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Synthesis and characterization of mono- and di-antimonide with the first transition metals in group 8B by mechanical alloying

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ABSTRACT

Mono- and di-anitimonide compounds between antimony and the first transition metals in group 8B were synthesized by mechanical alloying method. All samples were investigated by the X-ray powder diffraction technique and differential thermal analysis. The single phase can be obtained only for CoSb, NiSb and $CoSb_2$ compounds. In this investigation, a single phase of a marcasite structure ($FeSb_2$ and $NiSb_2$) and $Fe_{0.56}Sb_{0.44}$ compound cannot be detected in the XRD patterns after 60 h of milling because of the instability of their structures at low temperature. They decomposed to their starting materials as seen by the characteristic peaks of the starting materials in the XRD patterns after 60 h of milling.

1. Introduction

Metal antimonides are advanced materials with various useful physical properties. Their binary compounds in their intermediate phases allow for various compositions that depend on each system. In M–Sb (M = the first transition metal) binary phase diagrams, mono- and di-antimonide compounds are usually found as intermediate phases, however, neither of them have been reported in the Cu–Sb binary system [1]. In addition di-antimonide compounds are not present in the Mn–Sb [2] and Zn–Sb [3] binary systems. For antimonide compounds with the first transition metals in group 8B, MSb_3 is found only with the Co–Sb system and this compound has found many applications for thermoelectric systems [4]. Di-antimonides (MSb_2) have been of interest as negative electrodes for lithium-ion batteries [5]. Mono-antimonides (MSb) have been used as the catalyst for the oxidative dehydrogenation of hydrocarbons [6]. In general, transition metal mono-antimonides usually crystallize in the NiAs-type structure but the ZnSb compound crystallizes in the CdSb structure [3]. Many structures such as pyrites, marcasite or arsenopyrite-type stuctures, can be produced using the annealing temperature for metal di-antimonides. A compilation of the binary phases of MSb and MSb_2 (M = Fe, Co and Ni) is given in Table 1 [7–9].

In general, these compounds are prepared by physical thermal processes in which the elements are melted in an evacuated or Ar partially filled quartz tube and then annealed at a high temperature for several days. Using this method, $CrSb_2$, $FeSb_2$, $CoSb_2$ and $NiSb_2$ crystallize in the orthorhombic marcasite structure. To reduce the reaction steps and costs, several new methods such as hydrothermal [10] and mechanical alloying (MA) techniques [11] have been developed. Zhao and co-workers [12] reported a new method to synthesize $NiSb_2$ compound by a solvothermal route. It shows the main diffraction peaks of $NiSb_2$ in a marcasite structure with small NiSb and Sb diffraction peaks. The application of MA for these systems has mainly focused on producing $CoSb_3$. This compound cannot be synthesized directly by MA [13]. The milled mixture undergoes a further recrystallization by a hot pressing or annealing process to obtain the required phase [14]. Although the high-energy ball milling technique has been an intensively developed technology for preparing many materials for more than 30 years because it can be operated at low temperature and is suitable for mass production, its main disadvantage is that many metal antimonide compounds such as $CoSb_3$ and Zn_4Sb_3, cannot be synthesized by this method.

In this study, we have tried to synthesize mono- and di-antimonide compounds of the first transition metals in group 8B using a mechanical alloying method.

2. Experimental

The starting material powders of Fe (99%, −325 mesh), Co (99.9%, −100 mesh), Ni (99.99%, −100 mesh) and Sb (99.5%, −100 mesh) were milled in the stoichiometric

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Table 1
Crystal structure data for MSb and MSb_2 (M = Fe, Co and Ni).

