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Original Article

Solid state transformation of non-equilibrium Ni-Sn powder with a eutectic composition

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Abstract

Solid state transformation of supersaturated solid solution to anomalous Ni-Sn eutectic has been studied. The metastable Ni-Sn solid solution was prepared via mechanical alloying of a mixed Ni+Sn powder containing 32.5 wt-% Sn powder. The milling conditions included ball to powder ratio (BPR) of 5:1 and milling speed of 300 rpm. Milling times were varied as 5, 15, and 25 hours. Milling the mixed powder for longer than 15 hours resulted in formation of supersaturated Ni-Sn solid solution. Differential thermal analysis of the supersaturated Ni-Sn solid solution revealed two reactions, namely peritectoid and peritectic reactions, occurring at 945 and 1,141°C, respectively. Heating of the supersaturated Ni-Sn solid solution to different temperatures such as 800, 850, 900, 950, 1,100, and 1,140°C with holding time of 10 minutes resulted in development of anomalous eutectic with Ni_3Sn phase matrix embedded with Ni solution particles. Sintering and coarsening of the eutectic was depending on heating temperatures.

Keywords: mechanical milling, anomalous N-Sn eutectic, solid state transformation

1. Introduction

Non-equilibrium alloys can be produced either by employing rapid solidification or mechanical alloying techniques. Rapid solidification of the alloy melts can be obtained by three methods, including rapid movement of a high energy source, high undercooling caused by large cooling rate, and high undercooling caused by the absence of nucleants (Kurz and Trivedi, 1994). The non-equilibrium Ni-Sn eutectic, containing about 32 wt-% or 19 at-% Sn, was prepared by casting without chilling of the melt undercooled up to 240°C (Kattamis and Flemings, 1970). The undercooled Ni-Sn eutectic showed mixed lamellar and irregular structure with the fraction of irregular structure increasing with increasing undercooling. Microstructural observation by microscopy revealed that both phases were interconnected along a polyhedral network. The mixed eutectic structure was also reported in the undercooled Ni-32.5 wt-% Sn (Xing *et al.*, 1993). An anomalous eutectic colony in the as-solidified microstructures of the undercooled Ni-18.7 at-% Sn was reassessed using electron backscatter diffraction pattern (EBDP) mapping and inverse pole figure (IPF) examination (Li *et al.*, 2005). Both EBDPs and IPFs indicated that the Ni_3Sn intermetallic compound was continuous and well oriented whereas the Ni slid solution was discontinuous and randomly oriented within an anomalous eutectic grain.

Metastable supersaturated solid solutions of binary alloys could be produced by using mechanical milling even in the systems with positive enthalpies of mixing in the solid state (Murty and Ranganathan, 1998). The extension of solid solubility by mechanical alloying was attributed to nanocrystalline structure formed during mechanical alloying. The large volume fraction of grain boundaries present in the nanocrystalline state is expected to enhance the solid solubility in the mechanically alloyed materials. Extension of terminal solid solubility achieved by mechanical alloying has

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been reported in Ni base systems such as Ni-Ag (Froes *et al*., 1995), Ni-Al (Suryanaryana, 1996), Ni-C (Tanaka *et al*., 1992), and Ni-Nb (Portnoy *et al*., 1995). The extended solid solubility was also observed in the Ni-Sn alloy prepared by mechanochemical synthesis (Grigorieva *et al.*, 1997). A series of solid solutions with lattice parameters increasing as a function of tin content were prepared. A supersaturated solid solution with a maximum lattice parameter of 0.3662 nm containing 17.7 at-% Sn was mentioned to be according to Vegard's law.

