Preparation and microstructural characterization of the 60Al-40V master alloy

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Abstract. The present study focused on preparation and characterization of 60Al-40V master alloy which was produced via aluminothermic process. The study assessed the production in order to provide the optimum Al requirement for maximum recovery of the V. V_2O_5 (Vanadium pentoxide) and Al metal were mixed in the proportion of producing 60Al-40V and Al_2O_3 (slag) through an exothermic reaction. Microstructural analysis and phase identification were done using Optical Microscopy (OM), Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDX) and X-Ray Diffraction (XRD) analyses. The XRD revealed diffraction peaks mainly of the Al_3V phase and some peaks of slightly homogenized Al_8V_5 intermetallic compounds. The chemical composition was found to be 65 ± 0.03 and 35 ± 0.03 wt. % Al and V respectively. Good agreement between the experimental results and the predicted phases using Thermo-Calc. Software was observed.

1. Introduction

Ti and its alloys are sought after for their mechanical and thermal properties [1]. For example, the Ti-6Al-4V alloy is one of the most widely used in applications requiring excellent oxidation resistance and high-temperature strength retention such as automobile and aerospace field especially [2]. Al-V alloys are important master alloys, they are used as Al and V sources to produce Ti-6Al-4V alloy. Two classical powder metallurgy (PM) methods for producing useful Ti alloys, such as Ti-6Al-4V are the blended elemental and pre-alloyed approach [3]. In the pre-alloyed method, the 60Al-40V master alloy can be added to pure Ti in order to produce the Ti-6Al-4V alloy, which is considered as the semi-finished product that is used as raw materials in the Ti industry. These pre-alloyed elements are produced via aluminothermic (thermite) smelting process within a refractory-lined or copper vessel. However, the aluminothermy processes are usually used in the manufacture of master alloys in the steel and superalloy industry. In this process refractory metal oxides or ores are reduced thereby offering a production method free of carbon. The greater difference in O affinity of Al and metal oxide, the higher is the ease of reaction [4]. For the 60Al-40V master alloy been in considerable demand to develop Ti-6Al-4V alloy; in this study, the aluminothermy technique has been proposed as a method to produce the master alloy. The produced pre-alloy must content about 60 at % Al. and 40 at % V. In the production of the master alloy, V_2O_5, and Al metal need to be mixed in such proportion to produce an exothermic reaction capable of generating the master alloy [5]. The exothermicity of the reaction is dependent on the level of V_2O_5 and the concentration levels of the starting materials [6]. This makes it difficult to produced pure V metal because V reacts and absorbs readily O, N, and C considered as impurities. The level of impurity pronounced the strengthening effect, therefore affecting the mechanical properties of V. Furthermore, dissolved C, O, and N levels of the order of 2000 to 4000 raises the ductile-brittle transition temperature

(DBTT) in unalloyed V at room temperature [7]. Hence, the presence of these impurities renders V brittle. The aluminothermy is a process for reducing metal oxides using finely divided Al powder. The mixture of Al and oxides is ignited, causing the Al to be oxidized and the metal oxide to be reduced to the metal [8]. The reduction of V_2O_5 in the electrical furnace leads to high carbon content, therefore, the aluminothermy technique may be an effective way of producing 60Al-40V master alloy if a suitable reaction vessel is used. In the current study, the 60Al-40V master alloy was produced through the aluminothermic reaction process. Analytical techniques were then employed to assess the aluminothermic process in terms of chemical element contamination and thermodynamic feasibility in order to provide the optimum Al requirement for maximum recovery of V.

2. Experimental procedure

The 60Al-40V master alloy supplied by the CSIR was produced through aluminothermic reaction. V_2O_5, pure Al and flux are produced in water cooler copper vessel. The different constituents were mixed in such proportion that the reaction is exothermic and reduction of V_2O_5 to V by Al is thermodynamically favourable, equation 1.

