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Thermodynamic investigation on phase formation in the Al–Si rich region of Al–Si–Ti system

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ABSTRACT

The thermodynamic condition for phase formation in the Al–Si–Ti system is crucial for understanding the reason behind deteriorations of grain refinement and castability of Al–Si–Ti alloys. Seven Al–Si–Ti alloys annealed between 550 and 650 °C were used to clarify the inconsistencies of phase equilibria in the Al–Si rich region. The existences of τ_1 ($Zr_3Al_4Si_5$-type tetragonal), τ_2 ($ZrSi_2$-type orthogonal) and the three-phase equilibrium of $\tau_1 + \alpha$-Al + Si were confirmed. Combined with a critical review of literature data, a CALPHAD-type thermodynamic description was developed for the phase equilibria in the Al–Si rich region of the Al–Si–Ti system between 550 and 900 °C. Meanwhile, edge-to-edge matching analysis according to the crystal structures of τ_1 and τ_2 shows that their nucleation efficacies for α-Al are both weaker than that of $Ti(Al,Si)_3$. From the calculated phase equilibrium of $L + \tau_2 + Ti(Al,Si)_3$ at 727 °C and the local equilibrium principle, τ_2 would form on the surface of $TiAl_3$ particle and deteriorate its grain refinement efficiency for α-Al. From the calculated liquidus projection, $Ti(Al,Si)_3$ is the primary phase within 0–10.3 wt.% Si and 0.08–0.30 wt.% Ti. To avoid the formation of τ_1 and τ_2 for retaining good grain refinement efficiency and castability, a Ti/Si threshold was determined by thermodynamic calculations.

1. Introduction

With their low thermal-expansion coefficient, high wear resistance, and good corrosion resistance, Al–Si casting alloys are widely used in automobile industry [1–3]. Ti is commonly added into the Al alloy system to form $TiAl_3$ for refining the grain of α-Al [4–6]. However, a series of phases containing Ti and Si would also form in the Al–Si–Ti alloys, such as $TiSi_2$, TiSi, Ti_5Si_3 and TiAlSi (a general expression for Al–Si–Ti ternary phases [7]). Using edge-to-edge matching model (E2EM) [8,9], Qiu et al. [10] investigated the possible poisoning effects of several phases containing Ti and Si on grain refinement for α-Al. They pointed out that Ti_5Si_3 was more likely to form on the surface of $TiAl_3$ than $TiSi_2$ and TiSi. On the contrary, Quested et al. [11] used a thermodynamic description without the TiAlSi phase in Al-rich system. They found that $TiSi_2$ and TiSi would form on the surface of $TiAl_3$ particle. The possible poisoning effect of TiAlSi phases on grain refinement for α-Al was rarely reported in literature. Meanwhile, Chen et al. [7] pointed out that TiAlSi phases induced by an excess amount of Ti would cause blockage during casting and wormhole in the final product, as indicated by A356/357 alloys containing Ti over 0.1 wt.%.

A fundamental knowledge about phase formation from the thermodynamic aspect is necessary to clarify the deteriorations of grain refinement for α-Al and the casting quality of the Al–Si–Ti alloys. However, the available Al–Si–Ti phase diagrams are partially inconsistent and cannot help us to understand the mechanism of grain refinement for Al–Si casting alloys using titanium from the thermodynamic aspect. Therefore, the purpose of the present work is to investigate the phase equilibria in the Al–Si rich region (≤50 at.% Ti) by analyzing equilibrated alloys using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS), with special attention on the TiAlSi phases. Then a CALPHAD-type thermodynamic description for the Al–Si rich region in the temperature range from 550 to 900 °C will be developed. E2EM will be used to examine the grain-refining efficacies for the interested phase α-Al in the Al–Si–Ti alloys. Based on the thermodynamic calculations of phase equilibrium and solidification

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process, the reason for the deterioration of grain refinement for α-Al will be explained and the Ti/Si threshold for keeping adequate quality of the Al–Si–Ti alloys will be also determined.