Mechanical milling/alloying is one of the promising methods for processing of advanced and conventional material phases from elemental powders. This article is a part of the study on mechanical milling of binary Ni-Sn alloy system aiming for investigation of the fundamental phenomena and interactions between processing parameters, microstructures, and properties. The binary Ni-Sn alloy system is interesting because some orderly structured compounds/phases in this system have potentials for industrial applications. Intermetallic Ni_3Sn_4 prepared from elemental powders (Lee *et al*., 2002; Cheng and Shi, 2005; Amadei *et al*., 2005; Ehinon *et al*., 2008) is one of new cathode candidates for Li-ion batteries. The Ni_3Sn_2 metallic is also used for Li-ion batteries applications (Kim *et al*., 2003, and Kosho *et al*., 2007). It is possible to say that all intermetallics appearing in the binary Ni-Sn phase diagram can be applied as an electrode for lithium ion batteries. The nickel-rich Ni_3Sn intermetallic was also investigated on the mechanism of Li insertion into interphase Ni_3Sn in Ni-Sn alloy for the anode of lithium iron battery (Hou *et al*., 2008).

In this study, mixed elemental Ni+Sn powders were mechanically milled using attrition to produce metastable phases, which were subsequently heat-treated to follow solid state transformation of the non-equilibrium phases.

2. Experimental Procedure

Mixed elemental Ni+Sn powders, with a eutectic composition, were prepared from 32.5 wt-% Sn and balance Ni powders. The mixed powders were then milled in an attritor. The milling conditions included ball to powder ratio (BPR) of 5:1 and milling speed of 300 rpm. Milling times were varied as 5, 15, and 25 hours. The milled powders were characterized by using X-ray diffraction technique and optical microscopy. The milled powders, being a supersaturated solid solution throughout the whole particles, were examined using differential thermal analysis (DTA). The supersaturated solid solution powders were heated with a heating rate of 10°C/min under N_2 atmosphere in a temperature range between 30-1400°C. The obtained DTA curves were interpreted by matching the endothermic peaks with the transformation temperatures in the Ni-Sn phase diagrams (Massalski *et al*., 1996 and Li *et al*., 2004) along the eutectic composition. The supersaturated solid solution powders were heated to different temperatures such as 800, 850, 900, 950, 1100, and 1140°C with holding time of 10 minutes. The heated powders were observed by using scanning electron microscopy (SEM) equipped with a backscattering mode.

3. Results and Discussion

3.1 Milled Ni+Sn powders

Milling of the mixed Ni+Sn powders for 15 hours or for longer durations resulted in complete dissolution of Sn into Ni powders. The X-ray diffraction patterns, given in Figure 1, showed no peaks corresponding to free Sn powder particles. The Sn peaks disappeared after milling for 15 hours. The XRD peaks, corresponding to Ni and/or Ni solid solution in the milled Ni+Sn powders for 15 hours or for longer durations, appeared as sharp peaks. Disappearance of the Sn peaks meant that all Sn atoms diffused into Ni powder particles and formed either solid solution or intermetallic compounds with Ni. X-ray peaks corresponding to Ni-Sn intermetallic compounds were not observed. This indicates that Sn presents in the form of solid solution rather than intermetallic compounds. The shape XRD peaks indicate that the milled Ni+Sn powders are crystalline and not amorphous. For further confirmation of complete Ni-Sn solid solution, metallographic method was employed. Microstructural observation using SEM with a backscattering mode revealed that a single phase was formed from two different phases. The Sn powder particles (brighter phases in Figure 2(a)) disappeared when milling times were equaling to or higher than 15 hours. Figure 2(b) and (c) showed only dark grey Ni powder particles. This indicates that the Ni-32.5 wt-% Sn solid solution can be obtained by mechanical milling. Dissolution of Sn atoms into face-centered cubic (fcc) structure of Ni powder particles was also checked by examination of Ni lattice parameter. It was expected that the presence of bigger foreign Sn atoms in the Ni unit cell would change Ni lattice parameter. It was found from Table 1 that