$$3V_2O_5+16Al \rightarrow 6AlV+5Al_2O_3+heat \qquad \text{(equation 1)}$$
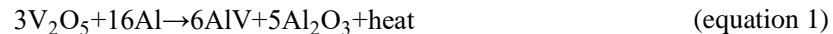
The Thermo-Calc. software with Al database was used for thermodynamic calculation and predictions of Al-V phases. The specimens of 60Al-40V produced were prepared for metallography investigation according to the ASTM standard E3-11 [9] (i.e. mounting, grinding, polishing and etching). The mounted samples were wet ground on SiC abrasive papers (P400-P1200) and polished up to 0.25 µm finished with colloidal silica (OP-S) suspension. The polished samples were thereafter etched in diluted Kroll's reagent followed by immediate rinsing under running water to avoid corrosive action of the etchant. The etched specimens were then examined using an optical microscope equipped with a high-resolution digital camera and Olympus Stream Essentials™ software. The phase identification was performed using XRD analysis with Cu Kα radiation and the results interpreted using X'Pert High Score Plus software. Zeiss Ultra PLUS FEG SEM, coupled with an Aztec X-Max energy dispersive spectroscopy (EDS) technique was used for imaging, and determination of chemical elements present in the different phases identified.

3. Results

3.1. Thermodynamic predictions

The equilibrium phase diagram of the given system is key in understanding the phase equilibria between constituents. The phase diagram of the Al-V binary and expected intermetallic phases have been investigated in this work using Thermo-Calc. software. Table 1. gives the list of phases of the Al-V predicted using Thermo-Calc. computer software.

Table 1. Phases in the Al-V system using Thermo-calc. computer software in this work.

Phase names	Other names	Weight range	strukturbericht	Space group	Pearson symbol	Model
liquid						(Al, V)
(Al)	fcc	0-0.05V	A1	Fm-3m	cF4	(Al, V)
Al$_{21}$V$_2$	Al$_{10}$V	8.7-4.9		Fd-3m	cF184	$(Al)_{10}(V)_1$
Al$_{45}$V$_7$	Al$_7$V	16.1V		C2/m	Mc104	$(Al)_7(V)_1$
Al$_{23}$V$_4$		21-24V		P63/mm	hP54	$(Al)_{23}(V)_4$
Al$_3$V		24-38V	D022	I4/mmm	tl8	$(Al)_3(V)_1$
Al$_8$V$_5$		38V	D82	I4-3m	cl2	$(Al)_8(V)_5$
(V)	bcc	51.5-100V	A2	Im-3m	cl2	(Al, V)

In the Al-V binary system, 8 known stable phases are found: the Al (fcc) liquid phase, in which a small amount of V is dissolved, the V (bcc, A2) dissolving a large amount of Al and 5 intermetallic compounds [10] [11]. In the specific composition of the pre-alloyed 60Al-40V study in this work, two intermetallic phases are expected (Al_3V and Al_8V_5). Figure 1. Shows the phase diagram corresponding to the Al-V binary system constructed and used in this work using Thermo-Calc.
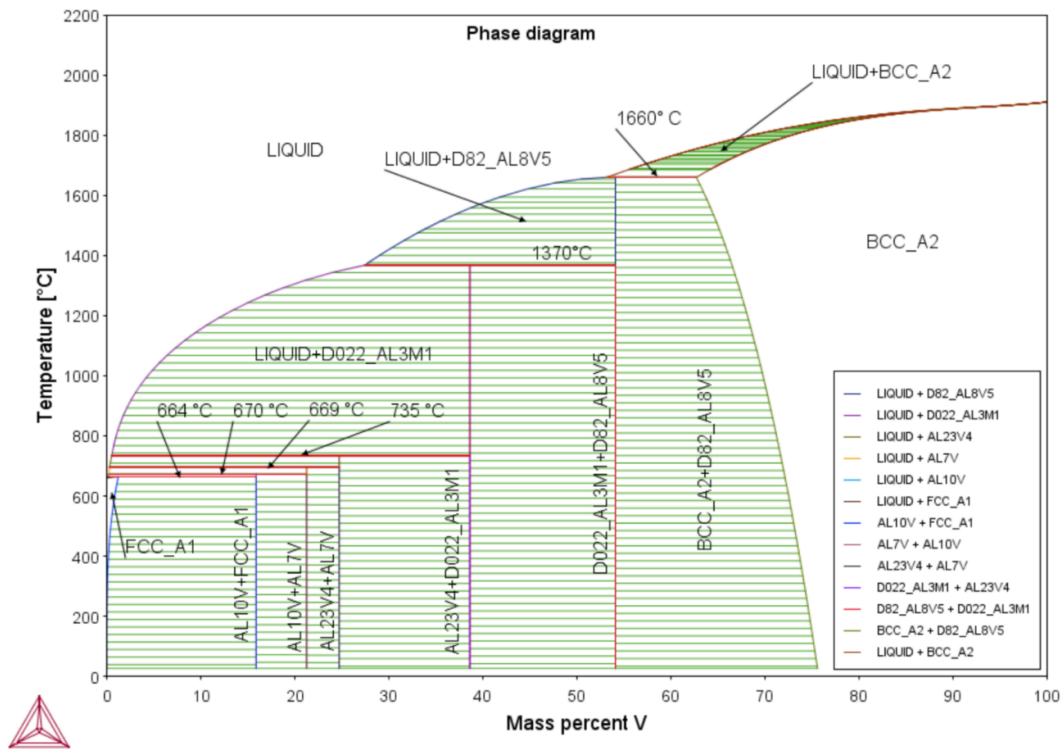
Figure 1. Al-V equilibrium binary phase diagram showing the various phases.

