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Thermodynamic investigation of phase equilibria in Al–Si–V system

Qun Luo[a], Kang Li[a], Qian Li[a,b,c,*]

[a] State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai, 200072, China
[b] Materials Genome Institute, Shanghai University, Shanghai, 200444, China
[c] Shanghai Institute of Materials Genome, Shanghai, 200444, China

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ABSTRACT

The Al–Si–V system is assessed to understand the phase equilibria of V-containing (3*d* transition metal) Al–Si alloys, which are generally of great importance for technical applications. Four annealed alloys were prepared to study the phase equilibria of Al-rich corner ($V \leq 23.3$ at.%, $Si \leq 57.6$ at.%) in the temperature range of 500–930 °C. The microstructure and phase constituents of the samples were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDS). The existence of ternary phase τ ($Al_{0.6}Si_{1.4}V$, $TiSi_2$-type) was confirmed with the composition ranging from 17.98 to 18.59 at.% Al and 48.89–49.20 at.% Si. However, it did not equilibrate with fcc(Al) below 868 °C, which was determined by differential scanning calorimetry (DSC). The Si_3V_5 appeared in $Al_{58.5}Si_{18.3}V_{23.2}$ and $Al_{64.7}Si_{20.2}V_{15.1}$ alloys annealed at 500 °C. It nearly disappeared after 3000 h-annealing and its thermodynamic stability was discussed. According to the measured phase relationships, the thermodynamic description of Al–Si–V system was optimized combing with the enthalpies of formation of binary and ternary compounds obtained by density functional theory (DFT). The Si–V system was modified to obtain the congruent liquidus of Si_3V_5 and enthalpy of formation of Si_3V_5 and Si_2V with experimental data. By comparing the calculated phase equilibria and phase transitions with experimental data, it showed that a good agreement was reached. The description of Al–Si–V system could be used to guide the development of Al–Si alloys.

1. Introduction

The Al–Si alloys are widely used for automotive parts, such as engine blocks, cylinder heads, chassis, and driveline due to their good castability, low density, excellent thermal conductivity, high strength and low thermal expansion coefficient [1–3]. However, the microstructure of conventional cast Al–Si alloys contains large brittle Fe-containing intermetallic and coarse Si phase, both of which are detrimental for mechanical properties [4,5]. The role of transition metals in cast Al–Si alloys has been a subject of many studies because of the significantly improved hardness and compressive strength [6–9]. Among the transition metals, vanadium has low diffusivity and limited solid solubility in Al–Si alloys. The intermetallic formed during solidification process would promote the strength of cast Al–Si alloys. However, it is still controversial which phase plays the important role. Pathak et al. [10] and Sahoo and Pathak [11] found that addition of V in Al–Fe–Si alloys led to the formation of ultrafine $Al_{13}(Fe, V)_3Si$, which hindered the growth of large brittle intermetallic compounds and coarse Si phases. The results of Yaneva et al. [12,13] revealed that a quaternary silicide as $Al_{13.18}(Fe, V)_{1.84}Si$ with lattice parameter of 1.2578 nm formed in low silicon alloys and a new phase nucleated and grew to be polyhedral particles as a fine α_{13} (α-AlFeSi) quaternary intermetallic when Si concentration exceeded 3 wt%. In addition, Kasprzak et al. [9] and Meng et al. [14,15] indicated that V stabilized the phase of Al_3V or $Al_{21}V_2$, which served as the site of heterogeneous nucleation and improved the hardness and yield strength of Al alloys. These investigations suggest that the phase constitution and phase formation in V-containing Al–Si alloys are not clear, which is obstructing our understanding of V affects. Therefore, the phase equilibria of Al–Si–V system needs to be investigated to explain the refinement mechanism in Al–Si alloy with the addition of V.

There are few reports concerning the thermal stability of intermetallic and phase equilibria in the Al–Si–V system. Gebhardt and Joseph [16] proposed a partial liquidus projection, a partial Scheil diagram and several vertical sections of Al–Si–V system up to

* Corresponding author at: State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China.
E-mail address: shuliqian@shu.edu.cn (Q. Li).