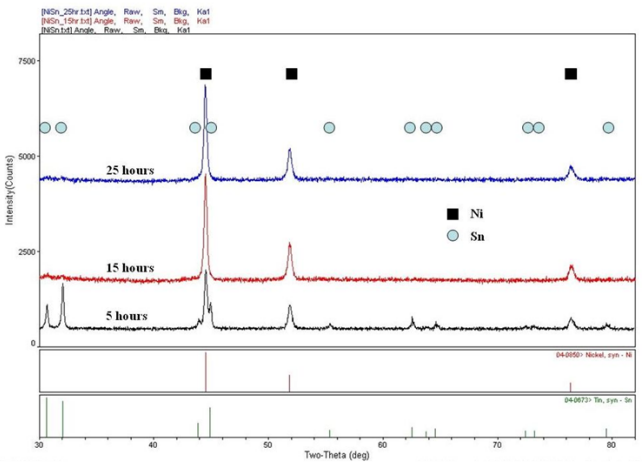
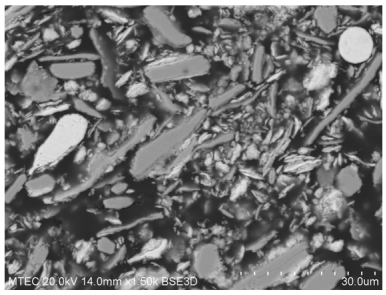
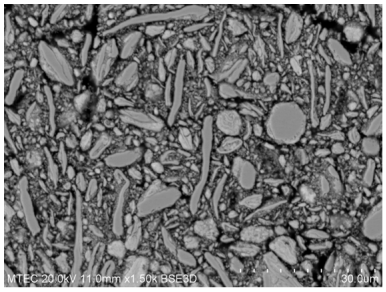


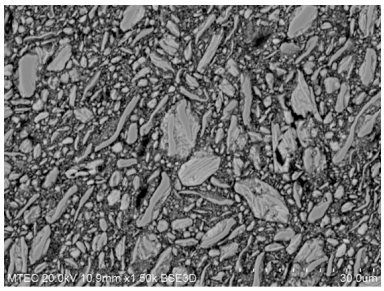
Figure 1. X-ray diffraction patterns of the Ni+Sn powders milled for different times.



(a) After 5 hours milling.



(b) After 15 hours milling.



(c) After 25 hours milling.

Figure 2. Backscattered SEM images of the Ni+Sn powders milled for different times.

Table 1. Observed lattice parameters of milled Ni+Sn powders.

Milling time (hrs)	Observed lattice parameters (A)	Average observed lattice parameter(A)
5	3.520 3.523 3.521	3.521±0.002
15	3.523 3.523 3.526	3.524±0.001
25	3.524 3.521 3.525	3.523±0.002
0	3.520	

the Ni lattice parameter was slightly increased. That indicates that spaces in the Ni unit cell are occupied by Sn atoms.

The solid solubility of Sn in Ni obtained in this experiment (19.23 at-% Sn) is higher than the maximum solubility value of 20 wt-% Sn at the eutectic temperature given in the equilibrium Ni-Sn phase diagram (Massalski *et al.*, 1996). The extended solid solubility was also observed in the Ni-Sn alloy prepared by mechanochemical synthesis (Grigorieva *et al.*, 1997). A series of solid solutions, with lattice parameters increasing as a function of tin content, were prepared. A supersaturated solid solution with a maximum lattice parameter of 0.3662 nm containing 17.7 at-% Sn was mentioned to be according to Vegard's law.

Extension of terminal solid solubility achieved by mechanical alloying has been reported in Ni base systems such as Ni-Ag (Froes *et al*., 1995), Ni-Al (Suryanaryana, 1996), Ni-C (Tanaka *et al*., 1992), and Ni-Nb (Portnoy *et al*., 1995). Departure from equilibrium solid solubility of each mechanically milled binary alloy was great. The extension of terminal solid solubility is attributed to nanocrystalline structure formed during mechanical alloying (Murty and Ranganathan, 1998). The large volume fraction of grain boundaries present in the nanocrystalline state is expected to enhance the solid solubility in these materials. It was reported that the diffusivity at grain boundary enhanced by 1,000 times or even greater as the size of the crystallites reached to a few nanometers (Schumacher *et al*., 1989). The extension of solid solubility is dominated by diffusion of solutes. According to literatures given above, complete solid solution Ni-Sn alloy, having eutectic composition, is possibly dominated by an interdiffusion process at grain boundary. The formation of an alloy from two different elemental powders may be explained by using the mechanism of ball-powder-ball collision (Gilman and Benjamin, 1983). At the initial collision, the ductile metal powders are flattened and worked harder when they are cold welded and heavily mechanically deformed. The layered structure of composites particles is formed when the flattened powders are brought into intimate contact. With further milling, cold welding, and deformation of layered particles result in refined microstructure. With increasing milling times, the lamellar spacing of the agglomerated particles is quickly reduced. An interdiffusion reaction takes place at the clean or fresh surfaces of the intimate layers in the powder particles to form an alloy.