Phase	Pearson symbol	Space group	Strukturebericht designation	Prototype
$Fe_{0.56}$ $Sb_{0.44}$	*hP*4	*P*6$_3$/*mmc*	B8$_1$	NiAs
$FeSb_2$	*oP*6	*Pnnm*	C18	FeS_2
CoSb	*hP*4	*P*6$_3$/*mmc*	B8$_1$	NiAs
$CoSb_2$ (low T)	*mP*12	*P*2$_1$/*c*	–	$CoSb_2$
$CoSb_2$ (high T)	*oP*6	*Pnnm*	C18	FeS_2
NiSb	*hP*4	*P*6$_3$/*mmc*	B8$_1$	NiAs
$NiSb_2$	*oP*6	*Pnnm*	C18	FeS_2

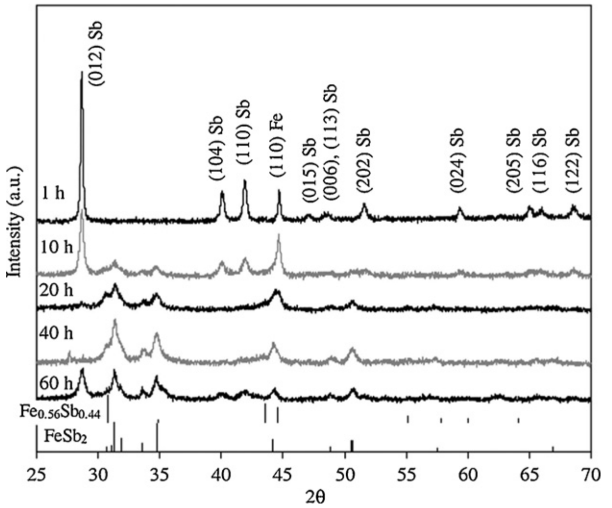

Fig. 1. XRD pattern of the mixture at a mole ratio of Fe:Sb = 0.56:0.44 after milling for 1, 10, 20, 40 and 60 h.

ratio of $Fe_{0.56}Sb_{0.44}$, CoSb, NiSb, $FeSb_2$, $CoSb_2$ and $NiSb_2$. The mechanical alloying process was performed in a Pulverisette 7 FRITSCH planetary ball mill in an argon atmosphere to prevent the powders from being oxidized during the milling process. The weight ratio of the balls to the powders was keep at 10:1 and the rotational speed was controlled at 650 rpm. The phase changes and crystal dimensions of the milled powders were characterized by X-ray diffraction (XRD, PHILIPS X'Pert MPD) using Ni-filled CuKα radiation. The thermal behavior of milled powders was performed by differential thermal analysis (DTA, PerkinElmer DTA 7) at a heating rate of 10 °C/min, in order to investigate the phase transformation after heating.

3. Results and discussion

3.1. Metal mono-antimonides (MSb, M = Fe, Co and Ni)

Figs. 1–3 show the XRD patterns of milled powders at different times in the stoichiometric ratio of $Fe_{0.56}Sb_{0.44}$ and MSb when M = Co and Ni, respectively. The successful preparation of a single phase of mono-antimonides was obtained in only the Co–Sb and Ni–Sb systems as shown in Figs. 2 and 3, respectively. For these binary systems, the peak intensities of the starting materials decreased as the milling time increased. After 5 h of milling, the XRD patterns of mono-antimonides corresponding to CoSb and NiSb were seen. The peaks of the starting materials were not observed and the XRD patterns show only the characteristic peaks of CoSb and NiSb after the mixture was milled for 20 h. After 60 h of milling, the CoSb and NiSb compounds do not change or decompose to another compound so this confirmed the stability of the synthesized compounds. Both compounds are crystallized in a nickel arsenide (NiAs) structure of a *P*6$_3$/*mmc* space group. The CoSb and NiSb powders show the lattice parameters $a = 0.3902(8)$ nm, 0.3957(9) nm and $c = 0.5182(8)$ nm, 0.5148(9) nm, respectively.

