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Experimental study of the Al-rich corner of the Al-Si-Ti system at 500 °C

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Abstract

The Al-Si-Ti ternary phase diagram and the correlated thermodynamic database play an important role in material design of high performance alloys for this system. In the present work, we have studied the phase equilibriums of the Al-rich corner of the Al-Si-Ti system at 500°C by means of the diffusion couple technique. The scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) results indicated that four phase layers had formed between two end-members. The X-ray diffraction (XRD) results confirmed that (Al), (Si), $Ti_7Al_5Si_{12}$ and $Ti(Al,Si)_3$ phases existed in the diffusion zoon. The confirmed reaction path way can be express as (Al) → $Ti_7Al_5Si_{12}$ → $Ti(Al,Si)_3$. Besides, the equilibriums of (Al) + $Ti_7Al_5Si_{12}$ and $Ti_7Al_5Si_{12}$ + $Ti(Al,Si)_3$ in Al-rich corner at 500°C were identified.

Introduction

Aluminum alloy is a very important light weight material in automobile. Cast Al-Si alloy is widely used in manufacturing cylinder blocks, cylinder heads, pistons and valve lifters due to its high strength, high hardness and high wear resistance. Ti is commonly added to the Al-Si alloy for its grain refining effect. Saheb et al. [1] reported that the increase of Ti content in the Al-Si alloy would lead to the formation of $TiAl_3$ and enlarged its volume fraction as well, which can improve the wear resistance of this alloy. Gao et al.[2] presented that blocky TiAlSi particles were helpful to enhance the high temperature strength of the Al-Si piston alloy, and that the increase of Ti content in the Al-Si-Ti alloy promoted the morphological transformation of TiAlSi from flake-like to block-like and primary Si was replaced by blocky TiAlSi particles, which can be a new method to modify primary Si particles in the hypereutectic Al-Si alloy. So, in order to predict the phase equilibriums in the Al-Si alloy added with Ti and further control the formation of phases like $TiAl_3$ and TiAlSi, it is essential to obtain an accurate Al-Si-Ti ternary phase diagram. However, the phases existed in the Al-rich corner of Al-Si-Ti system and their equilibrium relationships are still unclear. Zeren, et al.[3] summarized the possible phases existing in the Al-rich corner of this system (Table I), and pointed out that because each ternary phase had a range of chemical compositions and lattice parameters, the identification toward these ternary compounds were quite difficult. In the present work, we thus focus on clarifying the phase equilibriums existing in the Al-rich corner of Al-Si-Ti system and building the reliable experiment data for the thermodynamic optimization toward this system.

Table I. Possible phases existing in the Al-rich corner of Al-Si-Ti system summarized by Zeren, etc.[3].

Phases	Formula	Composition Range
$Ti(Al,Si)_3$	$Ti(Al_{1-x}Si_x)_3$	$0 \le x \le 0.15$
τ_1 or $Ti_7Al_5Si_{12}$	$(Ti_{1-x}Al_x)_8(Al_ySi_{1-y})_{16}$	$x \approx 0.12$, $0.06 \le y \le 0.25$
τ_2 or $Ti(Al,Si)_2$	$Ti(Al_xSi_{1-x})_2$	$0.15 \le x \le 0.30$

Experimental Procedures

The specimen is a solid state diffusion couple. Two end-members are Al-10wt.%Si alloy and Ti with the purity of 99.99%. Both end members were processed into bulks with the size of 8mm×8mm×3mm by wire-electrode cutting.

In order to let a sufficient diffusion happen, the interact surfaces of two end-members were ground and polished flat, clamped together intimately. Having been encapsulated in a vacuum quartz glass capsule, the sample was annealed at 500°C for 152 days. After the heat treatment, the sample was quenching in water for rapid cooling.

Having been grounded and polished transversely, the morphology and compositions of the diffusion zoon were investigated by SEM (HITACHI-1500) and EDS, respectively. Then the couple was broken apart along the initial bonding face, and XRD (8°/min, 20°-100°) was used to identify the phases sticking on the crack surfaces of both end-members.

Results and Discussion

Fig. 1(a) is the full view of the diffusion zoon forming in the Al-10wt.%Si/Ti couple. Fig. 1(b) is the enlarged image of Al-10wt.%Si side. Table II shows the compositions of the points marked in Fig. 1(b). According to the results showed in Table II. the dark gray matrix in Fig. 1(b) is (Al), and the bright gray particles is (Si). Due to the small solubility of Al in (Si) and Si in (Al) as well, the Al content in (Si) and the Si content in (Al) are both very low. Meanwhile, (Si) and (Al) have reached equilibrium after annealing. According to Fig. 1(a), several phase layers have been formed at the right side of the initial bonding face. It indicates that Al atoms and Si atoms have diffused into the Ti end-members and reacted with Ti atoms. Furthermore, the layer of 100 μm thick neighboring to the initial bonding face in Al-10wt.%Si side is no (Si) particles, which is caused by the migration of Si atoms to Ti side.

