

Contents lists available at [ScienceDirect](http://www.sciencedirect.com/science/journal/09258388)

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Interaction of the components in the Ag–Er–Sn system at 400 ◦C

Jianlie Liang∗, Changzhong Liao, Yiyuan Tang, Cailiu Yin, Yanmei Han, Liangqin Nong, Shibiao Xie

Institute of Materials Science, College of Physics and Electronic Engineering, Guangxi University for Nationalities, Nanning Guangxi 530006, PR China

article info

Article history: Received 22 February 2010 Received in revised form 7 April 2010 Accepted 22 April 2010 Available online 15 May 2010

Keywords: Phase diagram Ag–Er–Sn X-ray diffraction Scan electron microprobe

1. Introduction

Phase diagram is the "roadmap" for the materials design. Experimental data of the phase equilibria are fundamental for the materials design based on the CALPHAD method [\[1\],](#page-5-0) and subsequent Phase Field Simulation [\[1,2\].](#page-5-0) Moreover, exploration on the phase diagram always accompanied the discovery of new intermetallics, which might be the potential functional materials. However, knowledge of the phase equilibria in some ternary alloys is incomplete and even scarce. As to the RE–Ag–Sn alloys, phase equilibria in the RE (RE = La, Ce, Pr, Nd, Gd, Dy, Yb) –Ag–Sn [\[3–9\]](#page-5-0) have been reported in the form of isothermal section. Up to now, the phase equilibria in the Ag–Er–Sn system are not yet studied. To extend our knowledge of the RE–Ag–Sn alloys, we aim to determine the phase relationship of the Ag–Er–Sn system in this work.

Massalski [\[10\]](#page-5-0) assessed the Er–Sn system mainly based on two incomplete phase diagrams established by Love [\[11\]](#page-5-0) in composition range from 0 to 33.3 at.% Sn and Kulagina et al. [\[12\]](#page-5-0) from 66.7 to 100 at.% Sn, respectively. According to Massalski [\[10\], fi](#page-5-0)ve intermetallic compounds formed in this system, i.e., $Er₂Sn, Er₅Sn₃$, $Er_{11}Sn_{10}$, $ErSn_{2}$ and $ErSn_{3}$. Palenzona and Manfrinetti [\[13\]](#page-5-0) later identified the existence of $Er₂Sn₅$ when reinvestigating the Snrich part of this system. Except $Er₂Sn$, recent investigations on the Co–Er–Sn [\[14\]](#page-5-0) and Cu–(Sm,Er)–Sn [\[15\]](#page-5-0) ternary systems confirmed the existence of Er_5Sn_3 , $Er_{11}Sn_{10}$, $ErSn_2$, Er_2Sn_5 and $ErSn_3$.

ABSTRACT

The phase equilibria in the Ag–Er–Sn ternary system at $400 °C$ were studied over the whole composition range by means of X-ray diffraction and scan electron microscope and energy dispersive X-ray spectroscopy. A new ternary compound with composition of $Er_{24.6}Ag_{18.9}Sn_{56.5}$, designed τ , and binary phase Er_3Sn_7 had been discovered. The Er_3Sn_7 phase adopts the Tb_3Sn_7 structure type with lattice constants of $a = 0.4377 (1)$ nm, $b = 2.5578 (9)$ nm and $c = 0.4333 (2)$ nm. Other two ternary compounds, i.e., AgErSn₂ and AgErSn, were confirmed, too.

© 2010 Elsevier B.V. All rights reserved.

Three compounds exist in the Ag–Er system: AgEr, AgEr₂ and Ag₅₁E r_{14} [\[16\]. A](#page-5-0)s regarding to the Ag–Sn binary system, two binary compounds, Ag_3Sn and Ag_4Sn , were reported [\[17\].](#page-5-0)

Two ternary compounds were known for the Ag–Er–Sn system, i.e., AgErSn $[18]$ and AgErSn₂ $[19]$. [Table 1](#page-1-0) summarized the crystallographic data of the binary boundary phases and ternary compounds in this system.