The DTA scans of CoSb and NiSb powders prepared from the elemental powders after 60 h of milling are presented in Fig. 4. In a heating scan, the samples display a simple thermal behavior of

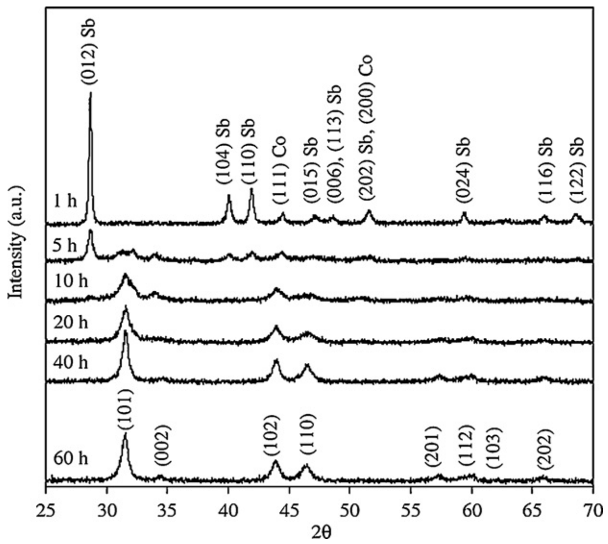

Fig. 2. XRD pattern of the mixture at a mole ratio of Co:Sb = 1:1 after milling for 1, 5, 10, 20, 40 and 60 h.

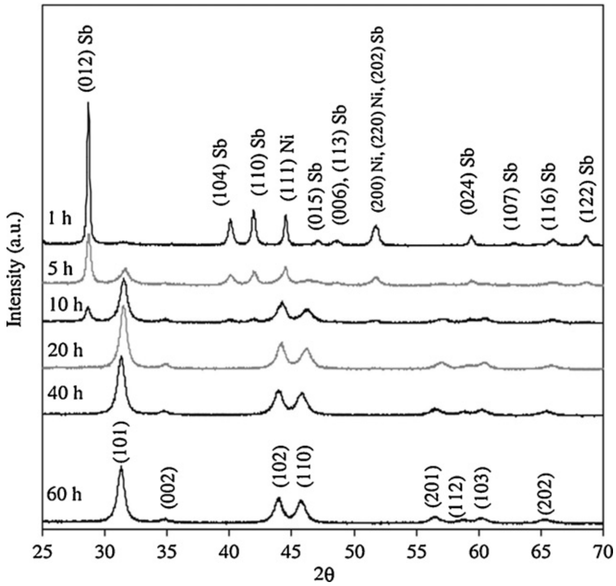

Fig. 3. XRD pattern of the mixture at a mole ratio of Ni:Sb = 1:1 after milling for 1, 5, 10, 20, 40 and 60 h.

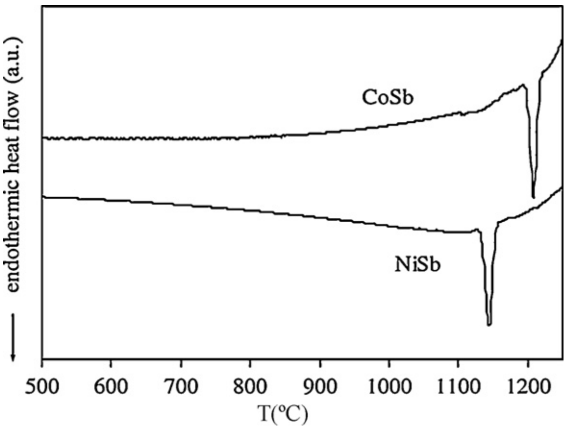

Fig. 4. DTA curves of CoSb and NiSb powders after 60 h of milling in a heating scan.

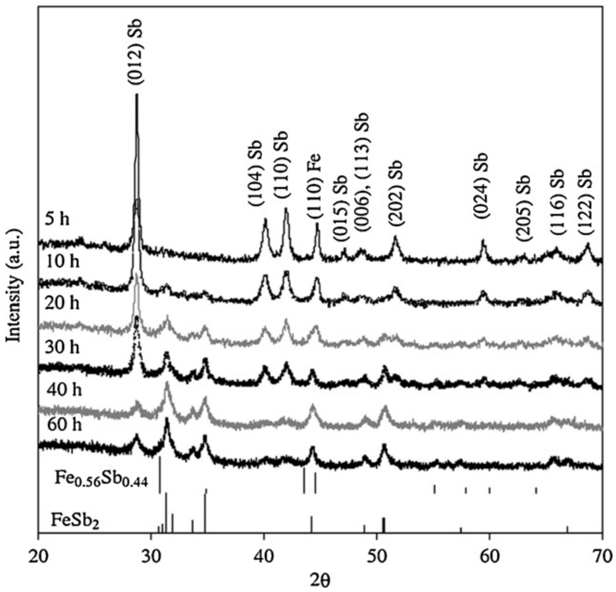

Fig. 5. XRD pattern of the mixture at mole ratio of Fe:Sb = 1:2 after milling for 5, 10, 20, 30, 40 and 60 h.

