

# Phase Equilibria in the Al-Sn-Co Ternary System

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Abstract The isothermal sections of the Al-Sn-Co ternary system at 800 °C and 1000 °C were constructed by twentynine key samples and two solid-liquid diffusion couples using electron probe microanalysis and x-ray diffraction analysis. The results show that: (1) No ternary intermetallic compound was found in this ternary system at 800 °C and 1000 °C. (2) The solid solubility of Sn in the Al-Co binary compounds is very small. (3) As-cast Al<sub>47</sub>Sn<sub>47</sub>Co<sub>6</sub>, Al<sub>46-</sub> Sn<sub>46</sub>Co<sub>8</sub> and Al<sub>45</sub>Sn<sub>45</sub>Co<sub>10</sub> (at.%) alloys exhibit the separated macroscopic morphologies. The reason is that the addition of Co can significantly promote the metastable liquid-phase separation in Al-Sn binary system. The newly determined phase equilibria may contribute to thermodynamic assessment and development of Al-based alloys.

**Keywords** Al-Sn-Co · phase diagram · phase equilibria · liquid miscibility gap

# **1** Introduction

Aluminum-water reaction is a cheap, effective, environment-friendly and safe method of preparing hydrogen.<sup>[1–3]</sup> Al-based alloys milled with low-melting-point metals<sup>[4–6]</sup>

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<sup>2</sup> State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Shenzhen 518005, People's Republic of China and other active metals<sup>[7–9]</sup> have good hydrogen production properties. Recently, using self-assembling egg-type powders with core/shell microstructure induced by liquid miscibility gap,<sup>[10]</sup> Wang et al. reported that a kind of selfassembling powder has better activity to generate  $H_2$ .<sup>[11]</sup> Al-Sn binary system has metastable liquid miscibility gap over a wide composition range, which is a good candidate for further optimizing of self-assembling powders.<sup>[12]</sup>

In practical application, the aim of adding the third element is to control the formation of some special macroscopic and microscopic morphologies of powders, because the third element can enhance or reduce the extent of liquid phase separation.<sup>[13,14]</sup> For example, in Al-Bi-Sn ternary system, Bi additions to the Al-Sn binary system can significantly promote the metastable liquid miscibility gap.<sup>[15]</sup> It is possible that the Co, Cu, Fe, Ni and other element additions may have an influence on liquid phase separation in Al-Sn binary system. In addition, according to the literature,<sup>[16]</sup> the addition of Co can significantly improve the production of hydrogen in Al-H<sub>2</sub>O reaction. Thus it is of great importance to obtain a clear understanding of the Al-Sn-Co ternary phase equilibria.

Three corresponding binary systems Al-Sn,<sup>[15,17–21]</sup> Al-Co<sup>[22–25]</sup> and Co-Sn<sup>[26–28]</sup> have been well investigated. Liu et al.<sup>[15]</sup> reported experimental investigation and thermodynamic calculation in Al-Bi-Sn ternary system. And there is metastable liquid miscibility gap in Al-Sn binary system. Stein et al.<sup>[23]</sup> updated thermodynamic description of Al-Co system which exhibits five stable compounds (AlCo, Al<sub>5</sub>Co<sub>2</sub>, Al<sub>3</sub>Co, Al<sub>13</sub>Co<sub>4</sub> and Al<sub>9</sub>Co<sub>2</sub>). Liu et al.<sup>[26]</sup> made thermodynamic assessment of Co-Sn binary system, where there are three stable compounds (Co<sub>3</sub>Sn<sub>2</sub>, CoSn and CoSn<sub>2</sub>). Three binary phase diagrams of Al-Sn, Al-Co and Co-Sn constituting the Al-Sn-Co ternary system are shown in Fig. 1. Information on the stable solid phases and crystal

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Fig. 1 Binary phase diagrams constituting the Al-Sn-Co ternary system<sup>[16,23,26]</sup>