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6.7 at.% V. The results showed that the solubility of Si was 0.3 at.% in $Al_{21}V_2$ and 1.5 at.% in $Al_{23}V_4$, whereas $Al_{45}V_7$ had little solubility of Si. They also determined the three-phase fields $Al_3V + Al_{23}V_4 + Si_2V$ and Fcc(Al) + $Al_{23}V_4 + Si_2V$ in the Al–Si–V system. The phase relations in V-rich part concerning the superconducting phase SiV_3 were provided by Müller [17]. It showed that the solubility of Al in SiV_3 was 3.5 at.% at 1000 °C and no ternary phase was found. Huber et al. [18,19] studied the phase equilibria and phase transitions of Al–Si–V system up to 50 at.% V in the temperature range from 500 to 850 °C. The electron probe microanalysis (EPMA) results indicated that the solubility of Si in $Al_{45}V_7$ was higher than that of other Al–V compounds, whereas the $Al_{23}V_4$ and $Al_{21}V_2$ showed no solubility of Si. A $TiSi_2$-type ternary compound τ-$Al_{0.6}Si_{1.4}V$ was discovered and the structure was determined to be a space group of *Fddd*, *a* = 8.091 Å, *b* = 4.697 Å and *c* = 8.501 Å by means of single crystal X-ray diffraction (XRD). The analysis of the morphologies of cast samples suggested that the extension of the Si_3V_5 crystallization field towards the Al-rich corner. Except the experimental investigations, few thermodynamic descriptions of the Al–Si–V system was reported.

Lack of thermodynamic investigation of the Al-rich corner in Al–Si–V system is the barrier to explain the phase transformation and refinement mechanism of V addition in Al–Si alloys. Therefore, the present work focuses on the experimental determination and thermodynamic analysis of the phase equilibria in the Al-rich corner of Al–Si–V system. The phase constitution and phase relationship in each sample ranging from 500 to 930 °C are determined by XRD, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

2. Experimental procedure

Each sample with a total weight of 20 g starting from the elemental Al (99.99 wt%), V (99.99 wt%) and Al–30 wt% Si alloys (99.99 wt%) was prepared by arc melting on a water-cooled copper tray with a non-consumable tungsten electrode under the protection of high purity argon atmosphere (99.999%). The samples were turned over and re-melted four times to ensure homogeneity. The weight loss of each sample was less than 1 wt%. Small strips of 5 mm × 5 mm × 10 mm were cut by wire electro-discharge machine. The samples were labeled as #1–#4 with approximate compositions of $Al_{58.5}Si_{18.3}V_{23.2}$, $Al_{64.7}Si_{20.2}V_{15.1}$, $Al_{73}Si_{18.3}V_{8.7}$ and $Al_{29.2}Si_{57.6}V_{13.2}$, respectively. Each sample was wrapped by a tantalum sheet, and sealed in evacuated quartz tubes. Because the V in the Al–Si–V alloys would react with the quartz tube (SiO_2) during the annealing process, the Ta foil was used to segregate the sample and quartz tube. Ta foil was chosen because of its high melting point and low solid solubility in Al. There is no reaction between Al and Ta below 661 °C, and the maximum solid solubility of Ta in Al is about 0.037 at.% at 661 °C. At high temperature, the intermetallic layer would form at the surface of the sample. However, the reaction layer is thin, about several microns. The intermetallic layer at the surface was removed by polishing on abrasive papers. In addition, the composition of sample was determined by inductively coupled plasma atomic emission spectrometry (ICP) after annealing. The content of Ta was low to 83 ppm. Therefore, the effect of impurity Ta was not considered in the present work. The samples were annealed at 500 °C for 1080 h, 600 °C for 144–1080 h, 654 °C for 72–20 h, 760 °C for 144 h, 850 °C for 43 h and 930 °C for 40 h, respectively, and then quenched in water.