3.2 Thermal analysis of the milled Ni+Sn powders

Since the supersaturated Ni-Sn solid solution was metastable, it was expected that this metastable phase in the milled Ni+Sn powders would be transformed to other more stable phases upon heating to the eutectic temperature. Thermal analysis of the milled Ni+Sn powders was performed in order to confirm this expectation. When the Ni+Sn powders, milled for 25 hours, were examined using differential thermal analysis (DTA) there were two endothermic peaks at temperatures of 945°C and 1,141°C (Figure 3). These two endo-

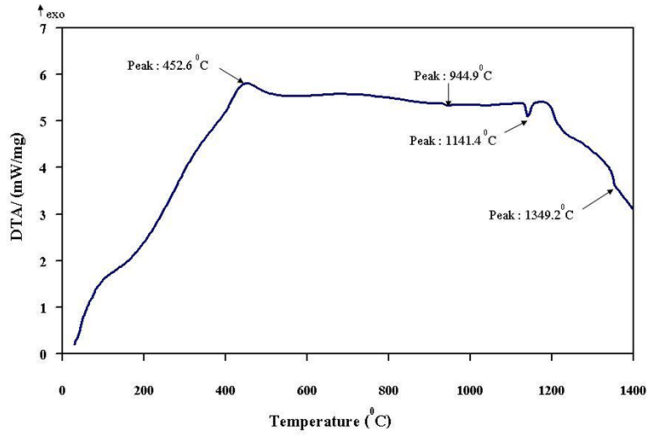


Figure 3. Differential thermal analysis of Ni+Sn powders milled for 25 hours.

thermic peaks were corresponding to the peritectoid reaction ($Ni + Ni_3Sn$ (HT) <=> Ni_3Sn (LT)) and the eutectic reaction (L <=> $Ni + Ni_3Sn$ (HT), respectively, in the binary Ni-Sn phase diagram along the Ni-rich eutectic composition. The temperatures (945°C and 1,141°C) obtained from this experiment were different from those (920.5 C and 1,130°C) given in the binary Ni-Sn phase diagrams, published in the compilation by Massalski *et al.* (1996) and reassessed through the CALPHAD method by Liu *et al*. (2004). However, a new investigation of the Ni-Sn system revealed that the peritectoid and eutectic reaction temperatures were 948°C and 1,139°C, respectively (Schmetterer *et al.*, 2007). The revised version of the binary Ni-Sn phase diagram is given in Figure 4. The temperatures (945°C and 1,141°C) obtained from this experiment were in agreement with the values given in Figure 4.

