Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 30(2020) 1005−1016
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Phase equilibria of Zn−Al−Ti ternary system at 450 and 600 °C

Wei WANG[1,2], Zhi LI[1,2,3], Wei-jun SHEN[1,2], Fu-cheng YIN[1,2], Ya LIU[3]

1. School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, China;
2. Key Laboratory of Materials Design and Preparation Technology of Hunan Province, Xiangtan University, Xiangtan 411105, China;
3. Jiangsu Key Laboratory of Materials Surface Science and Technology, Changzhou University, Changzhou 213164, China

Received 14 July 2019; accepted 16 December 2019

Abstract: The phase relationships in the Zn−Al−Ti system at 450 and 600 °C were experimentally determined using equilibrated alloys method. The specimens were investigated by means of scanning electron microscopy coupled with energy dispersive spectroscopy and X-ray diffractometry. Eleven and eight three-phase regions are confirmed in the 450 and 600 °C isothermal sections, respectively. The Ti_2Al_5 which only exists at high temperature (990−1199.4 °C) in Ti−Al binary system is confirmed in two isothermal sections due to the dissolution of zinc. The *T* phase is confirmed as a ternary compound rather than an extension phase of $TiZn_3$ at 450 °C. The T_2 phase is a new ternary phase stable at 450 and 600 °C in Zn−Al−Ti ternary system.

Key words: Zn−Al−Ti ternary system; phase diagram; X-ray diffraction; compound

1 Introduction

Hot-dip galvanizing has been widely used to protect steel products from oxidation and corrosion. However, galvanizing Si-containing steels remains a technical challenge as it produces dull and excessively thick coatings with poor adhesion. This phenomenon is referred to the Sandelin effect or Si reactivity [1−3]. A practical method to solve this problem is to galvanize the steel in an alloy bath. The Sandelin phenomenon disappears when the Al or small amount of Ti is added into the zinc bath [4−8]. CULCASI et al [9] investigated the synergistic effect of Ti and Al on the structure and the surface quality of the coating, and the results showed that addition of Ti could serve as a catalyst for the Fe−Al reaction, allow a great development of the inhibition layer and delay the growth of the Fe−Zn intermetallic. XU et al [10] investigated the influence of Ti and La additions on the formation of intermetallic compounds in the Al−Zn−Si bath. Ti is added as a grain refiner into the Al−Zn−Si bath to enhance the nucleation rate [11,12]. Therefore, more studies on the phase equilibria of Zn−Al−Ti ternary system are necessary for understanding mechanism on the interfacial reactions and developing Zn−Al−Ti alloy coating.

SU et al [13,14] experimentally investigated the Zn−Al−Ti isothermal section at 450 and 350 °C in order to get a better understanding of the effect of Al and Ti on galvanizing, and the Ti_2Al_5 phase which only exists at high temperature (990−1199.4 °C) in Ti−Al binary system was not found in this isothermal section. While in research of LUO et al [15], the Ti_2Al_5 phase can be stable in

Foundation item: Project (51971189) supported by the National Natural Science Foundation of China; Project (2019JJ60011) supported by Zhuzhou Joint Fund of Hunan Natural Science Foundation, China; Project (KFBM20180001) supported by Jiangsu Key Laboratory of Materials Surface Science and Technology (Changzhou University), China
Corresponding author: Zhi LI, Tel: +86-731-58292213, E-mail: lizhiclsj@xtu.edu.cn; Fu-cheng YIN, E-mail: fuchengyin@xtu.edu.cn
DOI: 10.1016/S1003-6326(20)65272-4

the Zn−Al−Ti ternary system at 400 and 500 °C due to the dissolution of zinc in the Ti_2Al_5 phase. LI et al [16] also confirmed the existence of the Ti_2Al_5 phase in Al68.6Zn4.1Ti27.3 alloy. In order to make sure of the existence of Ti_2Al_5 in Zn−Al−Ti at 450 °C and obtain reliable phase relations and enough data for thermodynamic model of Zn−Al−Ti ternary system, the isothermal sections at 450 and 600 °C in the Zn−Al−Ti system were determined experimentally in the present work.

2 Literature review

The Al−Zn binary system has been investigated repeatedly due to the importance of aluminum−zinc alloy in hot dip galvanizing and other applications [17−19]. For Zn−Al system, there are only three condensed phase, i.e., Al-based fcc, Zn-based hcp and liquid.

The thermodynamic calculations of phase diagram for Ti−Al system was presented by KAUFMAN and NESOR [20] in 1978, and then MURRY [21], OKAMOTO [22] and ZHANG et al [23] investigated this system respectively. RAGHAVAN [24], SCHUSTER and PALM [25] reassessed the Ti−Al system again. The latter critically reevaluated all available literature data. The result of the assessment is accepted in this work.

The intermetallics existing in the Zn−Ti system are still in dispute. The binary phase diagram of Zn−Ti evaluated by MURRAY [26] contains seven compounds including $TiZn_{15}$, $TiZn_{10}$, $TiZn_5$, $TiZn_3$, $TiZn_2$, TiZn and Ti_2Zn. However, VASSILEV et al [27,28] obtained Zn−Ti binary system by differential scanning calorimetry and diffusion couples, and they found another five Ti−Zn compounds, i.e., $TiZn_{16}$, $TiZn_8$, Ti_3Zn_{22}, $TiZn_7$ and Ti_2Zn_3. Whether the $TiZn_{10}$ and $TiZn_5$ phases exist has yet to be confirmed, because these two phases were not found in the diffusion couples. GLORIANT et al [29] found that the compound $TiZn_7$ was the only phase between $TiZn_{15}$ and $TiZn_3$. CHEN et al [30] studied the crystal structure of Ti_3Zn_{22} and $TiZn_{16}$, and confirmed that $TiZn_{16}$ and $TiZn_{15}$ were the same phase, and they believed that only $TiZn_{16}$ and Ti_3Zn_{22} existed between $TiZn_3$ and η-Zn. In Ref. [30], it was first tested that Ti_3Zn_{22} is a tetragonal structure and its space group is *P*42/*mbc*. The exact composition of Ti_3Zn_{22} phase is Ti2.841Zn22.159, and thus it is also named as $TiZn_8$ phase [31].

3 Experimental

The isothermal section of Zn−Al−Ti at 600 and 450 °C was determined with equilibrated alloys. Samples were prepared from metal powders with purity of 99.99%. Each sample was carefully weighed with electronic balance, 3 g in total. Due to the fact that Al and Ti will react with quartz at high temperature and to avoid oxygen diffusion, the mixed powders were first put into a corundum crucible and then sealed in an evacuated quartz tube. The samples were heated to 1200 °C and kept for two days, followed by quenching in water. The quenched samples were re-sealed in evacuated quartz tube, and then annealed at 600 and 450 °C respectively, for 60 days to make sure to reach equilibrium state.

The specimens were prepared in the conventional way for microstructure examination. The nital solution was used to reveal the microstructure of the samples. A JSM−6360LV scanning electron microscope equipped with energy-dispersive spectrometric (SEM−EDS) was utilized to study the morphology and chemical composition of various phases in the samples. The phases were further confirmed by analyzing their X-ray powder diffraction patterns by a D/max-rA X-ray diffractometer, operating at 40 kV and 100 mA with Cu K_α radiation.

4 Results and discussion

To determine the phase relationships of the 600 and 450 °C isothermal sections in the Zn−Al−Ti ternary system, a series of specimens were prepared. Table 1 and Table 2 list the nominal composition of the ternary alloy samples. All phases formed in the specimens, together with the chemical composition of the phases are included in Table 1 and Table 2.