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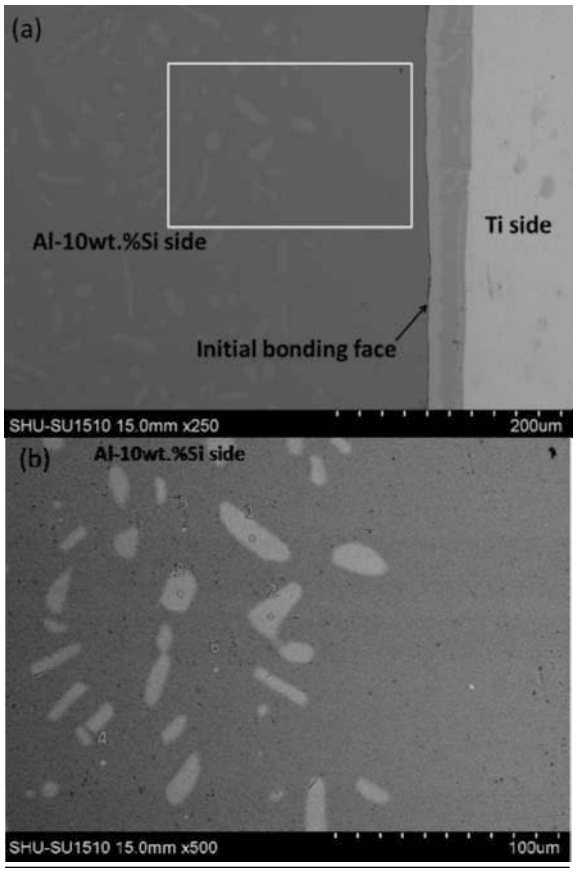

Figure 1. BSE images of the diffusion zoon forming in the Al-10wt.%Si/Ti couple: (a) full view image; (b) the enlarged image of Al-10wt.%Si side.

Table II. The compositions of EDS analyzed points marked in Figure 1(b).

Points	Al (at.%)	Si (at.%)	Ti (at.%)	Phases
1	0.6	99.4	0.0	(Si)
2	0.5	99..5	0.0	
3	1.0	99.0	0.0	
4	99.1	0.9	0.0	(Al)
5	98.9	1.1	0.0	
6	99.6	0.4	0.0	

Fig. 2 is the enlarged image of the diffusion zoon, which is also marked with the points analyzed by EDS. Table III shows the compositions of corresponding analyzed points. In this image three new phase layers can be observed at the right side of the initial bonding face, and their interfaces are almost straight. According to the results showed in Table III, the dark gray region at the left side of the initial bonding face is (Al). The first bright gray layer at the right side of the initial bonding face is a ternary phase, and its composition is closed to τ_1. Next in order is the dark gray layer. Its composition agrees well with $Ti(Al,Si)_3$ reported by Zeren, et al.[3]. The next layer also consists of three elements, however, its composition is different from any ternary compound reported by Zeren, et al.[3]. Considering its largely changing composition and thinness as well, it is reasonable to conceive that a series of Ti-Al and Ti-Si compounds are nucleating and growing up in this layer. The bright gray region at most right part of the image is pure Ti. Form the EDS results, the sequence of phase layers formed in the diffusion zoon of the sample is: (Al) → τ_1 → $Ti(Al,Si)_3$ → a series of Ti-Al and Ti-Si compounds → Ti.

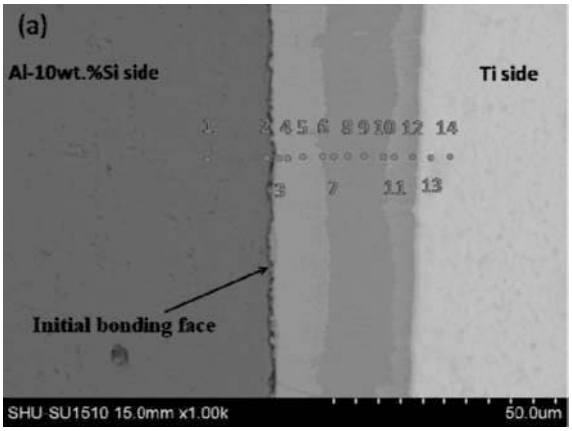

Figure 2. The enlarged BSE image of the diffusion zoon forming in the Al-10wt.%Si/Ti couple. The EDS analyzed points are marked on the image.

Table III. The compositions of EDS analyzed points marked in Figure 2.

Points	Al at.%	Si at.%	Ti at.%	phases
1	99.3	0.7	0.0	(Al)
2	99.0	1.0	0.0	
3	11.7	55.2	33.1	τ_1
4	12.6	54.8	32.7	
5	16.4	51.3	32.3	
6	62.2	11.8	26.0	$Ti(Al,Si)_3$
7	63.0	11.5	25.5	
8	61.9	12.4	25.8	
9	62.4	12.4	25.2	
10	62.1	12.2	25.7	
11	26.2	42.6	31.3	Ti-Al and Ti-Si Compounds
12	45.1	27.1	27.7	
13	0.0	0.0	100.0	Ti
14	0.0	0.0	100.0	