**Table 1** Stable solid phases in<br/>the three binary systems [21,25,28]

System	Phase	Phase symbol	Prototype	Strukturbericht	Space group	References
Al-Sn	(Al)	cF4	Cu	A1	Fm-3 m	20
	(BSn)	tI4	βSn	A5	I4 <sub>1</sub> /amd	20
Al-Co	(aCo)	cF4	Cu	A1	Fm-3 m	24
	(eCo)	hP2	Mg	A3	P6 <sub>3</sub> /mmc	24
	AlCo	cP2	CsCl	$B_2$	<i>Pm-3 m</i>	24
	Al <sub>5</sub> Co <sub>2</sub>	hP28	Al <sub>5</sub> Co <sub>2</sub>	D811	P6 <sub>3</sub> /mmc	24
	Al <sub>3</sub> Co					24
	Al <sub>13</sub> Co <sub>4</sub>	oP102	Al <sub>13</sub> Co <sub>4</sub>		$Pmn2_1$	24
	Al <sub>9</sub> Co <sub>2</sub>	mP22	Al <sub>9</sub> Co <sub>2</sub>		$P2_l/a$	24
Co-Sn	(aCo)	cF4	Cu	A1	Fm-3 m	27
	(eCo)	hP2	Mg	A3	P6 <sub>3</sub> /mmc	27
	(BSn)	tI4	βSn	A5	I4 <sub>1</sub> /amd	27
	$\alpha Co_3 Sn_2$	oP20	Ni <sub>3</sub> Sn <sub>2</sub>		Pnma	27
	$\beta Co_3 Sn_2$	hP6	Ni <sub>2</sub> In	B82	P6 <sub>3</sub> /mmc	27
	CoSn	hP6	CoSn		P6/mmm	27
	CoSn <sub>2</sub>	<i>tI</i> 12	CuAl <sub>2</sub>	C16	I4/mcm	27

structures in three binary systems are summarized in Table 1.<sup>[21,25,28]</sup> However, there is no information about Al-Sn-Co ternary system in the relevant literature.

The purpose of this work is to experimentally investigate phase equilibria in the Al-Sn-Co ternary system at 800 and 1000 °C. The results acquired in the present work are expected to contribute to the available thermodynamic and phase diagram information to enable more extensive application of this system.

## **2** Experimental Procedures

In order to obtain phase relations, twenty-nine key samples together with two solid–liquid diffusion couples were prepared. The diffusion couple is a powerful and efficient technique for mapping the phase diagrams of ternary systems.<sup>[29–31]</sup> Within diffusion layers the equilibrium phases occur, whereas local equilibria take place at the interface. However, it is possible that phases may be missed by the

βCo<sub>3</sub>Sn 30un  $(\mathbf{d})$ AlCo βCo<sub>3</sub>Sn<sub>2</sub> CoSn )µm Al<sub>3</sub>Co 0um 30um

**Fig. 2** Typical ternary BSE images obtained from: (a)  $Al_{34}Sn_{10}Co_{56}$  alloy annealed at 800 °C for 30 days; (b)  $Al_{40}Sn_6Co_{54}$  alloy annealed at 800 °C for 30 days; (c)  $Al_8Sn_{40}Co_{52}$  alloy annealed at 800 °C for 30 days; (d)  $Al_{25}Sn_{30}Co_{45}$  alloy annealed at 800 °C for 4 days; (e)  $Al_{71}Sn_4Co_{25}$  alloy annealed at 800 °C for 4 days; (f)  $Al_{76}Sn_4Co_{20}$  alloy annealed at 800 °C for 4 days; diffusion couple for determining the phase diagram.<sup>[31,32]</sup> Because slow nucleation of the phase can prevents formation of the diffusion layer. In order to obtain more reliable information, Kodentsov et al.,<sup>[31]</sup> among others, suggested combining key sample analysis with the diffusion couple method. Therefore, two technologies were used in the present work.

