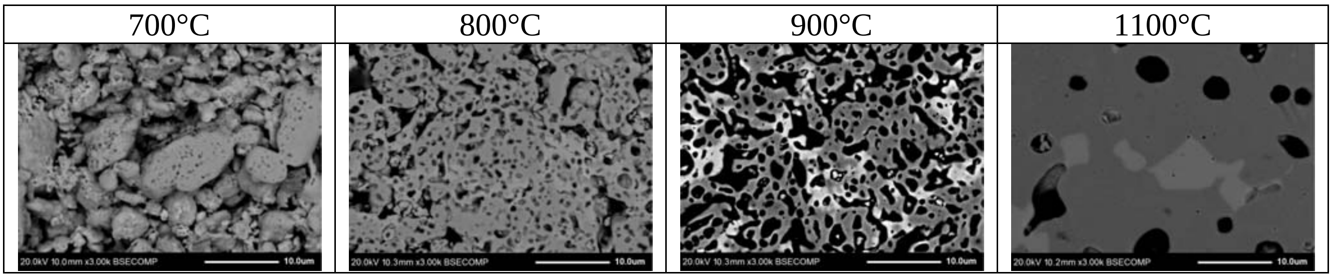


(c) Ni-73 wt. % Sn

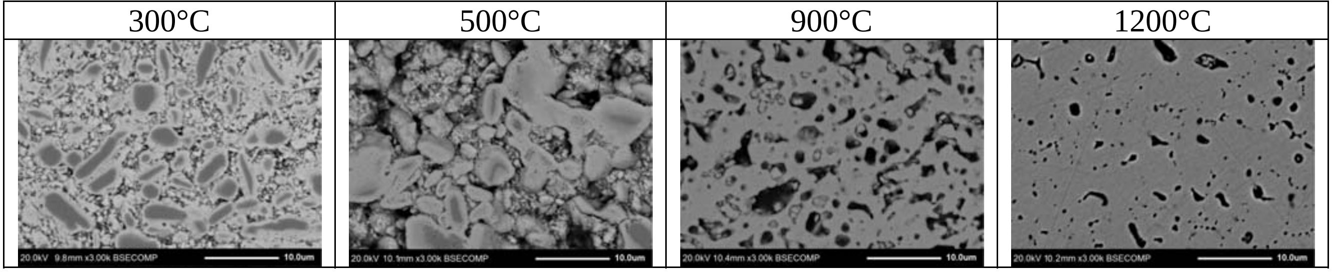
Figure 5 XRD patterns of the Ni-Sn materials mechanically alloyed for 25 hours and heated for 10 minutes at different temperatures

Electrical conductivity of porous Ni-Sn IMCs.

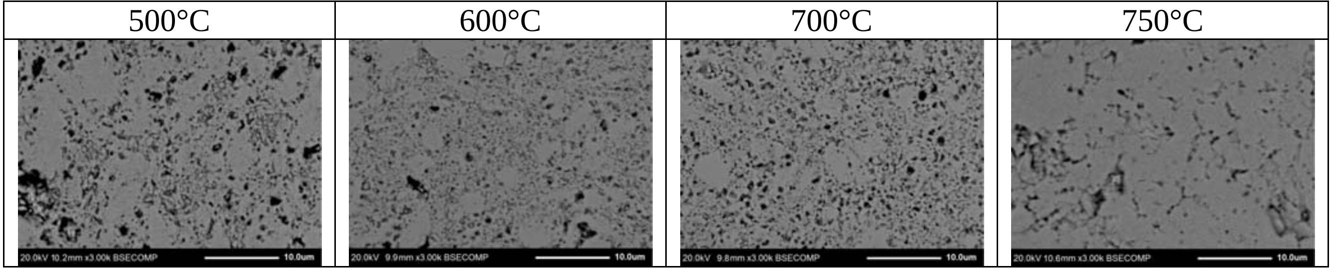
After heating of the mechanically alloyed Ni-Sn powders at different temperatures, porous Ni-Sn IMCs with different compositions corresponding to those of the nominal powder blends were obtained. Table 1 shows electrical conductivity data of the Ni-Sn materials heated at different temperatures. It was found that electrical conductivity increased with increasing heating temperatures due to generating higher degree of bonding between IMCs, as given in increased temperature of either composition in Figure 6 (increasing temperature enhances sintering neck growth). Since electricity is conducted via the IMC, increase of material connectivity results in increased electrical conductivity.



(a) Ni-41wt.%Sn



(b) Ni-58wt.%Sn



(c) Ni-73wt.%Sn

Figure 6 SEM images of the Ni-Sn materials mechanically alloyed for 25 hours and heated for 10 minutes at different temperatures

Table 1 Electrical conductivity data of the Ni-Sn materials mechanically alloyed for 25 hours and heated for 10 minutes at different temperatures

Materials	**Temperature**	**%IACS***
Ni-41wt.%Sn	700°C	1.759
	800°C	2.064
	900°C	3.748
	1100°C	6.748
Ni-58wt.%Sn	300°C	0.5557
	500°C	0.8469
	900°C	1.180
	1200°C	4.144
Ni-73wt.%Sn	500°C	2.351
	600°C	2.421
	700°C	3.316
	750°C	3.548

* %IACS: International annealed copper standard

Conclusions

The Ni-Sn IMCs were successfully obtained by mechanical alloying of Ni and Sn powder blends. However, with mechanical alloying times of up to 25 hours, formation of the IMCs was not governed by the blended powder compositions but influenced by Ni/Sn interfacial reactions. Heating of the Ni-Sn powders mechanically-alloyed for 25 hours resulted in the formation of IMCs having compositions with respect to nominal blended powder compositions. By adjusting heating temperatures, porous Ni-Sn IMCs could be obtained. In addition, electrical conductivity of the Ni-Sn IMCs increased with increasing heating temperature.

Acknowledgements

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