only one endothermic peak indicating a congruent melting event. Because the peak is at about 630 °C which corresponds to the melting point of Sb was not observed, there was no amorphous pure Sb that cannot be detected by XRD, in the final products. The melting points of CoSb and NiSb are 1209 and 1145 °C, respectively, and these are close to their reports in the binary phase diagrams (1120 °C for CoSb and 1147 °C for NiSb) [15,16].

The XRD patterns of mixtures between Fe and Sb powders are different from those two binary systems as seen in Fig. 1. When the starting materials were reacted together as indicted by a decrease of their peak intensities, the mono- and di-antimonide compounds as $Fe_{0.56}Sb_{0.44}$ and $FeSb_2$, respectively, were observed in the XRD patterns. As the milling time was prolonged, the intensities of the characteristic peaks of $FeSb_2$ tended to increase. However, a decrease of the peak intensities of $Fe_{0.56}Sb_{0.44}$ was observed and could not be detected after 60 h of milling. It is possible that this phase decomposed to their starting materials and at that time the characteristic peaks of Sb are present in the XRD pattern. Similar evidence can be seen when the mixture of Co:Sb at a mole ratio of 1:3 was milled for more than 40 h [11]. The instability of $Fe_{0.56}Sb_{0.44}$ may be explained by the presence of an extra Fe in the interstitial sites 2*d*. Occupied atoms on the both sites probably increase the strain due to short interactomic distance between metal and metalloid atoms [17]. This structure may be less stable than the normal MSb compound that crystallizes into the NiAs-structure.

3.2. Metal di-antimonides (MSb_2, M = Fe, Co and Ni)

Figs. 5–7 show the XRD patterns of milled powders at different times in the stoichiometric ratio = MSb_2 when M = Fe, Co and Ni, respectively. These figures, show that only the $CoSb_2$ compound can be successfully synthesized by the MA method. After 30 h of milling, the diffraction pattern of this phase just appeared and the intensities of the starting material peaks had decreased. The starting materials were no longer detectable after 40 h of milling as shown in Fig. 6. The prepared powders are crystallized in the monoclinic arsenopyrite structure of a $P2_1/c$ space group and do not transform to another phase after 60 h of milling. The lattice parameters of the prepared $CoSb_2$ show $a = 0.6510(3)$ nm, $b = 0.6341(4)$ nm and $c = 0.6537(8)$ nm. In the phase diagram of the Co–Sb binary system [8], $CoSb_2$ has two stable phases at different temperatures. At a high temperature, this compound crystallizes in a marcasite structure however an arsenopyrite structure is obtained at a lower temperature.

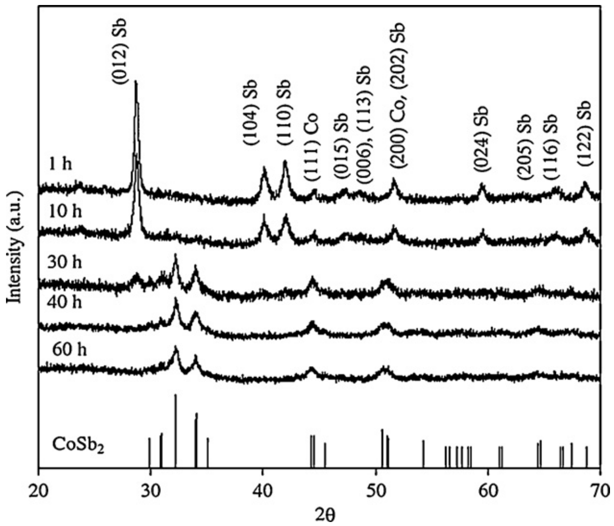

Fig. 6. XRD pattern of the mixture at mole ratio of Co:Sb = 1:2 after milling for 1, 10, 20, 30, 40 and 60 h.