The buttons of the key samples were melted from 99.99 wt.% Al and 99.99 wt.% Sn and 99.99 wt.% Co in an argon arc furnace, using a nonconsumable tungsten electrode. In order to achieve homogeneity, the ingots were melted four times. After each melt, ingots were reversed to promote mixing. The sample weight was around 15 g and the

weight loss during melting was generally < 0.20% of the sample weight. Then ingots of alloys were cut into small pieces which are about 2 g. After wrapped in tantalum foil, specimens were sealed into silica tubes under purified Ar gas. Specimens were annealed at 800 °C and 1000 °C for different time. The annealing time depends on the annealing temperature and the composition of specimens. Then specimens were quenched into ice water. Solid–liquid diffusion couples were prepared from two end-members of pure Co and Al<sub>50</sub>Sn<sub>50</sub> (at.%) which were prepared in argon arc furnace. Then the button of Co was cut into cubes with a volume of  $4 \times 4 \times 7$  mm<sup>3</sup>. After standard metallographic preparation, Co and Al<sub>50</sub>Sn<sub>50</sub> (at.%) were put into

Fig. 3 Typical ternary BSE images obtained from: (a) Al<sub>3</sub>Sn<sub>7</sub>Co<sub>90</sub> alloy annealed at 1000 °C for 15 days; (b) Al<sub>19</sub>Sn<sub>1</sub>Co<sub>80</sub> alloy annealed at 1000 °C for 15 days; (c) Al<sub>22</sub>Sn<sub>5</sub>Co<sub>73</sub> alloy annealed at 1000 °C for 15 days; (d) Al<sub>25</sub>Sn<sub>30</sub>Co<sub>45</sub> alloy annealed at 1000 °C for 2 days; (e) Al<sub>55</sub>Sn<sub>11</sub>Co<sub>34</sub> alloy annealed at 1000 °C for 2 days; (f) Al<sub>70</sub>Sn<sub>7</sub>Co<sub>23</sub> alloy annealed at 1000 °C for 2 days



the alumina crucible. Crucibles wrapped in sealed silica tubes under purified Ar gas were annealed at 800 °C for 40 min and at 1000 °C for 20 min. After quenching in ice water, samples were cut from the middle for observation. Solid–liquid diffusion couples of Co/Al<sub>50</sub>Sn<sub>50</sub> annealed at 800 °C for 40 min and Co/Al<sub>50</sub>Sn<sub>50</sub> annealed at 1000 °C for 20 min are denoted as diffusion couple 1 and diffusion couple 2, respectively.

standard metallographic After preparation, the macrostructural observations were carried out by high resolution camera. The equilibrium compositions of the phases and microstructural observations were measured by electron probe microanalysis (EPMA) (JXA-8100R, JEOL, Japan). Pure elements were used as standards and the measurements were carried out at 20.0 kV and  $1.0 \times 10^{-8}$  mA. Energy Dispersive Spectrometer (EDS) was used to determine the compositions of the liquid phase. The liquid phase was measured by EDS analysis at least 10 times. Then the data was averaged. The x-ray diffraction (XRD) was used to identify the constituent phases. The XRD measurement was carried out on a Phillips Panalytical X-pert diffractometer using Cu K<sub>a</sub> radiation at 40.0 kV and 40 mA. The data were collected in the range of  $2\theta$ from  $10^{\circ}$  to  $90^{\circ}$  at a step with of  $0.0167^{\circ}$ .

## **3** Results and Discussion

#### 3.1 Microstructure

Figure 2 and 3 show the BSE (back-scattered electron) images of typical ternary Al-Sn-Co alloys. Phase identification depends on equilibrium compositions and XRD results. All the mentioned chemical compositions in this work were given in form of atomic ratio (at.%). The L in this work means liquid phase. In Fig. 2(a, b), there are two two-phase equilibria of AlCo +  $\beta$ Co<sub>3</sub>Sn<sub>2</sub> and AlCo + CoSn that were found in alloys Al<sub>34</sub>Sn<sub>10</sub>Co<sub>56</sub> and Al<sub>40-</sub> Sn<sub>6</sub>Co<sub>54</sub> annealed at 800 °C for 30 days. The EPMA results indicated that  $\beta Co_3 Sn_2$  and CoSn are matrices where AlCo is distributed in them. As illustrated in Fig. 2(c, d), two three-phase equilibria of AlCo  $(black) + \beta Co_3 Sn_2 (dark gray) + CoSn (light gray) and$ AlCo (black) + CoSn (gray) + L (white) were detected in alloy Al<sub>8</sub>Sn<sub>40</sub>Co<sub>52</sub> annealed at 800 °C for 30 days and alloy Al<sub>25</sub>Sn<sub>30</sub>Co<sub>45</sub> annealed at 800 °C for 4 days, respectively. Figure 2(e) illustrates that three-phase equilibrium of  $Al_5Co_2 + Al_3Co + L$  existed in alloy