4.1 Phase equilibria of Zn−Al−Ti ternary system at 600 °C

Figure 1(a) shows the microstructure of Alloy A1. SEM−EDS analysis indicates that it contains a three-phase region, i.e., the dark α(Al) phase, stripy

Table 1 Compositions of samples and phases of 600 °C isothermal section in Zn−Al−Ti ternary system

Sample	Designed composition/at.%	Phase	Content/at.%		
			Al	Ti	Zn
A1	Al84Ti3Zn13	α(Al)	90.8	0.5	8.7
		Liquid	77.2	0	22.8
		$TiAl_3$	71.5	27.1	1.4
A2	Al72Ti13Zn15	Liquid	76.6	0	23.4
		$TiAl_3$	70.4	28.0	1.6
		Ti_2Al_5	68.2	28.1	3.7
A3	Al48Ti12Zn40	Ti_2Al_5	68.4	27.3	4.3
		$TiZn_3$	53.7	26.4	19.9
		Liquid	42.3	0	57.7
A4	Al60Ti33Zn7	Ti_2Al_5	67.3	29.1	3.6
		$TiAl_2$	60.8	35.6	3.6
		$TiZn_3$	57.4	27.9	14.7
A5	Al30Ti40Zn30	TiAl	37.5	49.4	13.1
		$TiZn_3$	33.3	30.1	36.6
		Ti_3Al	25.7	62.0	12.3
A6	Al18Ti47Zn35	T_2	18.4	57.3	24.3
		Ti_3Al	21.9	66.2	11.9
		$TiZn_3$	20.5	29.8	49.7
A7	Al8Ti42Zn50	T_2	12.1	52.5	35.4
		TiZn	3.4	51.6	45.0
		$TiZn_3$	10.0	29.1	60.9
A8	Al15Ti60Zn25	T_2	17.1	58.8	24.1
		Ti_3Al	22.2	66.7	11.1
		TiZn	4.2	52.3	43.5
A9	Al38Ti18Zn44	$TiZn_3$	44.7	25.8	29.5
		Liquid	31.4	0	68.6
A10	Al20Ti10Zn70	$TiZn_3$	41.3	25.6	33.1
		Liquid	6.7	0	93.3
A11	Al6Ti19Zn75	$TiZn_3$	9.4	24.7	65.9
		Liquid	0	1.3	98.7
A17	Al68.6Ti27.3Zn4.1	Ti_2Al_5	68.9	27.2	3.9

$TiAl_3$ phase and white liquid phase. The solubilities of Zn and Ti in α(Al) reach 8.7 and 0.5 at.%, respectively. On the other hand, the solubility of Zn in $TiAl_3$ reaches 1.4 at.%.

The microstructure of Alloy A2 is shown in Fig. 1(b). With the help of SEM−EDS, it can be found that Alloy A2 consists of three phases, i.e., $TiAl_3$, Ti_2Al_5 and Liquid phase. The dark $TiAl_3$ and Ti_2Al_5 phases exist in the matrix of liquid phase. Since the samples were put into a corundum crucible and sealed in a quartz tube, the cooling rate was not quick enough as the samples were quenched into the water, and then the liquid phase

Table 2 Compositions of samples and phases of 450 °C isothermal section in Zn−Al−Ti ternary system

Sample	Designed composition/at.%	Phase	Content/at.%		
			Al	Ti	Zn
B1	Al75Ti13Zn12	$TiAl_3$	71.9	27.3	0.8
		Ti_2Al_5	68.8	27.4	3.8
		α(Al)	82.2	0.2	17.6
B2	Al67Ti13Zn20	Ti_2Al_5	68.0	27.3	4.7
		T	59.9	25.9	14.2
		α(Al)	78.0	0.2	21.8
B3	Al21Ti55Zn24	T_2	19.7	60.3	20.0
		Ti_3Al	21.7	68.6	9.7
		T	24.6	29.3	46.1
B4	Al14Ti44Zn42	T	21.1	29.2	49.7
		TiZn	1.8	49.6	48.6
		T_2	9.6	54.4	36.0
B5	Al63Ti27Zn10	T	59.3	26.6	14.1
		$TiAl_2$	64.3	33.1	2.6
		Ti_2Al_5	67.9	28.1	4.0
B6	Al54Ti40Zn6	T	52.6	29.1	18.3
		TiAl	48.1	46.2	5.7
		$TiAl_2$	63.6	33.1	3.3
B7	Al42Ti43Zn15	T	42.1	29.2	28.7
		TiAl	44.0	48.1	7.9
		Ti_3Al	26.3	67.0	6.7
B8	Al35Ti8Zn57	α(Al)	76.2	0.1	23.7
		T	48.5	25.3	26.2
		Liquid	30.6	0.1	69.3
B9	Al3Ti14Zn83	T	17.4	26.1	56.5
		$TiZn_{16}$	0.6	6.6	92.8
		$TiZn_8$	0.5	12.1	87.4
B10	Al3Ti19Zn78	$TiZn_8$	0.4	13.3	86.3
		TiZn	1.6	49.5	48.9
		T	14.6	27.9	57.5
B11	Al5Ti5Zn90	T	22.3	25.2	52.5
		Liquid	2.0	0.1	97.9
		$TiZn_{16}$	0.3	6.5	93.2
B12	Al30Ti47Zn23	T_2	14.9	61.4	23.7
		Ti_3Al	16.3	71.5	12.2
B13	Al38Ti58Zn4	Ti_3Al	30.5	66.3	3.2
		TiAl	46.4	51.0	2.6
B14	Al16Ti50Zn34	T_2	15.9	54.2	29.9
		T	22.7	29.2	48.1
B15	Al75Ti8Zn15	α(Al)	5.6	0.1	94.3
		T	28.9	25.3	35.8
B16	Al62Ti13Zn25	T	58.3	25.7	16.0
		α(Al)	77.2	0.1	22.7
B17	Al72Ti13Zn15	Ti_2Al_5	68.5	27.3	4.2
		α(Al)	81.7	0.1	18.2

decomposed into Al-rich and Zn-rich phases during the quenching process.

The XRD patterns of Alloy A1 and A2 are shown in Figs. 1(c) and (d), respectively, which further confirm the two three-phase regions of α(Al)+$TiAl_3$+Liquid and Ti_2Al_5+$TiAl_3$+Liquid, respectively.

According to above results, the Ti_2Al_5 phase, which should not exist in the binary system below 990 °C, appears in Alloy A2. To confirm the existence of the Ti_2Al_5 phase, Alloy A17 (the nominal composition is Al68.6Ti27.3Zn4.1) was smelted and annealed at 600 °C for 60 days. The sample is found to be in single phase state under SEM−EDS examination and the phase is confirmed as Ti_2Al_5 by its XRD shown in Fig. 2. According to LUO et al [15], the existence of Ti_2Al_5 is due to the dissolution of Zn in Ti−Al. Therefore, the Ti_2Al_5 can stably exist at a lower temperature. In Alloy A17, the solubility of Zn in Ti_2Al_5 reaches 3.9 at.%.

The coexistence of $TiZn_3$, Ti_2Al_5 and Liquid is found in Alloy A3 from the microstructure and XRD analyses, as shown in Figs. 3(a) and (c). The dark phase is Ti_2Al_5 phase, and the liquid phase decomposes into white Zn-rich phase and dark Al-rich phase due to inadequate quenching rate. The grey big block phase is $TiZn_3$ and the Al content reaches 53.7 at.%. In our previous work [16], five