3.3 Heat treatment of the milled Ni+Sn powders

Heat treatment of the milled Ni+Sn powders with different holding temperatures of the Ni+Sn powders milled for 25 hours resulted in three phenomena (Figure 5). The first one involved sintering among the milled Ni+Sn powder particles. Separated milled powder particles (Figure 2(c)) formed metallic bonds between them (Figure 5). Sintering evidences, characterized by lighter Ni_3Sn phase joining and pore diminishment, were clearly observed in Figures 5. The second involved dark grey Ni grain coarsening that was evidenced by the growth of large particles, which were drawing materials from smaller particles that shrunk or disappeared. This phenomenon is corresponding to Ostwald ripening (Voohees, 1985). The last involved transformation from supersaturated solid solution (Figure 2(c)) to anomalous eutectic structures Figure 5. The irregular eutectic structure obtained by solid state transformation was similar to the anomalous eutectic structures present in the as-solidified microstructures of the undercooled Ni-Sn eutectic. The atypical eutectic, coexisted with typical lamellar structure, was reported previously in the Ni-Sn alloy cast without chilling at undercoolings of 75°C and 240°C (Kattais and Flemings, 1970). The fraction of the irregular eutectic increased with increasing undercooling. In the highly undercooled Ni-32.5 wt–% Sn melt, the dendrite tip velocity of the Ni_3Sn phase was significant larger than that of Ni (á) phase during recalescence, resulting in formation of dendrite cluster morphology (Xing *et al*, 1993). The dendrite clusters subsequently developed into anomalous eutectic structure by ripening of Ni_3Sn dendrites and growth of Ni (α) phase between the Ni_3Sn arms. Complete anomalous eutectic structure was observed in this alloy if the undercooling before nucleation was above about 130 K. A similar explanation for a mechanism of anomalous eutectic formation in the highly undercooled Ni-32.5 wt –% Sn was also given by Da *et al*. (2007). A transition from lamellar eutectic to anomalous eutectic in the undercooled Ni-Sb alloy started if undercooling was higher than a critical undercooling and completed if was even higher (Han and Wei, 2002). Dependency of eutectic morphology on undercooling degree was also reported in the undercooled Ni-Mo alloys (Wenjing and Bingbo, 2003). The threshold undercooling for anomalous eutectic to form in the undercooled Ni-47.7% Mo eutectic alloy melt was 54 K.

The anomalous eutectic colony in the as-solidified microstructures of the undercooled Ni-18.7 at-% Sn was reassessed using electron backscatter diffraction pattern (EBDP) mapping and inverse pole figure (IPF) examination (Li *et al*., 2005). Both EBDPs and IPFs indicated that the Ni_3Sn intermetallic compound was continuous and well oriented, whereas the Ni solid solution was discontinuous and randomly oriented within an anomalous eutectic grain. Anomalous eutectics in the solidification structure of undercooled Ni–18.7 at-% Sn eutectic alloy were examined by optical metallography and electron backscattered diffraction (Li *et al*., 2008). It was revealed that a–Ni particulates are, in principle, randomly distributed in the anomalous eutectics in

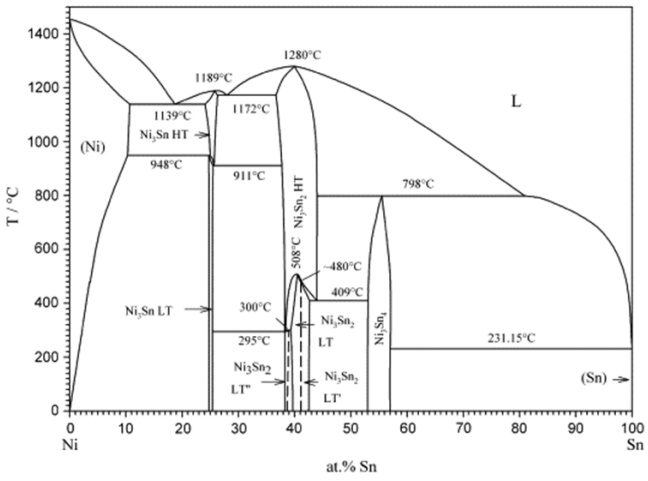
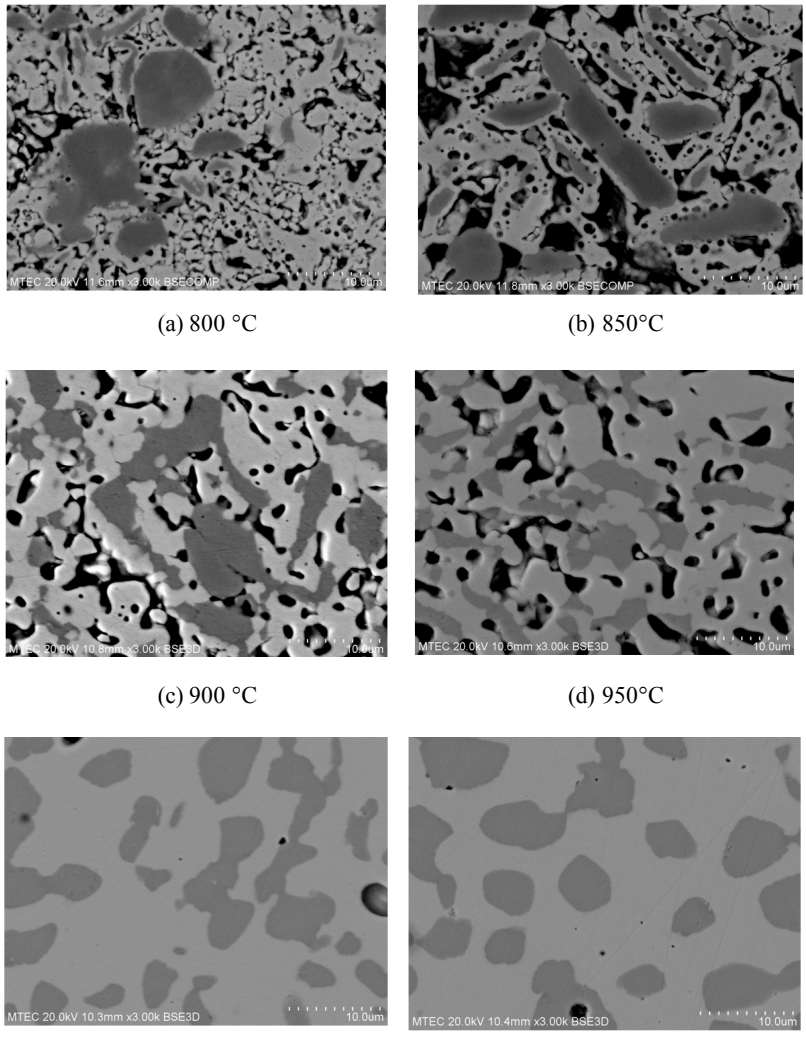