The Thermo-calc software was used to construct the Al-V phase diagram as well as the property diagram (Figure 1 and Figure 2). The intermetallic phases in this master alloy were predicted using the TC Binary Solutions V1.1 and SSOLOL4: Alloys Solutions Database V4.9 g. The predicted phases were calculated based on 60 wt. % Al. and 40 wt. % V. composition and were as follows: As expected, intermetallic phases namely $Al_{23}V_4$, Al_3V, and Al_8V_5 were obtained. The $Al_{23}V_4$ dissolve completely at a temperature of 800°C while the Al_3V started to dissolve at a temperature of 800°C and ended at 1380°C. The high-temperature Al_8V_5 phase only existed between 1380°C to 1450°C. Therefore, for high applications two intermetallic phases, namely Al_3V, and Al_8V_5 can be expected for temperatures above 800°C.
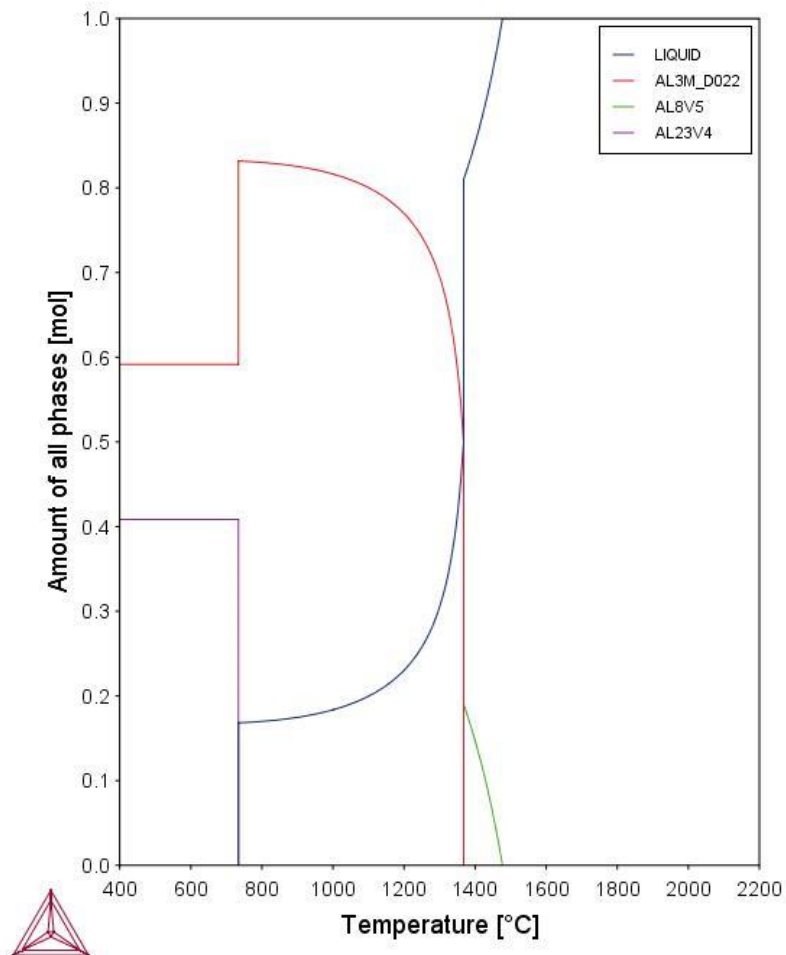
Figure 2. The amount of phases as a function of temperature in the 60Al-40V binary alloy system.