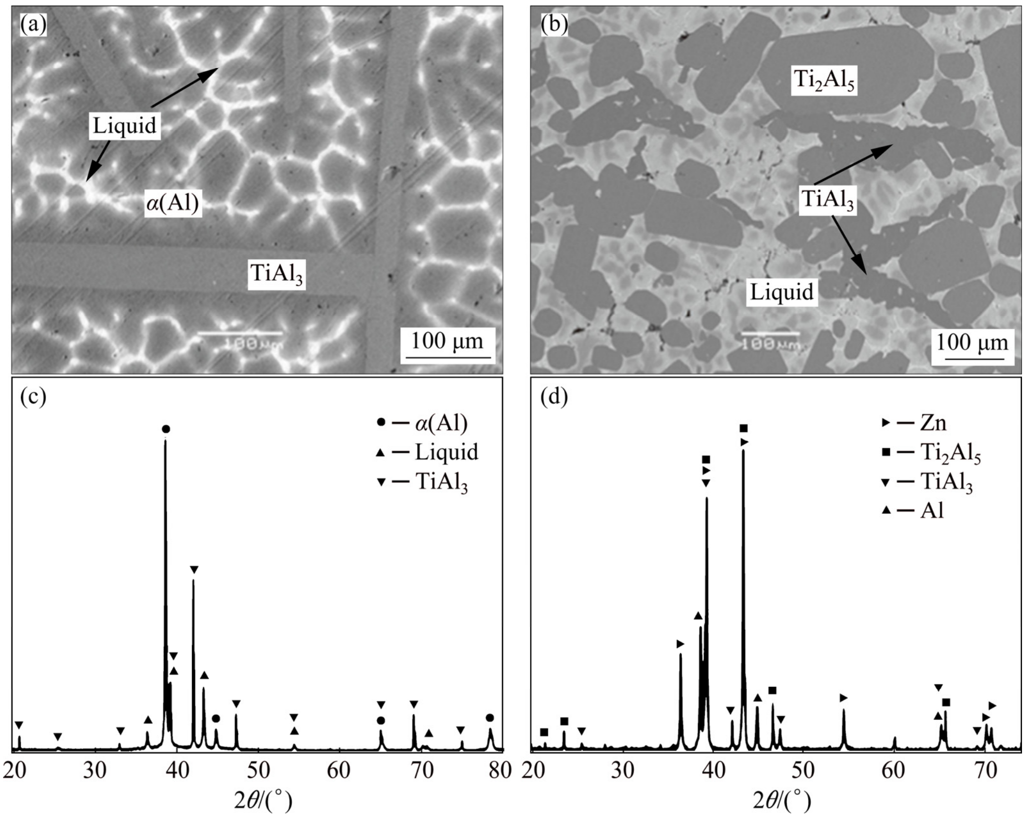

Fig. 1 SEM images (a, b) and XRD patterns (c, d) of Alloy A1 (a, c) and Alloy A2 (b, d)

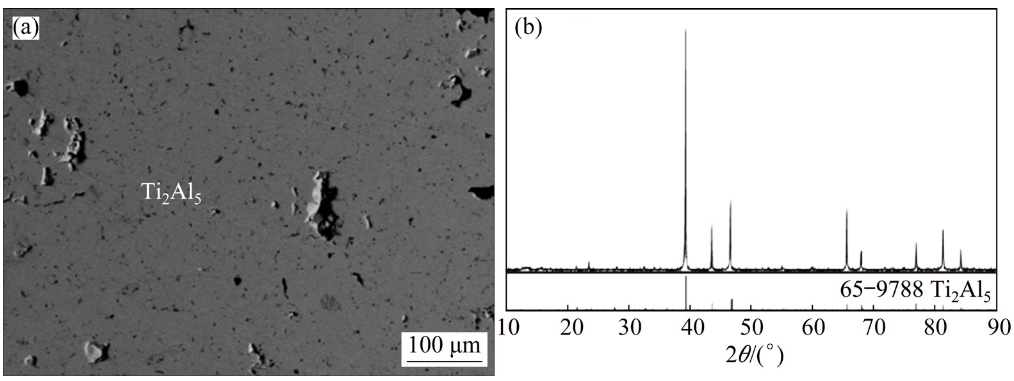

Fig. 2 SEM image (a) and XRD pattern (b) of Alloy A17

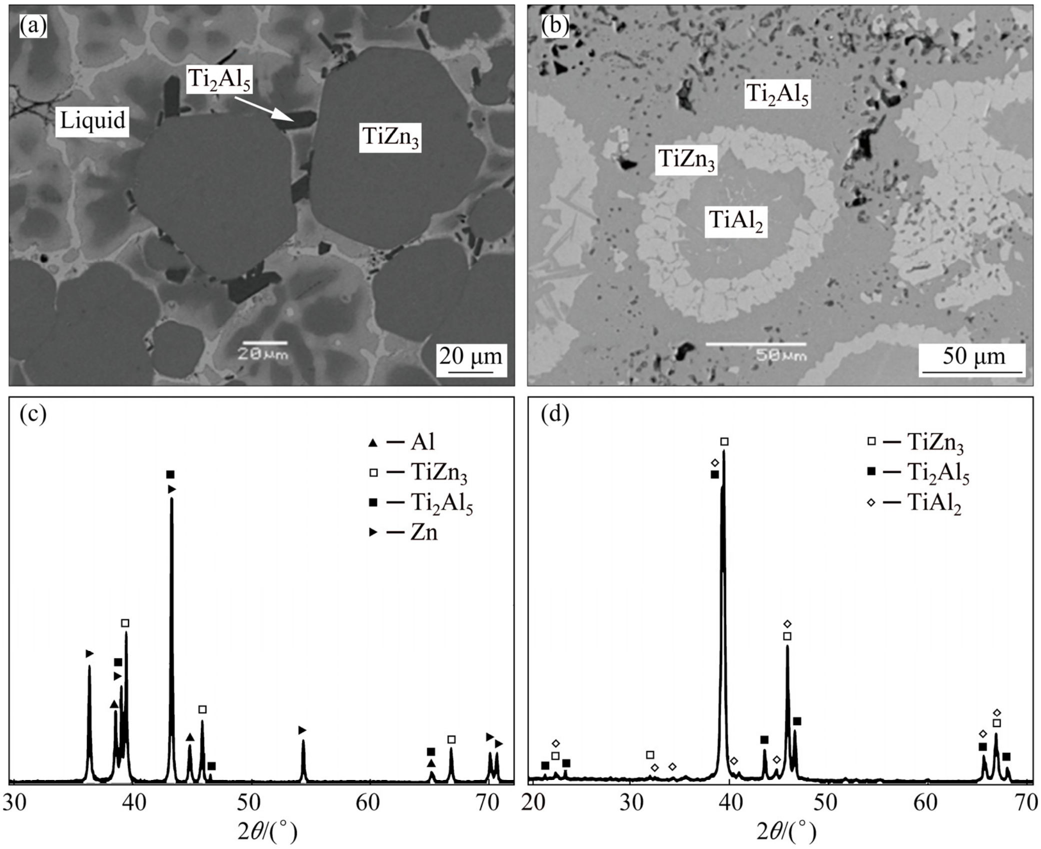

Fig. 3 SEM images (a, b) and XRD patterns (c, d) of Alloy A3 (a, c) and Alloy A4 (b, d)

alloys were prepared to determine the existence of the $TiZn_3$ phase of isothermal section in Zn−Al−Ti system at 600 °C. By scanning electron microscopy and X-ray diffraction analyses, these five samples were all in single-phase state which was proven to be the $TiZn_3$ phase.

SEM−EDS analyses indicate that Alloy A4 corresponds to a three-phase equilibrate state, as shown in Fig. 3(b), and XRD pattern in Fig. 3(d) further confirms the three-phase region of $TiZn_3$+Ti_2Al_5+$TiAl_2$.

Figure 4(a) presents the microstructure of Alloy A5. According to the results of SEM−EDS analyses, there is a three-phase region of Ti_3Al+$TiZn_3$+TiAl in Alloy A5. The white part is the $TiZn_3$ phase and the grey dark part is the TiAl phase. The grey white Ti_3Al phase occurs inside the TiAl phase. The Zn solubility in Ti_3Al phase and TiAl phase reaches 12.3 and 13.1 at.%, respectively.

Figure 4(b) shows the three-phase region of Ti_3Al+$TiZn_3$+T_2 of Alloy A6. The composition of T_2 in this sample is Al18.4Ti57.3Zn24.3 and it is a new ternary phase in Zn−Al−Ti ternary system which has not been reported in previous literatures. Due to the difficulty of sample preparation, alloys containing only the T_2 single phase have not been obtained for further study.

Figures 4(c) and (d) show the XRD patterns of Alloys A5 and A6, which help to further identify the two three-phase regions of Ti_3Al+$TiZn_3$+TiAl and Ti_3Al+$TiZn_3$+T_2, respectively.