Al<sub>71</sub>Sn<sub>4</sub>Co<sub>25</sub> annealed at 800 °C for 4 days, which was confirmed by the XRD result shown in Fig. 4(a). As can be seen from the Fig. 2(e), the black phase is Al<sub>3</sub>Co, the gray one is Al<sub>5</sub>Co<sub>2</sub> and the rest is liquid (*L*). All phases' diffraction peaks show good consistency and characteristic peaks of liquid phase originate from the Sn-rich phase. In addition, the microstructure of Al<sub>13</sub>Co<sub>4</sub> + Al<sub>9</sub>Co<sub>2</sub> + *L* in alloy Al<sub>76</sub>Sn<sub>4</sub>Co<sub>20</sub> annealed at 800 °C for 4 days is shown in Fig. 2(f) and substantiated by XRD result as shown in



**Fig. 4** X-ray diffraction patterns obtained from: (a)  $Al_{71}Sn_4Co_{25}$  alloy annealed at 800 °C for 4 days; (b)  $Al_{76}Sn_4Co_{20}$  alloy annealed at 800 °C for 4 days; (c)  $Al_{25}Sn_{30}Co_{45}$  alloy annealed at 1000 °C for 2 days; (d)  $Al_{55}Sn_{11}Co_{34}$  alloy annealed at 1000 °C for 2 days

Fig. 4(b). Two two-phase equilibria of  $\alpha Co + \beta Co_3 Sn_2$ and  $\alpha Co + AlCo$  were detected in alloys  $Al_3Sn_7Co_{90}$  and  $Al_{19}Sn_1Co_{80}$  in Fig. 3(a, b). As shown in Fig. 2(a), the  $\beta Co_3 Sn_2$  is gray matrix where the  $\alpha Co$  (black) is uniformly distributed. In Fig. 3(c), there is a three-phase microstructure of  $\alpha Co$  (gray) + AlCo (black) +  $\beta Co_3 Sn_2$ 