2. Experimental procedures

Fifty-five alloy buttons with the weight of 2 g each were prepared by arc-melting the pure elemental Ag (99.9 wt.%), Er (99.9 wt.%) and Sn (99.9 wt.%) under high purity argon atmosphere. To improve the homogeneity, each of the alloys were turned over and remelted for three times. Weight losses for the specimens range from about 1 to 1.5 wt%. No chemical analysis was carried out for the alloys. The ingots were then sealed in evacuated silica capsules, and annealed at 400 ◦C for 30 days. After completion of annealing, the samples were quenched in water with the tubes not broken.

X-ray diffraction (XRD) was performed with Rikagu-2500 diffractometer with CuK α operating at tube voltage of 40 kV and current of 250 mA. The lattice parameters were calculated by using the WinPLOTR program package [\[20\]. M](#page-5-0)icrostructural examination and composition microanalysis were carried out by using Hitachi 3400N scanning electron microscope (SEM) equipped with EDAX energy dispersive spectrometer (EDS).

3. Results and discussion

[Table 2](#page-1-0) summarizes the experimental results of XRD for the selected alloys. Those severely oxidized alloys are rejected in [Table 2. S](#page-1-0)ome off-equilibrium alloys were also collected in [Table 2,](#page-1-0) as they substantiated the existence of some binary or ternary phases. Based on the data available in [Table 2,](#page-1-0) the phase equilibria in Ag–Er–Sn are drawn in [Fig. 1.](#page-3-0) Similar to other M(M = Cu, Ag, Au)–RE–Sn systems, the alloys within or close to the region

[∗] Corresponding author. Tel.: +86 771 3260135; fax: +86 771 3261718. E-mail address: jianlieliang@126.com (J. Liang).

^{0925-8388/\$ –} see front matter © 2010 Elsevier B.V. All rights reserved. doi:[10.1016/j.jallcom.2010.04.148](dx.doi.org/10.1016/j.jallcom.2010.04.148)

Table 1

Crystallographic data of already known binary boundary phases and ternary compounds in the Ag–Er–Sn system.

^a High temperature phase.

^b Low temperature phase.

Table 2

Summary of experimental results of XRD for the selected alloys.

Table 2(Continued)

^a The alloys are off-equilibrium.

 b Ag₃Sn and (Sn) in these alloys resulted from the solidification of liquid during the quench.

of Er_5Sn_3 to $Er_{11}Sn_{10}$ were found sensitive to moisture and oxygen and were readily discarded. For this reason, we could not observe $Er_{11}Sn_{10}$ in the ternary alloys. Thus, the $Er_{11}Sn_{10}$ related tie-triangles are connected with dot line. Single $AgErSn₂$ phase was obtained in alloy 40 ($Ag_{25}Er_{25}Sn_{50}$), and its lattice parameter was calculated to be $a = 0.45095(7)$ nm. For AgErSn₂, its lattice constant was found significant change in alloys 11–14 with the variation of the alloys' composition. The fact implies that there is a small homogeneity for this compound. $Ag_{51}Er_{14}$ and liquid should occupy a certain area considering the adjacent phase relationships. However, no the effort was made to measure the phase boundaries of AgErSn₂ as well as $Ag_{51}Er_{14}$ and liquid. Thus, the boundaries of these phases were drawn tentatively in [Fig. 1. T](#page-3-0)o support the proposed tie triangles, [Figs. 2–5](#page-3-0) present XRD results of several equilibrated alloys.

In the present work, a new ternary compound, designed τ , was found and identified. [Fig. 6](#page-3-0) presents the XRD results of alloys 28

Fig. 1. Phase equilibria of the Ag–Er–Sn ternary system at 400 ◦C. The boundaries of AgErSn₂ and liquid phase and $\overline{Ag_{51}E_{14}}$ are tentative.

Fig. 2. XRD result of alloy 4 annealed at 400 ◦C for 30 days, showing the co-existence of AgErSn and (Ag) and Ag₅₁Er₁₄.