Figure 5(a) shows the microstructure of Alloy A7. According to the analyses with SEM−EDS and XRD, a three-phase region of TiZn+$TiZn_3$+T_2 is confirmed. The black T_2 phase and the grey TiZn phase exist in the matrix of $TiZn_3$ phase. The XRD pattern of A7 shown in Fig. 5(c) further ascertains the three-phase region of TiZn+$TiZn_3$+T_2. Figure 5(b) shows the microstructure of Alloy A8. The SEM−EDS analyses indicate that it is in the three-phase region of TiZn+T_2+Ti_3Al. The three phases can be judged from their contrast.

4.2 Phase equilibria of Zn−Al−Ti ternary system at 450 °C

Figure 6(a) shows the microstructure of Alloy B1. SEM−EDS analyses indicate that Alloy B1 consists of three phases, i.e. α(Al)+$TiAl_3$+Ti_2Al_5.

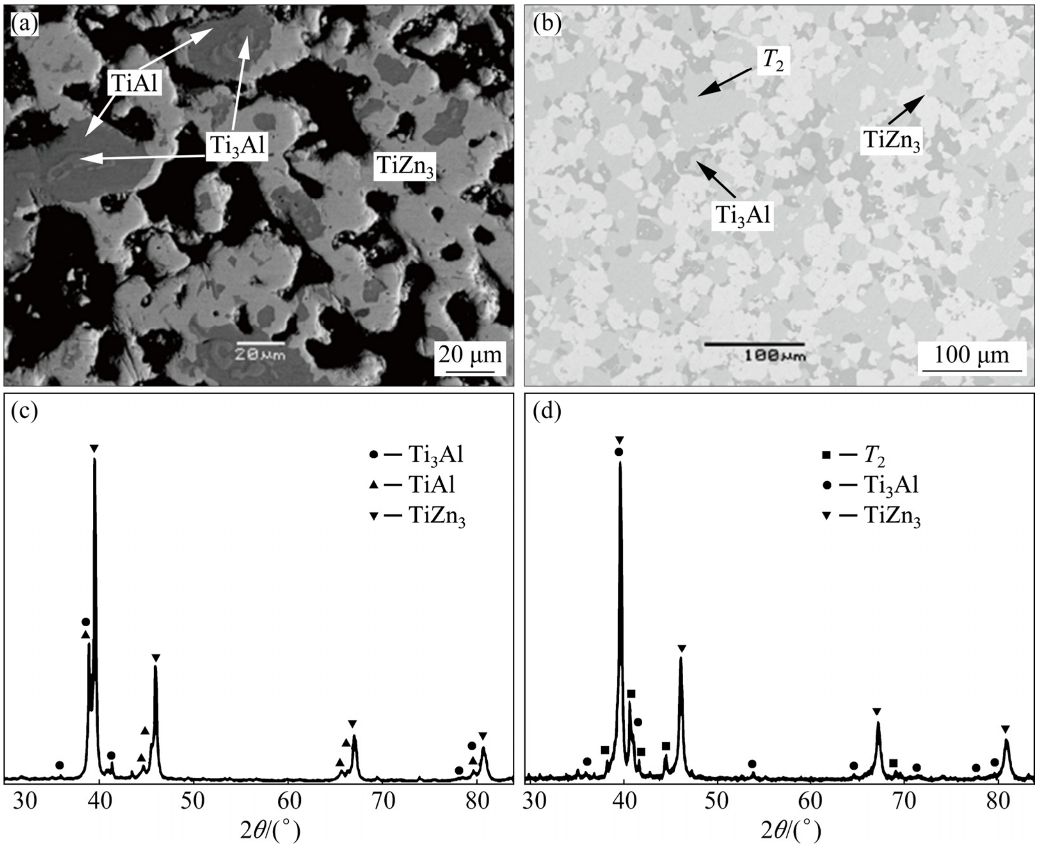

Fig. 4 SEM images (a, b) and XRD patterns (c, d) of Alloy A5 (a, c) and Alloy A6 (b, d)

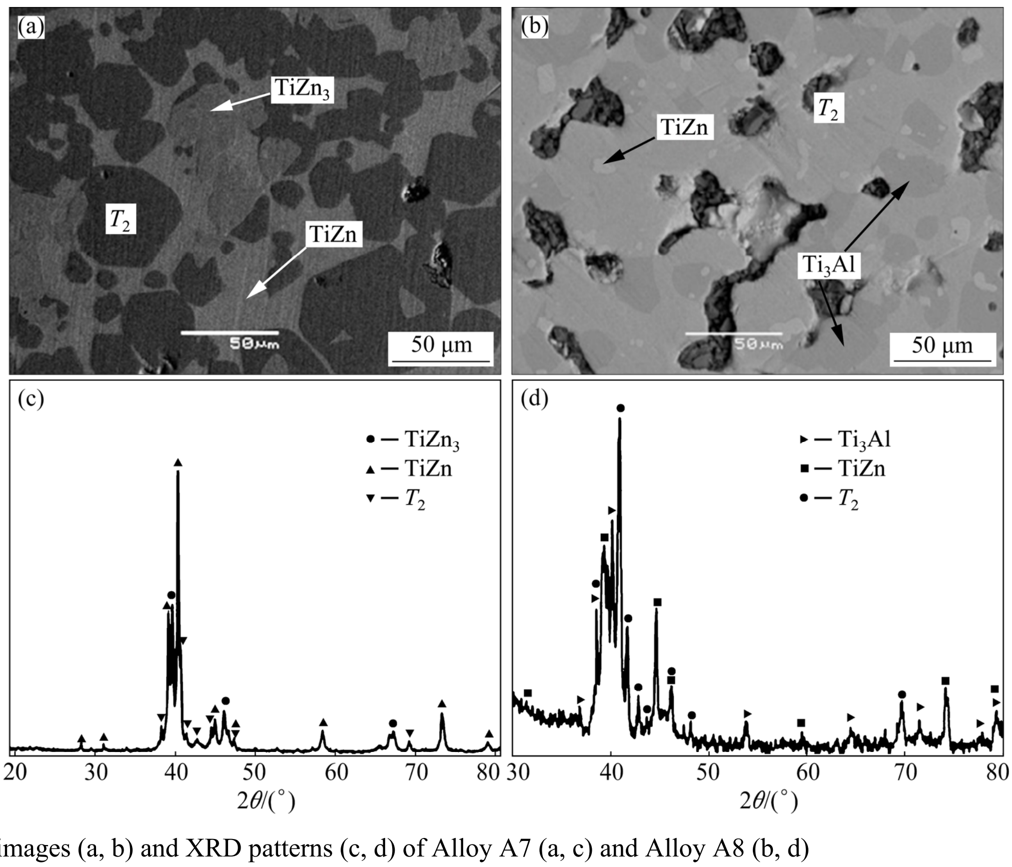

Fig. 5 SEM images (a, b) and XRD patterns (c, d) of Alloy A7 (a, c) and Alloy A8 (b, d)