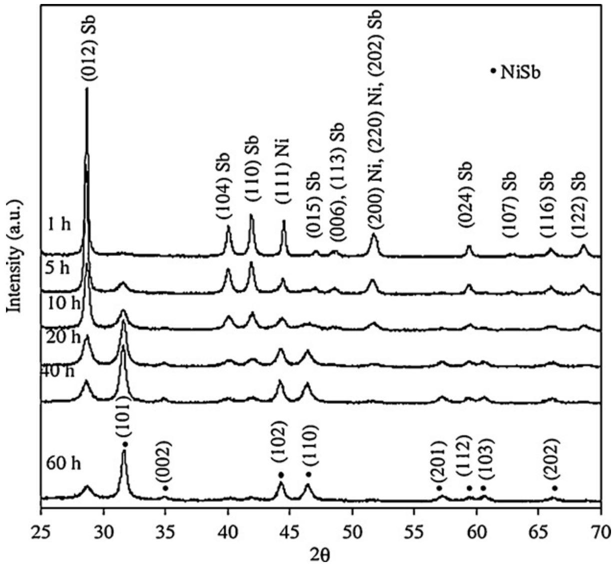

Fig. 7. XRD pattern of the mixture at mole ratio of Ni:Sb = 1:2 after milling for 1, 5, 10, 20, 40 and 60 h.

Fig. 7 shows the XRD patterns of powders that were mixed in an atomic mole ratio of Ni:Sb = 1:2, for different milling times. After 5 h of milling, some atoms of Ni and Sb have converted into the NiSb compound. After prolonging the milling time to 40 h, this phase has continued to increase and the residual Sb peaks have decreased. Mixing of the NiSb and Sb phases was still apparent in the XRD pattern when the powders were milled for 60 h. It indicates that no $NiSb_2$ phase can be formed in these conditions. On the other hand, the $FeSb_2$ phase can be detected in the XRD pattern after the mixture was milled for 10 h. The XRD patterns of a powder that was mixed with an atomic mole ratio of Fe:Sb = 1:2, for different milling times, is presented in Fig. 5. After 10 h of milling, the $Fe_{0.56}Sb_{0.44}$ and the $FeSb_2$ were formed together by the reaction between Fe and Sb. After 30 h of milling, the peak intensity of $FeSb_2$ increased while the $Fe_{0.56}Sb_{0.44}$ was either not presented or showed as only a very low peak in the XRD pattern. As the $FeSb_2$ is an unstable phase at low temperature, the singles phase of this compound cannot be synthesized with these conditions.

3.3. Stability of MSb and MSb_2

For the mono-antimonide (MSb), the CoSb and NiSb compounds can be synthesized by a direct MA method while the $CoSb_2$ compound is the only stable phase for di-antimonide (MSb_2) preparing by the MA method. Both $FeSb_2$ and $NiSb_2$ crystallize in a marcasite structure which is a stable phase at high temperature while $CoSb_2$ can be crystallized in an arsenopyrite structure at low temperature and transforms to a marcasite structure at high temperature [18]. Because of the existence of a stable phase at low temperature, the $CoSb_2$ can be successfully prepared by the MA method.

Li and co-workers [15] calculated the formation enthalpies of all intermetallic compounds in the Ni–Sb binary system. At 800 K, the NiSb structure is the lowest. As the marcasite structure ($NiSb_2$) is unstable at low temperature and NiSb is the prefered form, the NiSb phase must be observed in the XRD pattern when the mixture is formed by milling at the mole ratio of Ni:Sb = 1:2. The residual Sb comes from the stoichiometric reaction of the NiSb phase as a reaction: $Ni + 2Sb \rightarrow NiSb + Sb$. On the other hand, the $FeSb_2$ has the lowest formation enthalpy at 893 K over all structures in the Fe–Sb binary system as calculated by Pei et al. [16]. In fact, FeSb is absent in the Fe–Sb binary system, the composition of its structure is $Fe_{0.56}Sb_{0.44}$ with the extra Fe being presence in the interstitial sites 2*d*. The short interatomic Fe(2*d*)-Sb distance may increase the strain and the energy required offer its formation. The $FeSb_2$ structure can be observed because it has lower formation enthalpies over $Fe_{0.56}Sb_{0.44}$. However, both structures are not stable at low temperature. Neither $Fe_{0.56}Sb_{0.44}$ nor $FeSb_2$ can be prepared in a single phase by the MA method. Then, the mixtures that correspond to the stoichiometric ratios of $Fe_{0.56}Sb_{0.44}$ and $FeSb_2$ show similar XRD patterns after 60 h of milling.