Table 2	Equilibrium	compositions	of the	Al-Sn-Co	ternary s	system	determined	in the	present	work
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T, ℃	Alloy, at.%	Annealed time	Phase equilibria Phase 1/Phase 2/Phase 3	Composition, at.%						
				Phase 1		Phase 2		Phase 3		
				Sn	Со	Sn	Co	Sn	Co	
800	Al <sub>3</sub> Sn <sub>7</sub> Co <sub>90</sub>	30 days	$\alpha Co/\beta Co_3 Sn_2$	1.6	94.8	37.9	61.1			
	$Al_{19}Sn_1Co_{80}$	30 days	$\alpha$ Co/AlCo/ $\beta$ Co <sub>3</sub> Sn <sub>2</sub>	0.5	91.7	0.7	61.0	37.3	61.5	
	Al <sub>29</sub> Sn <sub>12</sub> Co <sub>59</sub>	30 days	AlCo/BCo3Sn2	0.8	57.5	38.8	60.0			
	$Al_{34}Sn_{10}Co_{56}$	30 days	AlCo/BCo3Sn2	0.6	55.3	39.3	59.5			
	$Al_8Sn_{40}Co_{52}$	30 days	AlCo/BCo3Sn2/CoSn	1.8	54.8	40.0	58.1	49.8	49.5	
	Al <sub>40</sub> Sn <sub>6</sub> Co <sub>54</sub>	30 days	AlCo/CoSn	0.6	54.0	49.4	49.1			
	Al <sub>25</sub> Sn <sub>30</sub> Co <sub>45</sub>	4 days	AlCo/CoSn/L	0.4	50.6	49.5	49.9	96.2	3.0	
	$Al_{44}Sn_{14}Co_{42}$	4 days	AlCo/L	0.2	48.2	97.6	1.3			
	Al <sub>55</sub> Sn <sub>11</sub> Co <sub>34</sub>	4 days	AlCo/Al <sub>5</sub> Co <sub>2</sub> /L	0.3	46.9	0.1	27.4	96.0	1.1	
	Al <sub>71</sub> Sn <sub>4</sub> Co <sub>25</sub>	4 days	Al <sub>5</sub> Co <sub>2</sub> /Al <sub>3</sub> Co/L	0.1	27.7	0.1	25.3	94.0	1.7	
	Al <sub>76</sub> Sn <sub>4</sub> Co <sub>20</sub>	4 days	Al13Co4/Al9Co2/L	0.1	23.9	0.2	18.3	93.1	1.6	
	Al <sub>48</sub> Sn <sub>48</sub> Co <sub>4</sub>	4 h	Al <sub>9</sub> Co <sub>2</sub> /L	0.1	17.8	56.6	0.4			
	Al <sub>81</sub> Sn <sub>5</sub> Co <sub>14</sub>	4 h	Al <sub>9</sub> Co <sub>2</sub> /L	0.1	17.2	20.7	0.5			
	Al <sub>87</sub> Sn <sub>2</sub> Co <sub>11</sub>	4 h	Al <sub>9</sub> Co <sub>2</sub> /L	0.1	17.6	5.1	0.4			
	Co/Al <sub>50</sub> Sn <sub>50</sub>	40 min	AlCo/L	0.4	48.7	98.1	1.2			
			Al <sub>5</sub> Co <sub>2</sub> /L	0.3	26.9	96.0	1.6			
			Al <sub>3</sub> Co/L	0.4	25.2	95.5	1.5			
			Al <sub>13</sub> Co <sub>4</sub> /L	0.5	23.7	94.9	1.2			
			Al <sub>9</sub> Co <sub>2</sub> /L	0.1	17.7	95.1	0.9			
1000	Al <sub>3</sub> Sn <sub>7</sub> Co <sub>90</sub>	15 days	$\alpha Co/\beta Co_3 Sn_2$	1.7	94.8	37.9	61.7			
	Al <sub>6</sub> Sn <sub>9</sub> Co <sub>85</sub>	15 days	$\alpha Co/\beta Co_3 Sn_2$	1.7	90.9	37.0	62.1			
	Al <sub>22</sub> Sn <sub>5</sub> Co <sub>73</sub>	15 days	$\alpha$ Co/AlCo/ $\beta$ Co <sub>3</sub> Sn <sub>2</sub>	1.4	86.7	1.4	66.5	34.3	62.8	
1000	Al <sub>19</sub> Sn <sub>1</sub> Co <sub>80</sub>	15 days	αCo/AlCo	1.1	86.9	0.8	65.5			
	Al <sub>15</sub> Sn <sub>22</sub> Co <sub>63</sub>	15 days	AlCo/βCo <sub>3</sub> Sn <sub>2</sub>	1.0	66.2	35.2	62.0			
	Al <sub>33</sub> Sn <sub>5</sub> Co <sub>62</sub>	15 days	AlCo/βCo <sub>3</sub> Sn <sub>2</sub>	0.7	62.4	35.9	61.0			
	Al <sub>29</sub> Sn <sub>12</sub> Co <sub>59</sub>	15 days	AlCo/βCo <sub>3</sub> Sn <sub>2</sub>	0.6	59.0	37.6	60.0			
	Al <sub>34</sub> Sn <sub>10</sub> Co <sub>56</sub>	15 days	AlCo/βCo <sub>3</sub> Sn <sub>2</sub>	0.8	55.1	37.9	59.5			
	Al <sub>25</sub> Sn <sub>30</sub> Co <sub>45</sub>	2 days	AlCo/βCo <sub>3</sub> Sn <sub>2</sub> /L	0.5	51.4	39.4	58.7	86.7	12.8	
	Al40Sn21Co39	2 days	AlCo/L	0.2	49.2	94.8	1.9			
	Al <sub>55</sub> Sn <sub>11</sub> Co <sub>34</sub>	2 days	AlCo/Al5Co2/L	0.1	46.7	0.1	27.6	94.9	1.2	
	Al <sub>70</sub> Sn <sub>7</sub> Co <sub>23</sub>	2 days	Al <sub>5</sub> Co <sub>2</sub> /Al <sub>3</sub> Co/L	0.1	27.1	0.1	24.7	93.9	1.3	
	Al <sub>48</sub> Sn <sub>48</sub> Co <sub>4</sub>	2 h	Al <sub>13</sub> Co <sub>4</sub> /L	0.1	24.0	53.2	0.6			
	Al <sub>57</sub> Sn <sub>40</sub> Co <sub>3</sub>	2 h	Al <sub>13</sub> Co <sub>4</sub> /L	0.1	23.6	42.9	0.9			
	Al <sub>81</sub> Sn <sub>5</sub> Co <sub>14</sub>	2 h	Al <sub>13</sub> Co <sub>4</sub> /L	0.1	24.5	7.4	9.6			
	Co/Al <sub>50</sub> Sn <sub>50</sub>	20 min	AlCo/L	0.3	49.4	90.7	8.8			
			Al <sub>5</sub> Co <sub>2</sub> /L	0.5	27.3	95.1	1.3			
			Al <sub>3</sub> Co/L	0.4	25.2	94.3	1.2			
			Al <sub>13</sub> Co <sub>4</sub> /L	0.4	23.4	94.0	1.0			