3.2. Phase identification

Figure 3 illustrates the XRD patterns of the 60Al-40V master alloy showing the phases identified in the alloy. The XRD patterns presented peaks of diffraction which corresponded to the crystalline intermetallic phases. The identified dominant peaks were the Al_3V (illustrated by high-intensity diffraction peaks) and some peaks of the Al_8V_5.
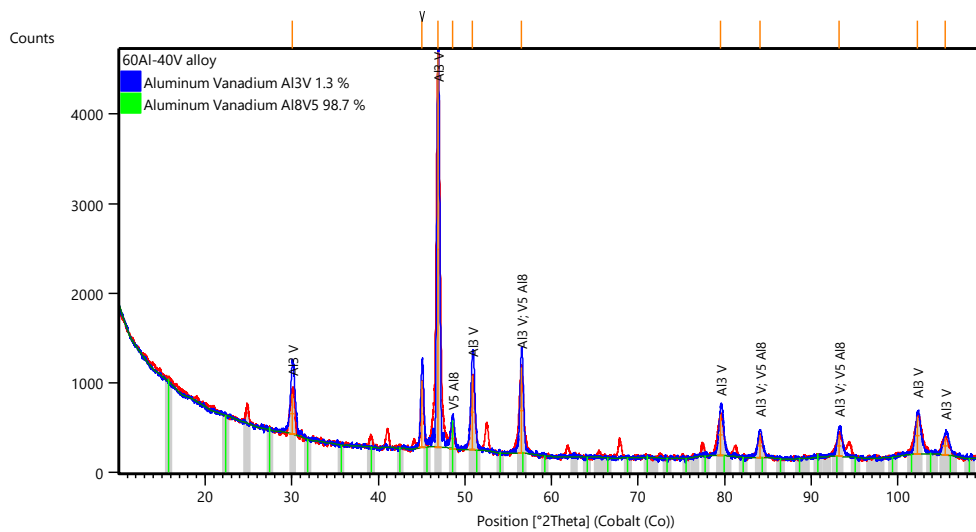
Figure 3. XRD patterns of the 60Al-40V master alloy showing the dominant phases in the alloy

3.3. Microstructural analysis

Figure 4.a shows SEM micrograph of the 60Al-40V master alloy, showing the microstructure which is typically dendritic structure. As may be seen, the microstructure of the alloy is composed of three phases i.e. the light grey, the dark grey, and the dark phases. The quantitative determination of the composition of each phase was done by EDS analysis (Figure 4.b.) illustrating the macrographs-EDS of the alloy by point scanning. The chemical compositions and the atomic percentage of the corresponding elements found in the phases are summarized in Table 2.
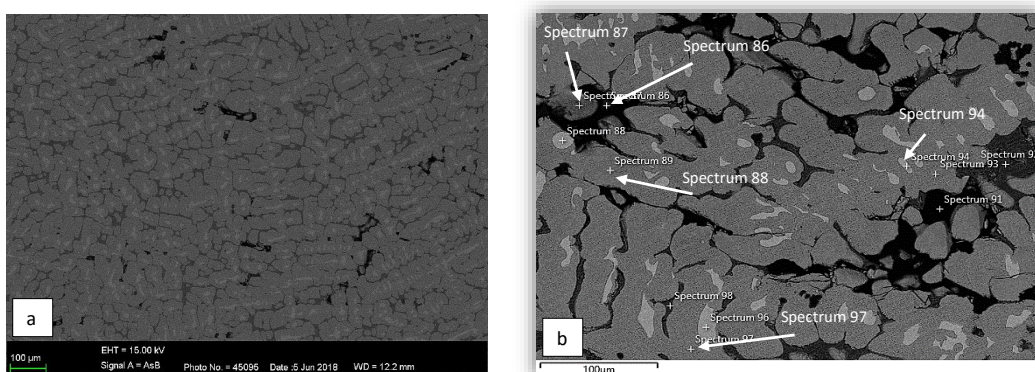

Figure 4.a) Electron Backscattered image; b) macrograph-EDS (point scanning) of the 60Al-40V master alloy. Magnification at 100 µm.