After the sample had been broken apart along the initial bonding face, the crack surfaces of both end-members had been analyzed by XRD, respectively. The XRD pattern (Fig. 3) shows that the phases sticking on the crack surface of Al-10wt.%Si bulk are (Al) and (Si), and the amount of (Al) is much larger. Meanwhile, the phases sticking on the crack surface of Ti bulk are $Ti_7Al_5Si_{12}$ and $Ti(Al,Si)_3$, and $TiSi_2$ may also exist. Thus, the diffusion path way can be further confirmed as: (Al)→$Ti_7Al_5Si_{12}$→$Ti(Al,Si)_3$. Furthermore, this experiment result reveals two two-phase equilibriums. One is the equilibrium between (Al) (its average composition is $Al_{99.2}Si_{0.8}$), and $Ti_7Al_5Si_{12}$ (its average composition is $Ti_{32.7}Al_{13.6}Si_{53.7}$). The other

is between $Ti_7Al_5Si_{12}$ and $Ti(Al,Si)_3$ (its average composition is $Ti_{25.6}Al_{62.3}Si_{12.1}$).

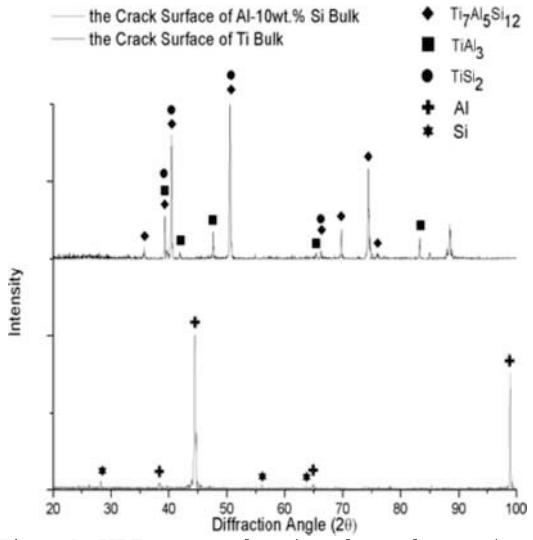

Figure 3. XRD pattern of crack surfaces of two end-members.

Fig. 4 is the calculated isothermal section of Al-Si-Ti system at 500°C. Two end points of the red solid line crossing the isothermal section denotes two end-members' compositions. The calculated ternary diagram and related thermodynamics database are extrapolated from binary systems of Al-Si[4], Al-Ti[5], Ti-Si[6]. The adopted ternary phases in this calculation are τ_1 ($Ti_7Al_5Si_{14}$) and τ_2 ($Ti_3Al_2Si_5$), which are reported by J. Gröbner, et al.[7]. According to this isothermal section, there are two three-phase equilibriums, including (Al) + (Si) + $Ti_7Al_5Si_{14}$ and (Al) + $Ti_7Al_5Si_{14}$ + $Ti(Al,Si)_3$, and three two-phase equilibriums, including (Al) + $Ti(Al,Si)_3$, (Al) + $Ti_7Al_5Si_{14}$ and $Ti_7Al_5Si_{14}$ + $Ti(Al,Si)_3$, in the Al-rich corner. Thus, it can be found that the equilibrium relationships identified by this experiment are consistent with the related equilibrium information from the calculated isothermal section.

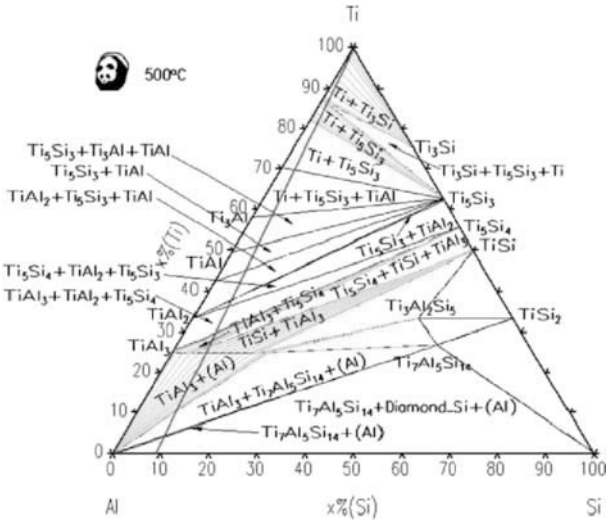

Figure 4. Calculated isothermal section of Al-Si-Ti at 500°C

Conclusions

Through Al-10wt.%Si diffusion couple experiment, the phase equilibriums in the Al-rich corner of the ternary Al-Si-Ti system at 500°C have been investigated. The experiment results can be concluded as follows:

1. The confirmed reaction path way in the diffusion zoon of the sample is (Al) → $Ti_7Al_5Si_{12}$ → $Ti(Al,Si)_3$.
2. The diffusion couple reveals two two-phase equilibriums existed in the Al-rich corner of the Al-Si-Ti system at 500°C, which are (Al) + $Ti_7Al_5Si_{12}$ and $Ti_7Al_5Si_{12}$ + $Ti(Al,Si)_3$. This result is consistent with the corresponding calculated isothermal section of the Al-Si-Ti system.

Acknowledgments

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