XRD was performed on samples using D/MAX 2500 diffractometer with the scanning range from 10° to 90° at a rate of 2°/min. The sample #2 used for the XRD examination was bulk because of its good ductility. Other samples used for XRD examination were powders. The microstructure and composition of phases in the samples were measured by HITACHI SU-1500 SEM equipped with EDS. The NETZSCH 404C DSC was used to examine the phase transition temperatures with heating rate of 5 °C/min under high purity argon atmosphere at a flowing rate of 50 mL/min. In addition, the heating

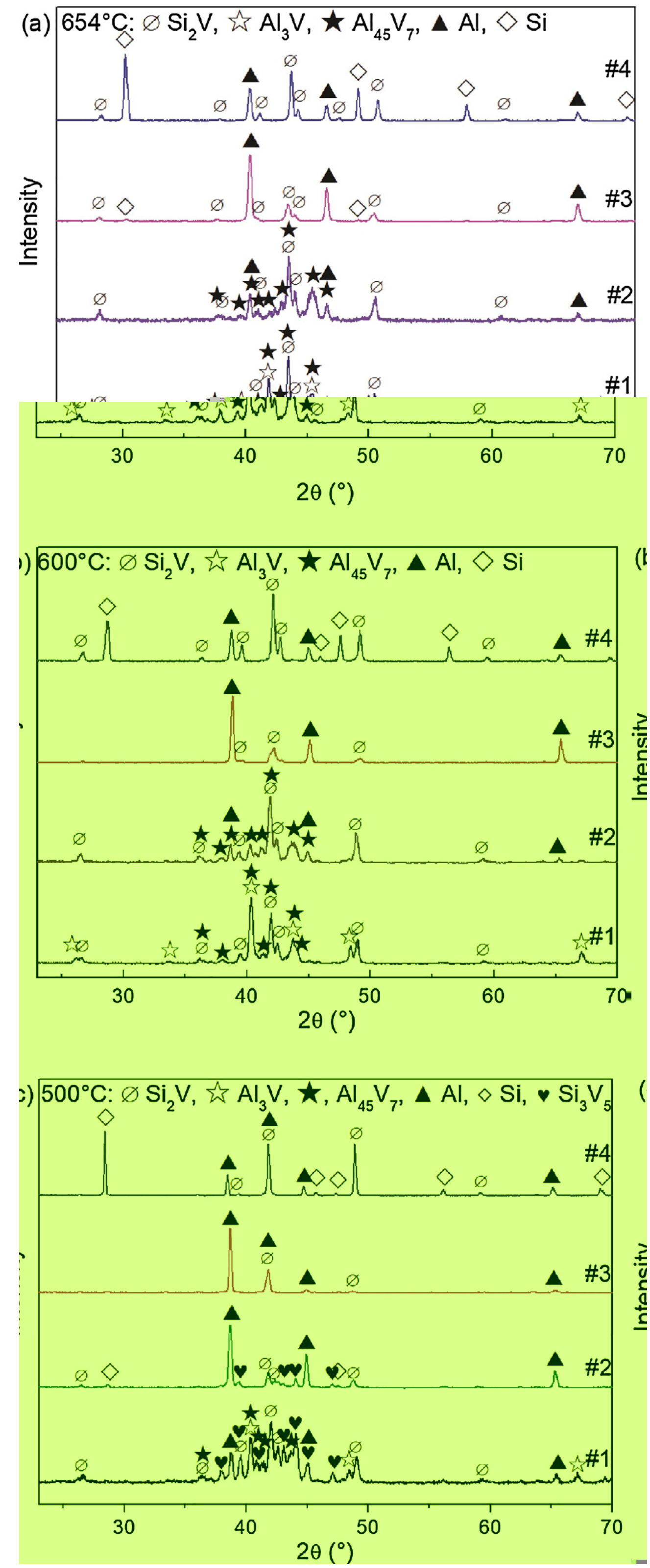

Fig. 1. XRD patterns of samples #1–#4 annealed at (a) 654 °C, (b) 600 °C and (c) 500 °C.