 $(Ag_{20}Er_{20}Sn_{60})$, 30 $(Ag_{20}Er_{22}Sn_{58})$ and 32 $(Ag_{28}Er_{20}Sn_{52})$, where the intense peaks labeled in full circle were identified as $\tau.$ The peak positions in two-theta attributed to this new ternary compound are listed as follows: 34.20◦, 36.45◦, 41.26◦, 56.27◦, 59.83◦, 64.28◦, 70.80° and 72.17°. However, except (Sn) and Ag₃Sn, there are many

Fig. 3. XRD result of alloy 11 annealed at 400 ◦C for 30 days, showing the coexistence of AgErSn₂ and AgErSn and ErSn₂.

Fig. 4. XRD result of alloy 23 annealed at 400 ℃ for 30 days, showing the coexistence of AgErSn₂ and AgErSn and Ag₃Sn.

Fig. 5. XRD result of alloy 7 annealed at 400 ◦C for 30 days, showing the co-existence of Ag₂Er and Er₅Sn₃.

unidentified weak peaks in Fig. 6. To clarify the composition of this new ternary compound, alloy 32 $(Ag_{28}Er_{20}Sn_{52})$ was subjected to SEM/EDS examination. Matrix τ phase and Ag₃Sn and (Sn) were observed in this alloy. The composition of τ was measured to be of 24.6 at.% Ag, 18.9 at.% Er and 56.5 at.% Sn, while that of Ag₃Sn was 73.6 at.% Ag, 1.1 at.% Er and 25.3 at.% Sn. In order to synthesize this compound, several other alloys, such as alloys $37 (Ag_{20}Er_{25}Sn_{55})$, 38 $(Ag_{20}Er_{27}Sn_{53})$ and 39 $(Ag_{18}Er_{27}Sn_{55})$, were melted and annealed

Fig. 6. The XRD results of alloys 28 $(Ag_{20}Er_{20}Sn_{60})$, 30 $(Ag_{20}Er_{22}Sn_{58})$ and 32 $(Ag_{28}Er_{20}Sn_{52})$. Except those of (Sn) and Ag₃Sn, peaks labeled in full circle were identified as to the new ternary compound τ .

Fig. 7. XRD patterns of alloy 37 (Ag₂₀Er₂₅Sn₅₅) annealed at 400 and 500 °C, respectively.

at 400 \degree C for 7 days. Due to the segregation of (Sn), we failed to obtain single ternary compound $\tau.$

The new ternary compound τ was found to disappear when the alloy was annealed at 500 \degree C for 7 days followed by water quenching. Fig. 7 compares the XRD results of alloy 37 $(Ag_{20}Er_{25}Sn_{55})$ heated at 400 and 500 $^{\circ}$ C, respectively. As shown in Fig. 7, new ternary phase τ and (Sn) and Ag $_3$ Sn as well as trace amount of Er₂O₃ co-exist in the alloy heated at 400 \degree C. When temperature rises to 500 \circ C, Ag₃Sn and those peaks attributed to the new ternary compound as well as the unknown weak peaks vanished with the formation of AgErSn_{2.} This fact suggested that those unknown weak peaks mentioned above might belong to τ phase, as shown in Fig. 7.

X-ray patterns similar to Tb_3Sn_7 were observed in several ternary alloys, which implied that Er_3Sn_7 might form in the Er-Sn side. Fig. 8 presents the XRD results of alloys 1 $(Ag_{25}Er_{10}Sn_{65})$ and 16 ($Ag_{10}Er_{20}Sn_{70}$), where the peaks labeled in full circle are attributed to Er_3Sn_7 . By assuming Er_3Sn_7 isostructural to Tb_3Sn_7 , fair agreement in the calculated and observed peak intensities was obtained. Therefore, Er_3Sn_7 was believed to exist in the Er–Sn system. This conclusion is in contradiction to the results of Palen-zona and Manfrinetti [\[13\],](#page-5-0) in which $RE₃Sn₇$ type phases were excluded in (Er, Ho, Tm, Lu)–Sn systems but included in (Gd, Tb, Dy, Y)–Sn systems. The cell parameters of $Er₃Sn₇$ are calculated to be $a = 0.4377$ (1) nm, $b = 2.5578$ (9) nm and $c = 0.4333$ (2) nm in alloy 1 ($Ag_{25}Er_{10}Sn_{65}$). As shown in Fig. 8, alloy 16 ($Ag_{10}Er_{20}Sn_{70}$)