Figure 4. Binary Ni-Sn phase diagram (Schmetterer *et al.*, 2007).



(a) 800 °C (b) 850°C

(c) 900 °C (d) 950°C

(e) 1100°C (f) 1140°C

Figure 5. Eutectic Ni-Sn alloy resulted from 10 minute-heating of milled Ni-Sn powders at temperatures of (a) 800°C, (b) 850°C, (c) 950°C, (d) 950°C, (e) 1100°C, and (f) 1140°C.

the undercooling range investigated. Another eutectic phase, β–Ni_3Sn, is well orientated at low undercoolings but gradually becomes inconsistent in orientation as undercooling increases, accompanied by an increasing number of grain boundaries in it. As the solidification structure changes from a mixture of anomalous eutectics plus lamellar eutectics to full anomalous eutectics beyond a critical undercooling of 130 K, however, misorientation in the β–Ni_3Sn phase disappears completely from the measurement area.

According to the works of Li *et al*. (2005) and Li *et al*. (2008) orientation of the Ni_3Sn and Ni (α) phases solidified from the highly undercooled binary N-Sn alloys is already studied. However, the orientation of these two phases resulted from solid state transformation cannot be instantly implied by referring to those works. Thus, the orientation of each phase in the solid state transformed anomalous eutectic is also worth further studies. Thermal stability of the anomalous eutectic has not been widely investigated. Aging of the anomalous Ni-Sn eutectic at different temperatures is also aimed for further study.

4. Conclusions

When the mixed Ni+Sn powders with a eutectic composition were mechanically milled for longer than 15 hours, complete Ni-Sn solid solution was obtained. Characterization of the milled Ni+Sn powders using XRD techniques and SEM revealed that neither eutectic structures nor Ni-Sn intermetallic was observed. Differential thermal analysis of the supersaturated Ni-Sn solid solution revealed two reactions, namely peritectoid and peritectic reactions, occurring at 945 and 1,141°C, respectively. Heating of the supersaturated Ni-Sn solid solution to different temperatures such as 800, 850, 900, 950, 1,100, and 1,140°C with holding time

of 10 minutes resulted in formation of anomalous eutectic. Sintering and coarsening of the eutectic was depending on heating temperatures.

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