2. Literature review of the Al–Si rich region

The phases in the Al–Si rich region (≤50 at.% Ti) of the Al–Si–Ti system have been reviewed by Perrot [12]. τ_1 ($Ti_7Al_5Si_{12}$) with $Zr_3Al_4Si_5$-type crystal structure has a wide homogeneity range of $(Ti_{1-x}Al_x)(Si_{1-y}Al_y)_2$ ($x = 0.12, 0.06 \le y \le 0.25$) on the isothermal section at 700 °C [12–14]. However, some researchers thought that its composition range was much narrower [15–17], such as $Al_{6.2–9.3}Si_{57.5–60.9}Ti_{32.4–34.0}$ [15]. τ_2 with $ZrSi_2$-type (C49) is usually described as $Ti(Si_{1-x}Al_x)_2$ ($0.15 \le x \le 0.3$) [18], and its composition range was given differently as $Al_{15–19}Si_{48–52}Ti_{32–33}$ [14] and $Al_{10.0–11.6}Ti_{34.2–34.5}Si_{53.9–55.6}$ [15]. Although the composition ranges of τ_1 and τ_2 remain controversial, it still can be concluded that τ_1 and τ_2 both contain about 33 at.% Ti and τ_2 has a higher Al/Si ratio than τ_1.

Whether τ_2 is evolved from β-$TiSi_2$ remains controversial. $TiSi_2$ has a C54-type structure (denoted as α-$TiSi_2$) and a C49-type structure (denoted as β-$TiSi_2$) [19]. Based on an obvious shrinkage of the electrical resistivity of $TiSi_2$ at about 1200 °C [20], Seifert et al. [19] suggested that α-$TiSi_2$ → β-$TiSi_2$ took place at 1200 °C. Meanwhile, Beyers et al. [21] pointed out that β-$TiSi_2$ was metastable and would transform to α-$TiSi_2$ during annealing below 800 °C. Bulanova et al. [22] thought that τ_2 was the Al-stabilized β-$TiSi_2$ below 1200 °C. However, there is a big difference between melting points of τ_2 (1338 °C [23]) and $TiSi_2$ (1448 °C [19]).

As for phase equilibria, Dezellus et al. [16] investigated the liquid–solid phase equilibria between 600 and 800 °C, and L + τ_2, L + τ_1 + τ_2 and L + τ_1 phase regions were determined. These phase equilibria were also presented in the isothermal sections of the Al–Si–Ti system at 700, 727 and 900 °C [15,17,23]. Li et al. [24] determined the three-phase equilibrium of α-Al + τ_1 + $TiAl_3$ at 500 °C by Al–10 wt.% Si/pure Ti diffusion couple. Li et al. [15] confirmed five three-phase equilibria of τ_1 + Si + liquid, τ_1 + α-$TiSi_2$ + TiSi, τ_1 + α-$TiSi_2$ + Si, TiSi + $TiAl_3$ + τ_2 and τ_1 + τ_2 + TiSi at 700 °C by eleven equilibrated alloys in the Al–Si rich region. However, in our previous work [25] a three-phase equilibrium of L + τ_2 + Si was obtained by regarding τ_1 as a metastable phase which was not found in the alloys annealed between 450 and 700 °C for 310–3360 h by XRD and SEM-EDS. So the stability of τ_1 is still under discussion.

Liu et al. [23] proposed L + τ_2 → τ_1 + α-Al taking place between 577 and 592 °C for the Al–Si–Ti system based on differential thermal analysis. By using differential scanning calorimetry (DSC), Luo et al. [25] determined that the reaction temperature of L + $TiAl_3$ → τ_2 + α-Al was 595 °C, which is consistent with 592 °C reported by Liu et al. [23]. According to the analyses on morphologies of crystals, chemical compositions of phases and temperatures of invariant reactions, Dezellus et al. [16] drew up a liquidus projection for the composition range of 0–25 at.% Si and 0–0.25 at.% Ti, in which the invariant reaction with the lowest temperature on a liquidus surface was L + τ_1 → α-Al + Si at 578.3 °C.

As for the thermodynamic description of the Al–Si–Ti system, Youdelis [26] did not consider $Ti(Al,Si)_3$, τ_1, τ_2 and even the binary Ti–Si silicides like TiSi and $TiSi_2$. Based on the isothermal section of the Al–Si–Ti system at 700 °C and a partial liquidus projection near the Al–Si binary eutectic [14,27], Gröbner et al. [28] developed a thermodynamic description of the Al–Si–Ti system in which $Ti(Al,Si)_3$, τ_1 and τ_2 were modeled as $(Al,Ti)_{0.25}(Al,Si,Ti)_{0.75}$, $(Ti)_3(Al)_2(Si)_5$ and $(Ti)_7(Al)_5(Si)_{12}$, respectively. In their work, the Gibbs energy of τ_1 was set to be inappropriately low and makes the calculated phase equilibria and invariant reactions concerning L, α-Al, $Ti(Al,Si)_3$, τ_1 and τ_2 between 550 and 900 °C inconsistent with the experimental results in Refs. [15–17,23]. Luo et al. [25] did not consider τ_1 as a stable phase in their thermodynamic modeling. Azevedo et al. [29,30] assessed only the Ti-rich corner of the Al–Si–Ti system between 700 and 1200 °C. Therefore, it is necessary to redevelop a reliable thermodynamic description in the Al–Si rich region of the Al–Si–Ti system.