(white) in alloy Al<sub>22</sub>Sn<sub>5</sub>Co<sub>73</sub> that was annealed at 1000 °C for 15 days. Two three-phase microstructures of  $AlCo + \beta Co_3Sn_2 + L$  and  $AlCo + Al_5Co_2 + L$  were found in alloys Al<sub>25</sub>Sn<sub>30</sub>Co<sub>45</sub> and Al<sub>55</sub>Sn<sub>11</sub>Co<sub>34</sub> annealed at 1000 °C for 2 days, respectively (Fig. 3d, e). And the XRD results show very good consistency in Fig. 4(c, d). As similar to the previously discussed alloy Al71Sn4Co25 annealed at 800 °C, these characteristic peaks of liquid



**Fig. 7** (a) BSE images of diffusion couple 1; (b) Magnified area of "A" in (a); (c) Magnified area of "B" in (a)

phases also originate from the Sn-rich phase. As shown in Fig. 3(f), three-phase equilibrium of  $Al_5Co_2$  (gray) +  $Al_3Co$  (black) + L (white) was discovered in the alloy  $Al_{70}Sn_7Co_{23}$  annealed at 1000 °C for 2 days. Since the average atomic numbers of  $Al_5Co_2$  and  $Al_3Co$  are approximate, their colors are also very similar.

#### 3.2 Isothermal Section

Equilibrium compositions of the Al-Sn-Co ternary system in the present study at 800 °C and 1000 °C determined by EPMA are listed in Table 2. According to the experimental data, two isothermal sections at 800 °C and 1000 °C are shown in Fig. 5 and 6. Six three-phase regions of  $\alpha Co + AlCo + \beta Co_3 Sn_2$ , AlCo +  $\beta$ Co<sub>3</sub>Sn<sub>2</sub> + CoSn, AlCo + CoSn + L,  $AlCo + Al_5Co_2 + L$ ,  $Al_5Co_2 + Al_{3-2}$ Co + L and  $Al_{13}Co_4 + Al_9Co_2 + L$  were experimentally determined at 800 °C. Four three-phase regions of  $\alpha Co + AlCo + \beta Co_3 Sn_2$ , AlCo +  $\beta$ Co<sub>3</sub>Sn<sub>2</sub> + L,  $AlCo + Al_5Co_2 + L$  and  $Al_5Co_2 + Al_3Co + L$  were also obtained at 1000 °C. It can be seen from Fig. 5 that there was small solid solubility of Sn in the Al-Co binary compounds at 800 °C. The solubility of Sn in aCo and AlCo phases was measured to be about 1.6 at.% and 1.8 at.%, respectively. The solubility of Sn in Al<sub>5</sub>Co<sub>2</sub>, Al<sub>3</sub>Co, Al<sub>13</sub>. Co<sub>4</sub> and Al<sub>9</sub>Co<sub>2</sub> was almost negligible. In addition, the solubility of Al in  $\beta$ Co<sub>3</sub>Sn<sub>2</sub> and CoSn was measured to be about 1.9 at.% and 0.7 at.%, respectively. Compared the isothermal section at 1000 °C with that at 800 °C, the solubility of Sn in Al-Co binary compounds and the solubility of Al in Co-Sn binary compounds were also small. At 800 and 1000 °C, both isothermal sections have large liquid regions. With increasing temperature, the solubility of Co in liquid phase increases in Al-rich corner.