Fig. 8. The XRD results of alloys 16 ($Ag_{10}Er_{20}Sn_{70}$) and 1 ($Ag_{25}Er_{10}Sn_{65}$) annealed at 400 °C for 30 days followed by water quenching. Alloy 16 ($Ag_{10}Er_{20}Sn_{70}$) is composed of Er₂Sn₅, Er₃Sn₇, Ag₃Sn and (Sn), while alloy 1 (Ag₂₅Er₁₀Sn₆₅) consists of Er₃Sn₇, Ag₃Sn and (Sn). The latter two phases are the liquid products during the solidification.

Fig. 9. XRD results of alloy 18 ($Er_{27}Sn_{73}$) annealed at (1) 700 °C for 30 days and (2) further annealed at 400 °C for 7 days.

is composed of Er_2Sn_5 , Er_3Sn_7 , Ag_3Sn and (Sn), while alloy 1 $(Ag_{25}Er_{10}Sn_{65})$ consists of Er_3Sn_7 , Ag₃Sn and (Sn). The latter two phases are the liquid products during the solidification.

Alloys 18 ($Er_{27}Sn_{73}$) and 19 ($Er_{30}Sn_{70}$) were prepared to verify the existence of Er_2Sn_5 . Er_3Sn_7 was thought to form through peritectic reaction at a temperature higher than that of $Er₂Sn₅$. Alloy 19 was expected to consist of single Er_3Sn_7 or $(Er_3Sn_7 + Er_2Sn_5)$, if the practical composition of alloy only slightly deviated from the nominal composition. Thus, a higher annealing temperature 700 \degree C was arbitrarily chosen for these two alloys for the first time. Apart from $Er₂Sn₅$ and Sn, XRD detected additional trace amount of $Ersn₂$ for alloy 19 ($Ers₃₀sn₇₀$) and orthorhombic $Ersn₃$ for alloy 18 ($Er_{27}Sn_{73}$), after annealed at 700 °C for 30 days followed by air-cooling. When both alloys were re-heated at 400 ◦C for 7 days and followed by water quenching, alloy 19 ($Er_{30}Sn_{70}$) was observed to consist of $Er₂Sn₅$ and $ErSn₂$ with (Sn) almost vanished, while alloy 18 ($Er₂₇Sn₇₃$) consisted of $Er₂Sn₅$ and (Sn) with ErSn₃ thoroughly disappeared. Fig. 9 presents the XRD results of alloy 18 ($Er₂₇Sn₇₃$). $Er₂Sn₅$ was reported to adopt the Y₂Sn₅ crystal structure [\[13\]. H](#page-5-0)owever, we could not find the crystal structural data of Y_2 Sn₅ in the public literature. Recently, Venturini et al. determined the crystal structure of $Er₂Ge₅$ (space group, Pmmn) [\[21\].](#page-5-0) We thought that $Er₂Sn₅$ might be isostructural to $Er₂Ge₅$. Thus, substituting Sn into the positions of Ge, the XRD pattern of $Er₂Sn₅$ was calculated by using the Powdercell program $[22]$. Comparing the calculated patterns, $Er₂Sn₅$ was found to show strong preferred orientation in all the investigated alloys. As shown in Fig. 9, the (007) peak was observed to be the most intense while the theoretical strongest peak (1 1 3) to be the third intense.

Palenzona and Manfrinetti [\[13\]](#page-5-0) indicated that the $RSn₂$ compounds showed very high stability, and could not be destroyed by annealing treatment unless remelting the alloy. This suggestion might be right for the binary alloys. However, for the ternary alloys, the suggestion might be questionable. In the present work, $ErSn₂$ and cubic-AgErSn₂ as well as (Sn) and Ag₃Sn were observed in the as-cast alloy 28 ($Ag_{20}Er_{20}Sn_{60}$). When this alloy is subjected to annealing at 400 \degree C for 20 days, ErSn₂ and cubic-AgErSn₂ vanished and the new ternary compound τ formed.