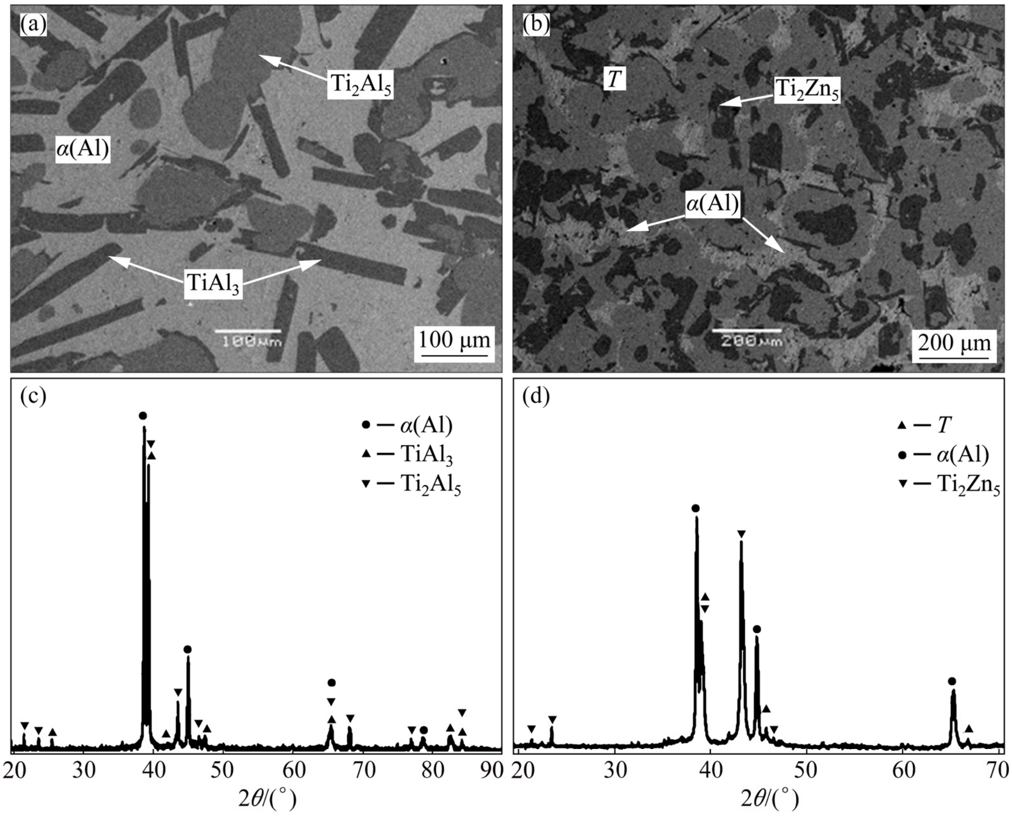

Fig. 6 SEM images (a, b) and XRD patterns (c, d) of Alloy B1 (a, c) and Alloy B2 (b, d)

Figure 6(b) shows the microstructure of Alloy B2, which presents the three-phase region of Ti_2Al_5+T+ α(Al). These two samples confirm the existence of Ti_2Al_5 which was ignored by SU et al [13,14]. The XRD patterns of Alloys B2 and B3 are shown in Figs. 6(c) and (d), respectively, which further confirm the existence of Ti_2Al_5 at 450 °C.

The inadvertence of the Ti_2Al_5 phase in the study of SU et al [13,14] is largely attributable to the following aspects. Firstly, the composition of Ti_2Al_5 is very close to that of $TiAl_3$, especially as zinc is dissolved in it. Secondly, the Ti_2Al_5 phase does not exist below 990 °C according to the Ti−Al binary system. So, the Ti_2Al_5 phase is probably treated as the $TiAl_3$ phase.

Figure 7(a) shows the microstructure of Alloy B3, and three phases, T, T_2 and Ti_3Al co-exist in this alloy. The light grey matrix is the T phase and the grey dark part is the T_2 phase. The darkest phase is Ti_3Al phase. The Zn solubility in Ti_3Al reaches 9.7 at.%. Figure 7(b) shows the three-phase region of T+TiZn+T_2 of Alloy B4. It is the same as the previous alloy: the light grey matrix presents the T phase, the grey dark part is the TiZn phase and the darkest phase surrounding the T phase corresponds to the T_2 phase. The Al solubility in TiZn and T_2 reaches 1.8 and 9.6 at.%, respectively. From these two samples, it can be concluded that the T_2 phase can exist stably at 450 °C.

The coexistence of Ti_2Al_5, $TiAl_2$ and T is found in Alloy B5 from the microstructure and XRD analyses, as shown in Figs. 8(a) and 8(c). The light grey matrix is the T phase, but the contrast between the Ti_2Al_5 and $TiAl_2$ phases is not clear. However, the Ti_2Al_5 phase appears in block shape and $TiAl_2$ appears in acicular shape. The XRD pattern of B5 is shown in Fig. 8(c), further confirming the three-phase region of T+Ti_2Al_5+$TiAl_2$.

SEM−EDS analyses indicate that Alloy B6 corresponds to T+TiAl+$TiAl_2$ three-phase equilibria state, as shown in Fig. 8(b) and the XRD pattern is shown in Fig. 8(d). The Zn solubilities in TiAl and $TiAl_2$ reach 5.7 and 3.3 at.%, respectively.

The microstructure of Alloy B7 is shown in Fig. 9(a). With the help of SEM−EDS and XRD, it can be found that Alloy B7 consists of three phases, i.e., Ti_3Al, TiAl and T. The dark TiAl and Ti_3Al phase exist in the matrix of T phase. The contrast of

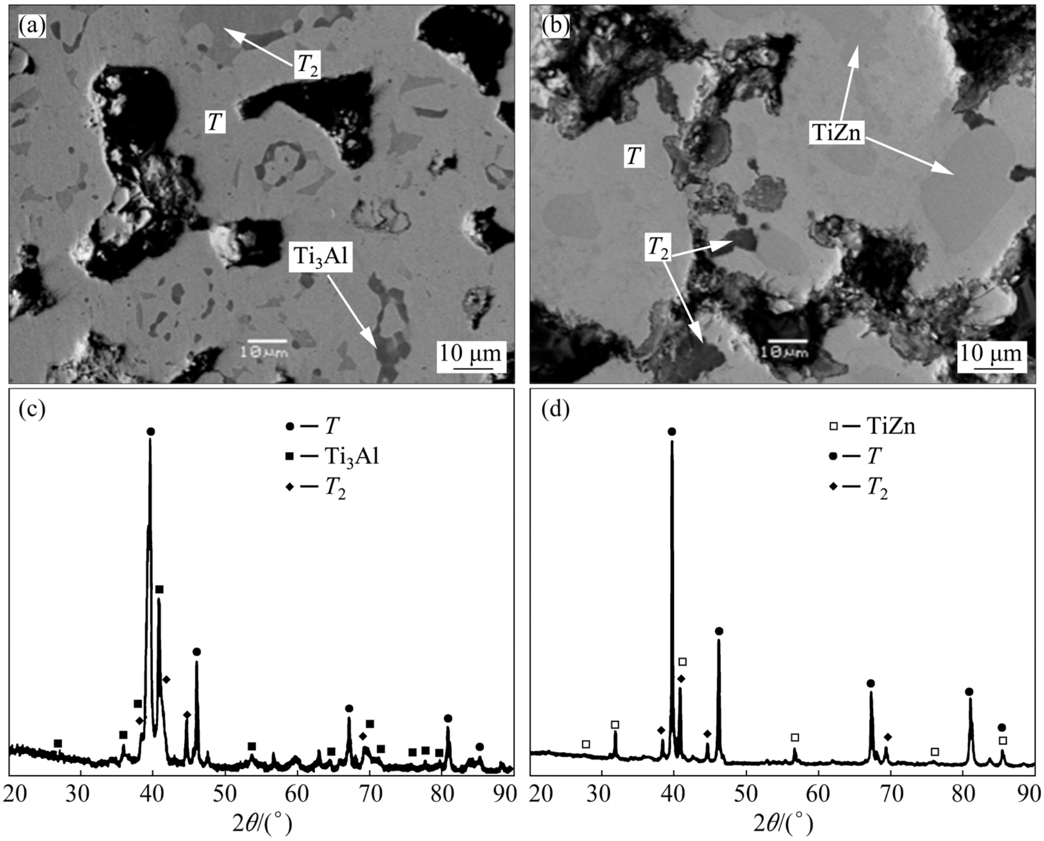

Fig. 7 SEM images (a, b) and XRD patterns (c, d) of Alloy B3 (a, c) and Alloy B4 (b, d)