When the phase equilibrium was constructed in Al-rich corner at 800 °C, the three-phase region of Al<sub>3</sub>. Co + Al<sub>13</sub>Co<sub>4</sub> + *L* was not determined by key sample because of the small range. Besides this reason, compositions of as-cast alloys that are in the small three-phase region were in the region of phase separation. There is also a three-phase region of Al<sub>3</sub>Co + Al<sub>13</sub>Co<sub>4</sub> + *L* that was not determined in the isothermal section at 1000 °C by key samples.

## 3.3 Solid–Liquid Diffusion Couples

Two diffusion couples were prepared. BSE images of diffusion couple 1 are shown in Fig. 7. During the heat treatment, extensive interdiffusion among Al, Sn and Co took place resulting in the formation of various equilibrium phases. It is very difficult to obtain a better diffusion layer due to the formation of cracks and uncontrolled diffusion time during the heat treatment. Usually, the use of diffusion couples in phase diagram studies is based on the assumption of local equilibrium at the phase interfaces. The solid– liquid diffusion is more complex because the diffusion of liquid phase is very quick thus it is difficult to find out the





proper time so that all liquid has diffused into the solid. But when the annealing time is proper, every diffusion layer could be treated as local two-phase equilibrium. In this study, each layer was considered to be local two-phase equilibrium. The WDS line scans were used to determine solubility ranges and phase equilibria. For liquid phase, surface analysis by EDS along the line scan was used to determine the solubility ranges. As shown in Fig. 8, the composition profile of diffusion couple 1 was described according to the data that have good consistency in line scan. The same approach was also used to study diffusion couple 2. Figure 7(a) is the microstructure of diffusion couple 1. There are five diffusion layers in diffusion couple 1. Diffusion layers containing three phases are impossible in a ternary system. The reason follows directly from the phase rule. In binary system, three degrees of freedom are required to fix temperature and pressure and vary the composition. Reaction morphologies consisting of twophase structures are, therefore, thermodynamically forbidden for binary system, assuming that only volume-diffusion take place. In ternary system, it is possible to develop two-phase areas in the diffusion zone because of the extra degree of freedom. That is also the reason why it is impossible to develop three-phase areas.<sup>[33]</sup> The sequence of phases along the diffusion path can be deduced as: AlCo + L,  $Al_5Co_2 + L$ ,  $Al_3Co + L$ ,  $Al_{13}Co_4 + L$  and  $Al_9Co_2 + L$ , which were confirmed by line scan (Fig. 8). According to the analysis, the first diffusion layer is AlCo + L, which is about 740  $\mu$ m. After that the diffusion path reached  $Al_5Co_2 + L$ ,  $Al_3Co + L$  and  $Al_{13}Co_4 + L$ , respectively. Because the average atomic numbers of Al<sub>5-</sub>  $Co_2$ , Al<sub>3</sub>Co and Al<sub>13</sub>Co<sub>4</sub> are very similar, these layers are not obvious. Figure 7(b, c) are magnifications of these areas. The last diffusion layer is  $Al_9Co_2 + L$ . This layer is about 180 µm in width. In diffusion couple 1, the solid solubility of Sn in the Al-Co binary compounds is less than 1 at.%. The phase relationship of  $Al_3Co + Al_{13}Co_4 + L$ was confirmed by diffusion couple 1.