4. Conclusion

By mixing the elemental powders of Co, Fe, Ni and Sb at the mole ratios of six intermetallic compounds (MSb and MSb_2) that occur in the Co–Sb, Fe–Sb and Ni–Sb binary phase diagrams, only three intermetallic compounds; CoSb, NiSb and $CoSb_2$ can be synthesized by the MA method. For mono-antimonide compounds, $Fe_{0.56}Sb_{0.44}$ has an extra Fe in its interstitial sites that perhaps increases the energy of formation and is not stable at low temperature.

For the di-antimonide compounds, all intermetallic phases occur with a marcasite structure and are usually observed at high temperature. But only $CoSb_2$ crystallizes in the arsenopyrite structure that is stable at low temperature. At the mole ratios of Fe or Ni:Sb = 1:2, the presence of the NiSb and $FeSb_2$ phases maybe be related to their formation enthalpies.

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References

[1] W. Gierlotka, D. Jendrzwjczyk-Handzlik, J. Alloys Compd. 484 (2009) 172–176.
[2] A.V. Tkachuk, Y.K. Gorelenko, Y.V. Stadnyk, O.I. Bodak, J. Alloys Compd. 317–318 (2001) 280–283.
[3] H. Okamoto, J. Phase Equilib. Diffus. 29 (2008) 290.
[4] Y. Kawaharada, K. Kurosaki, M. Uno, S. Yamanaka, J. Alloys Compd. 315 (2001) 193.
[5] L. Monconduit, C. Villevieille, C.-M. Inoic-Bousquet, B. Ducourant, J.-C. Jumas, J. Power Source 172 (2007) 388–394.
[6] I.P. Parkin, C.J. Carmalt, D.B. Morrison, Polyhedron 19 (2000) 829–833.
[7] H. Okamoto, J. Phase Equilib. Diffus. 12 (1991) 244–245.
[8] H. Okamoto, J. Phase Equilib. Diffus. 22 (2001) 166.
[9] H. Okamoto, J. Phase Equilib. Diffus. 30 (2009) 301–302.
[10] J.L. Mi, X.B. Zhao, T.J. Zhu, J.P. Tu, G.S. Cao, J. Alloys Compd. 417 (2006) 269–272.
[11] Y. Yang, Y. Chen, J. Peng, X. Song, W. Zhu, J. Su, R. Chen, J. Alloys Compd. 375 (2004) 229–232.
[12] J. Xie, X.B. Zhao, G.S. Cao, M.J. Zhao, S.F. Su, J. Alloys Compd. 393 (2005) 283–286.
[13] L. Kegao, Z. Jiuxing, X. Dong, J. Mater. Process. Technol. 184 (2007) 257–260.
[14] J. Yang, Y. Chen, J. Peng, X. Song, W. Zhu, J. Su, R. Chen, J. Alloys Compd. 375 (2004) 229–232.
[15] Y. Zhanf, C. Li, Z. Du, T. Geng, Comput. Coupling Phase Diag. Thermochem. 32 (2008) 378–388.
[16] B. Pei, B. Bjorkman, B. Sundman, B. Jansson, CALPHAD 19 (1995) 1–15.
[17] L. Noren, R.L. Withers, Y. Tabira, J. Alloys Compd. 309 (2000) 179–187.
[18] K. Ishida, T. Nishizawa, Binary Alloy Phase Diagram, second ed., ASM International, Mterials Parks, Ohio, 1990, p.1232.