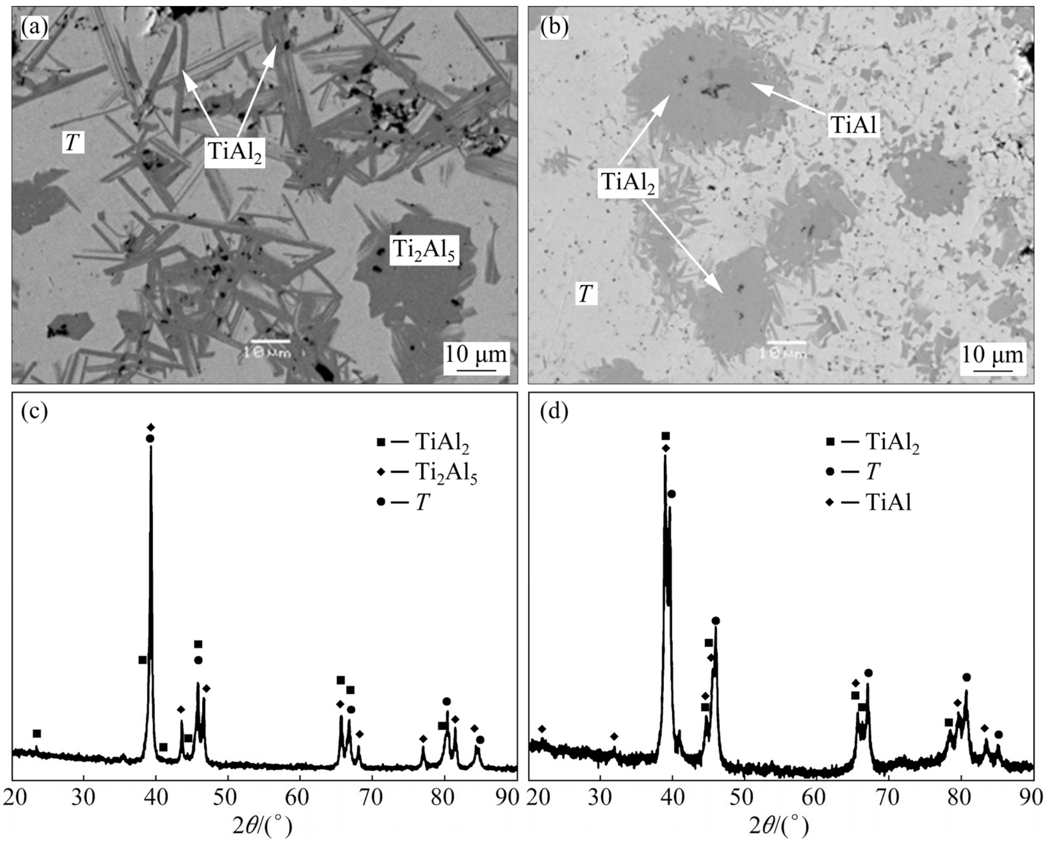

Fig. 8 SEM images (a, b) and XRD patterns (c, d) of Alloy B5 (a, c) and Alloy B6 (b, d)

Ti_3Al phase is deeper than that of TiAl. The Zn solubilities in Ti_3Al and TiAl reach 6.7 and 7.9 at.%, respectively.

Figure 10 shows the microstructures of Alloys B8−B11. According to the results obtained by SEM−EDS analyses, there are four three-phase regions of T+α(Al)+Liquid, $TiZn_8$+$TiZn_{16}$+T, $TiZn_8$+TiZn+T and Liquid+$TiZn_{16}$+T. These results are consistent with the phase relationship obtained by SU et al [13]. Unlike the result obtained in Zn−Al−Ti ternary system at 600 °C, the T phase in the isothermal section at 450 °C is a ternary phase rather than an extension of the $TiZn_3$ phase.

Based on the results of microstructures observation and phase analyses, the 600 and 450 °C isothermal sections of Zn−Al−Ti ternary system are constructed, as shown in Fig. 11 and Fig. 12, respectively. Figure 11 turns out that eight three-phase regions are confirmed in the Zn−Al−Ti system at 600 °C, i.e., α(Al)+$TiAl_3$+Liquid, Liquid+$TiAl_3$+Ti_2Al_5, Ti_2Al_5+Liquid+$TiZn_3$, Ti_2Al_5+$TiAl_2$+$TiZn_3$, Ti_3Al+$TiZn_3$+TiAl, Ti_3Al+$TiZn_3$+T_2, $TiZn_3$+T_2+TiZn, Ti_3Al+T_2+TiZn and two three-phase regions could be deduced, viz., Ti_2Al_5+$TiAl_3$+$TiAl_2$ and TiAl+$TiZn_3$+$TiAl_2$. Figure 12 presents the isothermal section of Zn−Al−Ti ternary system at 450 °C, which consists of eleven ternary phase regions, i.e., $TiAl_3$+Ti_2Al_5+α(Al), α(Al)+T+Ti_2Al_5, T+Liquid+α(Al), T+TiZn+$TiZn_8$, T+$TiZn_8$+$TiZn_{16}$, T+Liquid+$TiZn_{16}$, T+T_2+TiZn, T_2+T+Ti_3Al, T+Ti_3Al+TiAl, T+TiAl+$TiAl_2$, T+Ti_2Al_5+$TiAl_2$. In addition, two three-phase regions could be derived in the 450 °C isothermal section, i.e., $TiAl_2$+$TiAl_3$+Ti_2Al_5 and TiZn+$TiZn_8$+$TiZn_3$.