The diffusion couple 2 was also used to confirm the three-phase region of  $Al_3Co + Al_{13}Co_4 + L$  at 1000°C. The BSE images in Fig. 9(a)-(c) show the formation of a small region with four diffusion layers. Based on the WDS



Fig. 9 (a) BSE images of diffusion couple 2; (b) Magnified area of "A" in (a); (c) Magnified area of "B" in (a)

line scan, as shown in Fig. 10, it reveals four two-phase regions. Phase relations confirmed by this diffusion couple are AlCo + L,  $Al_5Co_2$  + L,  $Al_3Co$  + L and  $Al_{13}Co_4$  + L. This is in agreement with the previous key sample analysis.

#### 3.4 Separated Microscopic Morphology

Furthermore, the as-cast alloy Al<sub>47</sub>Sn<sub>47</sub>Co<sub>6</sub> had separated macroscopic morphologies, which was caused by liquid miscibility gaps. At a certain temperature, the reaction of Liquid  $\rightarrow$  Liquid<sub>1</sub> + Liquid<sub>2</sub> occurs. After quenching into ice water, separated microscopic morphology has been retained. Separated macroscopic morphology is shown in Fig. 11(b), where the interlayer is Sn-rich. The insets are microscopic morphologies. This phenomenon is considered to be jointly induced by the degree of subcooling and the density difference of the Al-rich and Sn-rich liquids during cooling under the gravity condition. In addition to these reasons, the magnetic stirrer in the argon arc furnace also has a great influence on this phenomenon. As shown in Fig. 11(a), the alloy Al<sub>48</sub>Sn<sub>48</sub>Co<sub>4</sub> does not have the separated macroscopic morphology. With the increase of Co content, the macroscopic morphology showed obvious interface between the Sn-rich and Al-rich phases. The Alrich in macroscopic morphologies is bright, but is dark in microscopic morphologies. Because the color of macroscopic morphologies taken by high resolution camera is based on metallic luster, the color of microscopic morphologies that were measured by EPMA depends on elements' atomic number. The color of the phase will be brighter as the atomic number increases. Same situations were also discovered in alloys Al<sub>46</sub>Sn<sub>46</sub>Co<sub>8</sub>, Al<sub>45</sub>Sn<sub>45</sub>Co<sub>10</sub>, Al<sub>70</sub>Sn<sub>10</sub>Co<sub>20</sub>, Al<sub>64</sub>Sn<sub>16</sub>Co<sub>20</sub>, Al<sub>60</sub>Sn<sub>20</sub>Co<sub>20</sub>, Al<sub>55</sub>Sn<sub>25</sub>Co<sub>20</sub>, Al<sub>83</sub>Sn<sub>10</sub>Co<sub>7</sub>, Al<sub>78</sub>Sn<sub>10</sub>Co<sub>12</sub>, Al<sub>73</sub>Sn<sub>10</sub>Co<sub>17</sub>, Al<sub>67</sub>Sn<sub>10</sub>Co<sub>23</sub> and Al<sub>66</sub>Sn<sub>10</sub>Co<sub>24</sub>. This result illustrated that Co can promote the liquid-phase separation.

## 4 Conclusions

- The isothermal sections of the Al-Sn-Co system at 800 and 1000 °C for the whole composition range were experimentally determined. A total of seven and five three-phase regions exist in the ternary system at 800 and 1000 °C, respectively. There is no ternary compound in this system.
- The homogeneity ranges of binary compounds were determined and the phase relations among them were established. The solid solubility of Sn in Al-Co binary compounds is small which is from 0.1 to 1.9 at.% at 800 and 1000 °C.
- Separated microstructure was found in certain Al-Sn-Co alloys. Furthermore, it was found Co additions to





Fig. 11 Macroscopic morphologies of the as-cast alloys (a)  $Al_{48}Sn_{48}Co_4$  and (b)  $Al_{47}Sn_{47}Co_6$  cooling in the arc-melting furnace, the insets are microscopic morphologies



the Al-Sn binary alloys can effectively promote the liquid phase separation.

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