4. Conclusions

Phase equilibria of the Ag–Er–Sn ternary system were determined. Two new compounds, i.e., Er_3Sn_7 and τ , were identified for the first time. The Er_3Sn_7 phase crystallizes in Tb_3Sn_7 structure type with cell parameters of $a = 0.4377$ (1) nm, $b = 2.5578$ (9) nm

and c = 0.4333 (2) nm. The compositions of τ were measured to be of 24.6 at.% Ag, 18.9 at.% Er and 56.5 at.% Sn.

Acknowledgements

Financial supports from the Guangxi Science Foundation (Contract Nos. 0448022, 0542009 and 0640040), and Guangxi Large Scale Apparatus Corporation Office are greatly appreciated.

References

- [1] Z.K. Liu, L.Q. Chen, P. Raghavan, Q. Du, J.O. Sofo, S.A. Langer, C. Wolverton, J. Comput. Aided Mater. Des. 11 (2004) 183–199.
- [2] J.Z. Zhu, Z.K. Liu, V. Vaithyanathan, L.Q. Chen, Scripta Mater. 46 (2002) 401– 406.
- [3] J. Liang, C. Lian, Y. Du, Y. Tang, Y. Han, Y. He, S. Liu, J. Alloys Compd. 493 (2010) 122–127.
- [4] P. Boulet, D. Mazzone, H. Noël, P. Riani, P. Rogl, R. Ferro, Intermetallics 7 (1999) 931–935.
- [5] D. Mazzone, P. Riani, G. Zanicchi, R. Marazza, R. Ferro, Intermetallics 10 (2002) 801–809.
- [6] P. Salamakha, O. Zaplatynsky, O. Sologub, O. Bodak, J. Alloys Compd. 239 (1996) 94–97.
- [7] J.L. Liang, Y. Du, Y.Y. Tang, C.Z. Liao, J.L. Meng, H.H. Xu, J. Alloys Compd. 481 (2009) 264–269.
- [8] V.V. Romaka, A. Tkachuk, V. Davydov, J. Alloys Compd. 439 (2007) 128–131.
- [9] G. Zanicchi, D. Mazzone, P. Riani, R. Marazza, R. Ferro, J. Alloys Compd. 317–318 (2001) 513–520.
- [10] T.B. Massalski, Binary Alloy Phase Diagrams, 2nd ed., ASM International, Metals Park, OH, 1990.
- B. Love, WADD Tech. Rep. 60-74, 1960, p. 226.
- [12] I.G. Kulagina, A.P. Bayanov, N.M. Kulagin, Izv. Akad. Nauk SSSR, Met. 3 (1985) 211–216 (in Russian).
- [13] A. Palenzona, P. Manfrinetti, J. Alloys Compd. 201 (1993) 43–47.
- [14] R.V. Skolozdra, Ya.S. Mudryk, L.P. Romaka, J. Alloys Compd. 296 (2000) 290– 292.
- [15] I.V. Senkovska, Ya.S. Mudryk, L.P. Romaka, O.I. Bodak, J. Alloys Compd. 312 (2000) 124–129.
- [16] K.A. Gschneidner, F.W. Calderwood, J. Phase Equilibr. 6 (1985) 17–19.
- [17] I. Karakaya, W.T. Thompson, J. Phase Equilibr. 8 (1987) 340–347.
- [18] P. Villar, Pearson's Handbook, Desk ed., ASM International, Materials Park, OH, 1997.
- [19] V.V. Romaka, V. Davydov, L. Romaka, Yu. Stadnyk, J. Alloys Compd. 457 (2008) 329–331.
- [20] T. Roisel, J. Rodriguez-Carvajal, WinPLOTR: A windows tool for powder diffraction patterns analysis, http://www-llb.cea.fr/fullweb/winplotr/winplotr.htm.
- [21] G. Venturini, I. Ijjaali, B. Malaman, J. Alloys Compd. 288 (1999) 183–187. W. Krau, G. Nolze, Powdercell, Available in: http://www.ccp14.ac.uk/ccp/webmirrors/powdcell/a v/v 1/powder/e cell.html.