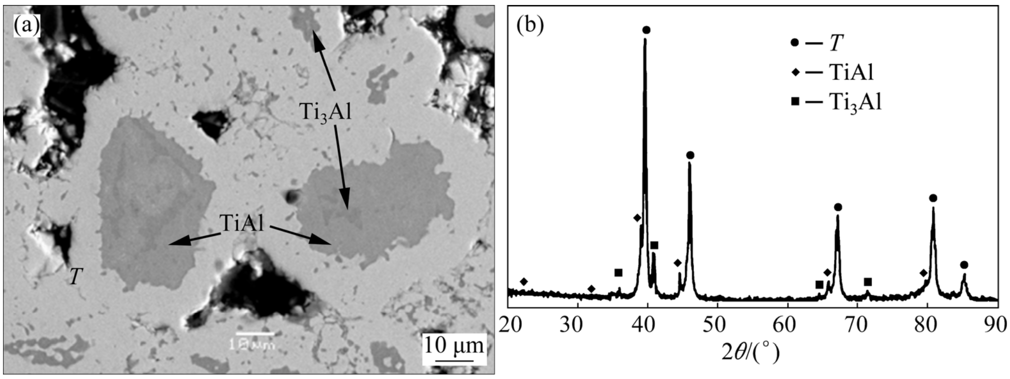

Fig. 9 SEM image (a) and XRD pattern (b) of Alloy B7

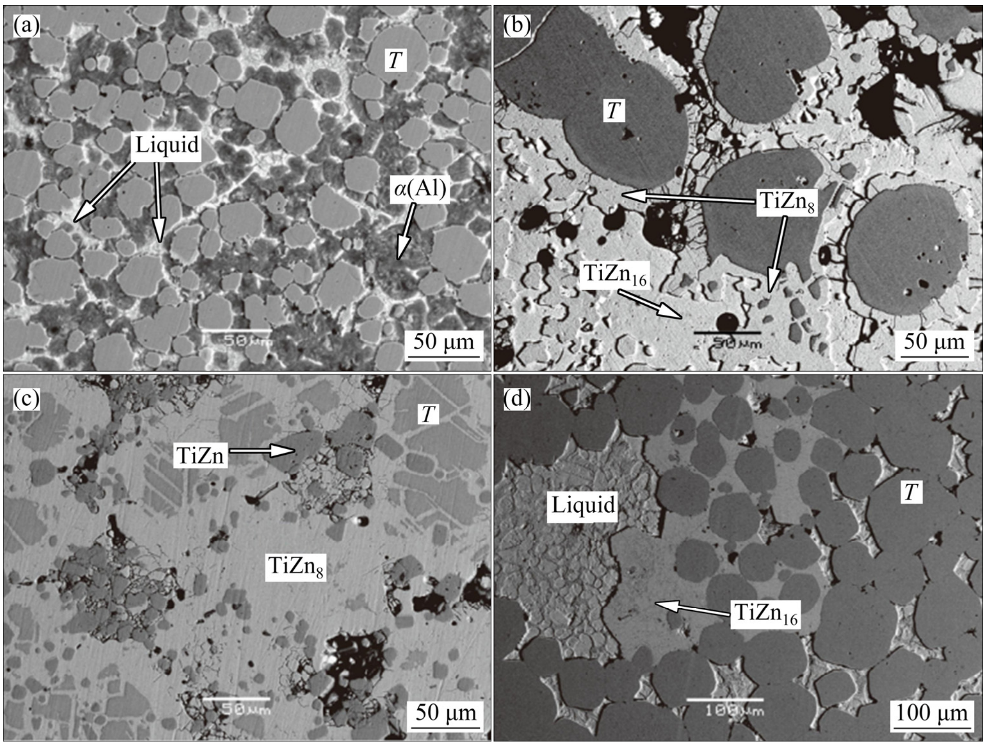

Fig. 10 Microstructures of Alloys B8−B11: (a) B8; (b) B9; (c) B10; (d) B11

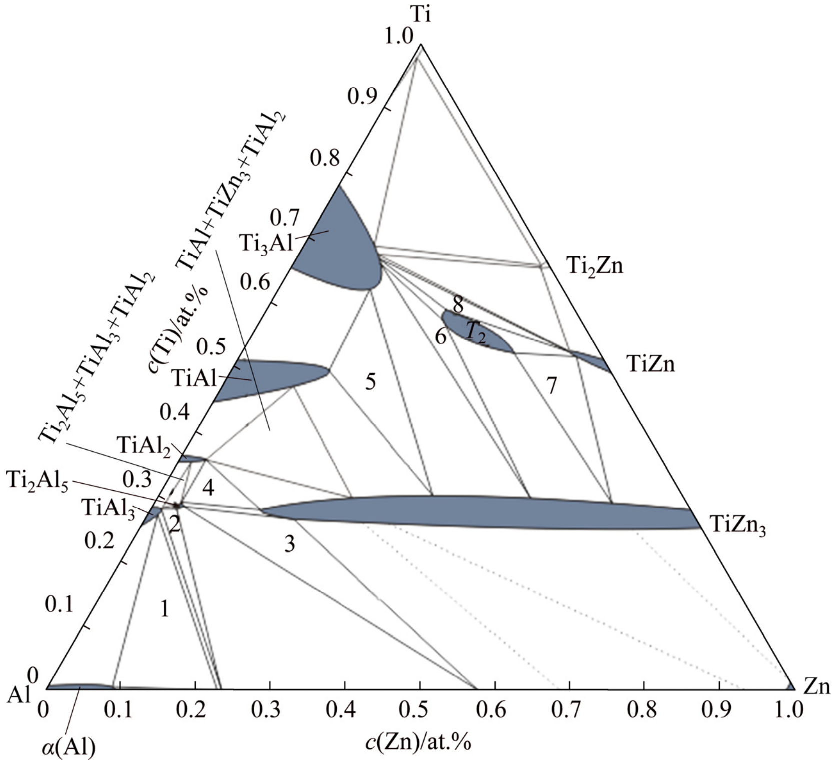

Fig. 11 Isothermal section of Zn−Al−Ti phase diagram at 600 °C: 1—$TiAl_3$+Liquid+α(Al); 2—$TiAl_3$+Ti_2Al_5+Liquid; 3—Ti_2Al_5+$TiZn_3$+Liquid; 4—$TiAl_2$+Ti_2Al_5+$TiZn_3$; 5—$TiZn_3$+TiAl+Ti_3Al; 6—$TiZn_3$+T_2+Ti_3Al; 7—T_2+TiZn+$TiZn_3$; 8—T_2+TiZn+Ti_3Al

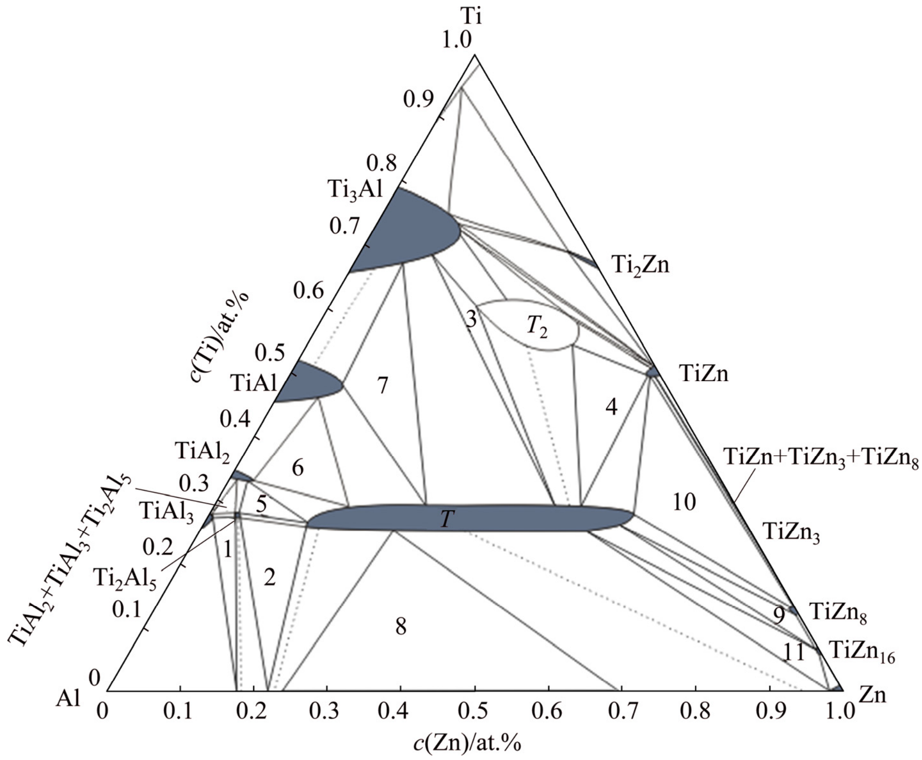

Fig. 12 Isothermal section of Zn−Al−Ti phase diagram at 450 °C: 1—$TiAl_3$+Ti_2Al_5+α(Al); 2—Ti_2Al_5+α(Al)+T; 3—T+T_2+Ti_3Al; 4—T+T_2+TiZn; 5—Ti_2Al_5+$TiAl_2$+T; 6—T+$TiAl_2$+TiAl; 7—Ti_3Al+TiAl+T; 8—Liquid+α(Al)+T; 9—T+$TiZn_8$+$TiZn_{16}$; 10—T+TiZn+$TiZn_8$; 11—T+$TiZn_{16}$+Liquid

The Ti_2Al_5 and T_2 phases are stable in both isothermal sections of Zn−Al−Ti ternary system at 450 and 600 °C, and the T_2 phase is a new ternary phase in the Zn−Al−Ti ternary system at 600 and 450 °C. The composition range of the T phase is similar to that of the $TiZn_3$ phase. However, the T phase in the isothermal section at 450 °C is a ternary phase rather than an extension phase of TiZn.

5 Conclusions

(1) Eight three-phase regions are confirmed in the 600 °C isothermal section and two three-phase regions can be deduced. Eleven three-phase regions are confirmed in the 450 °C isothermal section and two three-phase regions can be deduced.

(2) The Ti_2Al_5 phase which could only exist at high temperature in Ti−Al binary system appears in 450 and 600 °C isothermal sections because of the dissolution of Zn.

(3) The ternary compound T phase in the isothermal section at 450 °C is not an extension phase of $TiZn_3$. However, the compositions of the T and $TiZn_3$ phases are similar.

(4) The T_2 phase is a new ternary compound stable in the isothermal section of the Zn−Al−Ti ternary system at 450 and 600 °C.