3. Experimental details

Ten alloys were prepared and their nominal compositions were listed in Table 1. The compositions of alloys #1–#7 were selected from the isothermal sections of the Al–Si–Ti system at 550, 600 and 650 °C calculated with the previous thermodynamic description [28] for clarifying the phase equilibria of τ_1 and τ_2. The alloys #8 and #9 were used to obtain the crystallographic information of τ_1 and τ_2, respectively. Alloy #10 was made to verify the existence of the transformation α-$TiSi_2$ → β-$TiSi_2$ at about 1200 °C.

All alloys were synthesized by a medium frequency induction furnace under high purity argon atmosphere (99.999%) from Al (99.999%), Ti (99.95%) and Si (99.9%) in a water-cooled copper crucible. Each alloy was re-melted at least five times to ensure their homogeneity. Alloys #1–#7 were cut into small blocks by a wire electro-discharge machine. These small blocks were individually wrapped by tantalum foils and sealed into evacuated quartz capsules. The annealing at 550, 600 and 650 °C was performed in muffle furnaces for 1368–4932 h followed by quenching in ice water. Setting such a long annealing time was to guarantee that the equilibrium state could be obtained, particularly for the samples containing τ_1. Alloys #8–#10 were annealed at 900 °C for 360 h followed by furnace cooling to obtain well crystallized τ_1, τ_2 and α-$TiSi_2$. It should be stressed that the raw materials for alloy #10 were 8.100 g of Si bulk and 6.897 g of Ti bulk, which were weighted strictly following the atomic ratio of Ti and Si in α-$TiSi_2$. To determine the thermodynamic stability of β-$TiSi_2$, a small block (about 1 g) of alloy #10 annealed at 900 °C was further annealed at 1350 °C for 10 h, followed by quenching in ice water.

Standard metallographic procedures were performed for alloys #1–#7, followed by SEM analysis on JSM-6700F equipped with Inca X-Max^N EDS (15 kV, live time is 60 s). The working distance was set to be 13–14 mm. The relative error for EDS measurements of Al, Si and Ti in this work was estimated to be ≤5%. Meanwhile, the powder samples of alloys #1–#7 were analyzed by a D/MAX 2500 diffractometer with Cu Kα radiation. The high resolution XRD (HRXRD) patterns of τ_1 and τ_2 were collected by a Mythen-II detector on the powder diffraction beamline at Australian synchrotron with $\lambda = 0.09995$ nm, followed by Rietveld refinement using Topas 4.2 version.

The allotropic transformation of α-$TiSi_2$ → β-$TiSi_2$ was investigated by thermal dilatometer (DIL) on a Netzsch DIL 402 at the flowing rate of 50 ml/min Ar and heating rate of 5°/min. The cylinder sample (Φ 6.0 × 10.0 mm) was cut from the center of alloy #10 annealed at 900 °C by a wire electro-discharge machine.

All the thermodynamic calculations in this work were performed by Pandat software [31].

Table 1
Nominal compositions of the Al–Si–Ti alloys.

No.	Nominal composition
#1	Al–46.4 at.% Si–29.5 at.% Ti
#2	Al–50.5 at.% Si–34.5 at.% Ti
#3	Al–54.0 at.% Si–39.0 at.% Ti
#4	Al–57.0 at.% Si–36.5 at.% Ti
#5	Al–68.5 at.% Si–26.6 at.% Ti
#6	Al–56.1 at.% Si–14.6 at.% Ti
#7	Al–53.0 at.% Si–31.0 at.% Ti
#8	Al–58.8 at.% Si–32.4 at.% Ti
#9	Al–55.0 at.% Si–33.2 at.% Ti
#10	Ti–66.7 at.% Si