References

[1] LIU Yong-xiong, YIN Fu-cheng, LI Zhi, OUYANG Xue-mei, CHEN Liang-ping. Experimental determination of 800 °C isothermal section in Al−Zn−Zr ternary system [J]. Transactions of Nonferrous Metals Society of China, 2019, 29: 25−33.

[2] FOCT J, PERROT P, GREUMNOT G. Interpretation of the role of silicon on the galvanizing reaction based on kinetics, morphology and thermodynamics [J]. Scripta Metallurgica et Materialia, 1993, 28(10): 1195−1200.

[3] GUTTMAN H, NIESSEN P. Reactivity of silicon steels hot-dip galvanizing [J]. Canadian Metallurgical Quarterly, 1972, 11(4): 609−615.

[4] MARDER A R. The metallurgy of zinc-coated steel [J]. Progress in Materials Science, 2000, 45(3): 191−271.

[5] MACKOWIAK J, SHORT N R. Metallurgy of galvanizing coatings [J]. International Metals Reviews, 1979, 24(1): 1−19.

[6] MUNROE P R, LAKSMI C S, GLEESON B. Effects of 0.1 and 0.2 wt.% aluminium addition to zinc on the interdiffusion between zinc and iron at 400 °C [J]. Materials Science and Engineering A, 1998, 251(1−2): 87−93.

[7] GROSS N, NASCH T, EITSCHKO W. Ternary intermetallics with high zinc content: TT′2Zn20 (T=Zr, Hf, Nb; T'=Mn, Fe, Ru, Co, Rh, Ni) with CeCr2Al20-type structure [J]. Journal of Solid State Chemistry, 2001, 161(2): 288−293.

[8] SU X, TANG N Y, OGURI J M. Thermodynamic evaluation of the Fe−Zn system [J]. Journal of Alloys and Compounds, 2001, 325: 129−136.

[9] CULCASI J D, SERE P R, ELSNER C I, DI SARLI A R. Control of the growth of zinc-iron phases in the hot-dip galvanizing process [J]. Surface and Coatings Technology, 1999, 122(1): 21−23.

[10] XU J, GU Q F, LI Q, LU H S. Influence of Ti and La additions on the formation of intermetallic compounds in the Al−Zn−Si bath [J]. Metallurgical and Materials Transactions A, 2016, 47(12): 6542−6554.

[11] LUO Qun, LI Qian, ZHANG Jie-yu, CHEN Shuang-lin, CHOU Kuo-chih. Experimental investigation and thermodynamic calculation of the Al−Si−Ti system in Al-rich corner [J]. Journal of Alloys and Compounds, 2014, 602: 58−65.

[12] LI Yang, GU Qin-fen, LUO Qun, PANG Yue-peng, CHEN Shuang-lin, CHOU Kuo-chih, LI Xun-wang, LI Qian. Thermodynamic investigation on phase formation in the Al−Si rich region of Al−Si−Ti system [J]. Materials and Design, 2016, 102: 78−90.

[13] YANG S, SU X P, WANG J H, YIN F C, LI Z, TU H, PENG H P. The Zn-rich corner of the Zn−Al−Ti system at 723 K [J]. Journal of Alloys and Compounds, 2010, 499: 194−199.

[14] XIAO Lai-rong, HUANG Jian-feng, CHEN Yi-lei, SU Xu-ping, WANG Jian-hua. Phase equilibria of the Zn−Al−Ti system at 370 °C in the Zn-rich region [J]. International Journal of Materials Research, 2015, 104(9): 843−848.

[15] LUO Q, LI Q, ZHANG J Y, CHEN S L, CHOU K C. Experimental investigation and thermodynamic optimization of the Al−Zn−Ti system in the Al-rich corner [J]. Intermetallics, 2013, 33: 73−80.

[16] LI Z, SHEN W J, YIN F C, WANG X M, WU Y, ZHAO M X. Phase equilibria of the Al−Zn−Fe−Ti quaternary system at 600 °C [J]. Journal of Phase Equilibria and Diffusion, 2013, 34(3): 211−220.

[17] CHEN S L, CHANG Y A. A thermodynamic analysis of the Al−Zn system and phase diagram calculation [J]. Calphad, 1993, 17(2): 113−124.

[18] MEY S A. Reevaluation of the Al−Zn system [J]. Zeitschrift fur Metallkunde, 1993, 84: 451−455.

[19] KHALFALLAH A, RAHOA A, AMZERT S, DJEMLI A, Precipitation kinetics of GP zones, metastable η' phase and equilibrium η phase in Al−5.46wt.%Zn−1.67wt.%Mg alloy [J]. Transactions of Nonferrous Metals Society of China, 2019, 29: 233−241.

[20] KAUFMAN L, NESOR H. Coupled phase diagrams and thermochemical data for transition metal binary systems—V [J]. Calphad, 1978, 2(4): 325−348.

[21] MURRAY J L. Phase diagrams of binary titanium alloys [J]. ASM International, 1987: 340−345.

[22] OKAMOTO H. Al−Ti (aluminium−titanium) [J]. Journal of Phase Equilibria, 1993, 14(1): 120−121.

[23] ZHANG F, CHEN S L, CHANG Y A, KATTNER U R. A thermodynamic description of the Ti−Al system [J].

Intermetallics, 1997, 5: 471−482.
[24] RAGHAVAN V. Aluminum−titanium [J]. Journal of Phase Equilibria and Diffusion, 2005, 26(2): 171−172.
[25] SCHUSTER J C, PALM M. Reassessment of the binary aluminum−titanium phase diagram [J]. Journal of Phase Equilibria and Diffusion, 2006, 27(3): 255−277.
[26] MURRAY J L. The Ti−Zn (titanium−zinc) system [J]. Bulletin of Alloy Phase Diagrams, 1984, 5(1): 52−56.
[27] VASSILEV G P, LIU X J, ISHIDA K. Reaction kinetics and phase diagram studies in the Ti−Zn system [J]. Journal of Alloys and Compounds, 2004, 375: 162−170.
[28] VASSILEV G P. Contribution to the zinc-rich side of the Ti−Zn system [J]. Zeitschrift fur Metallkunde, 2004, 95: 813−817.
[29] GLORIANT T, REUMONT G, PERROT P. The Fe−Zn−Ti system at 450 °C [J]. Zeitschrift fur Metallkunde, 1997, 88: 539−544.
[30] CHEN X A, JEITSCHKO W, DANEBROCK M, EVERS C B H, WAGNER K. Preparation, properties, and crystal structures of Ti3Zn22 and TiZn16 [J]. Journal of Solid State Chemistry, 1995, 118(2): 219−226.
[31] FAN S, WU C, LIU Y, TU H, SU X P, WANG J H. 600 and 450 °C isothermal sections of the Zn−Ce−Ti system [J]. Journal of Alloys and Compounds, 2017, 709: 842−849.

Zn−Al−Ti 三元体系 450 和 600 °C 等温截面的相关系

汪 娓[1,2]，李 智[1,2,3]，沈玮俊[1,2]，尹付成[1,2]，刘 亚[3]

1. 湘潭大学 材料科学与工程学院，湘潭 411105；
2. 湘潭大学 湖南省材料设计与制备技术重点实验室，湘潭 411105；
3. 常州大学 江苏省材料表面科学与技术重点实验室，常州 213164

摘 要：通过平衡合金法实验确定 Zn−Al−Ti 三元系 450 和 600 °C 等温截面的相关系。采用扫描电镜−能谱仪以及 X 射线衍射对样品进行分析。在 450 和 600 °C 等温截面中分别存在 7 和 8 个三相区，由于锌在 Ti_2Al_5 相中的溶解，使得仅在高温下(990~1199.4 °C)存在的 Ti_2Al_5 相能够在较低温度下稳定存在。450 °C 等温截面中的 T 相并非 $TiZn_3$ 的延伸相，而是一个三元化合物。T_2 相是 Zn−Al−Ti 三元体系中一个新的三元相，并且在 450 和 600 °C 下稳定存在。

关键词：Zn−Al−Ti 三元系；相图；X 射线衍射；化合物

(Edited by Bing YANG)