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Table 2. Phase color and chemical composition

Phase color	Element content	
	Al [At. %]	V [At. %]
Dark	35.4	64.6
Light grey	63.4 / 65.3	36.6 / 34.7
Grey	75.0 / 74.9	25.0 / 25.1

Figure 5 (b) Shows the EDS elemental map showing that the alloy consisted of Al and V elements. The average proportions of these elements in the bulk material were 65 ± 0.03 and 35 ± 0.03 wt. %.; 77.81 and 22.19 at. %. respectively (Table 3).

(a)   **(b)**
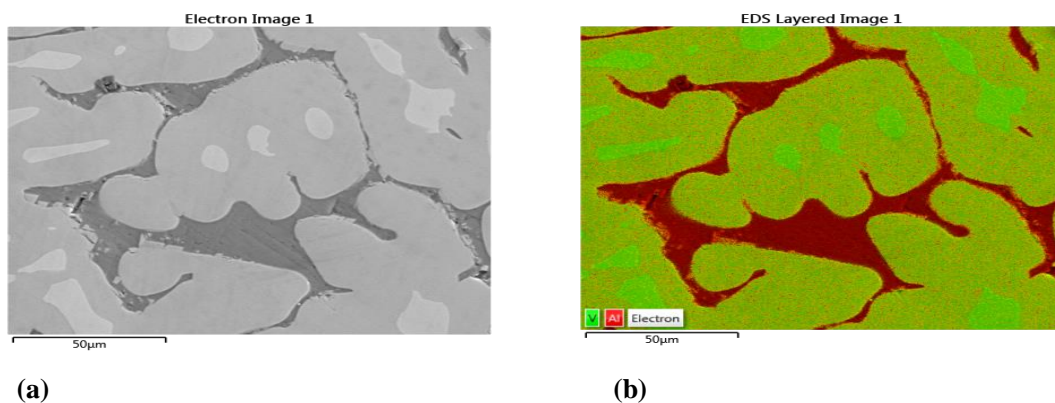
Figure 5. (a) SEM micrograph, (b) SEM-EDS layered image.

Table 3. EDS analysis-overall chemical composition

Elements	mass %	mass % sigma	At. %
Al	65.00	0.03	77.81
V	35.00	0.03	22.19
Total	100		100

4. Discussion

The Al-V binary phase diagram and property diagram calculated in this work using Thermo-calc, the proposed diagrams in Figure 1 and Figure 2, gave information on the phases formed (Table 1), and invariant temperatures as compared to the work of others [2][10] [12]. The solubility of V in liquid Al calculated from the temperature of 1100°C to 2200 °C, the liquidus was nicely reproduced as well as invariant temperatures. As can be observed, the corresponding phase diagrams and property diagrams of the system are similar in all features. Two intermetallic phases, namely the Al_3V and Al_8V_5 with the highest melting composition in Al-V to be the Al_8V_5 were obtained. It was therefore, observed that the melting reactions of peritectic type gave as transformation temperatures for Al_3V and Al_8V_5 of 1370°C and 1660°C respectively, while in their studies Richter gave peritectic temperatures of 1270°C and 1408°C for Al_3V and Al_8V_5 [13], and Massalki of 1360°C and 1670°C for Al_3V and Al_8V_5 respectively [14]. As can be seen, the results agree with those found in literature, the main difference of the phase diagram data is in the solubility of Al in bcc at the invariant reaction liquid $+bcc \rightarrow Al_8V_5$ which agrees with results observed by Massalki but deviate from the findings of Richter and Ipser. The XRD patterns revealed the presence of high-intensity diffraction Al_3V and the Al_8V_5 intermetallic phases (Figure 3) with Al_3V (cubic I4/mmm tL8) and the Al_8V_5 (cubic I-43m cl2) as illustrated in the ICSD data, which indicates that the system is not amorphous but crystalline. The qualitative determination of the alloy

through optical microscopy, the SEM micrograph in Figure 4.a showed a predominance of grey phases typically dendritic structure which was quantitatively identified by EDS technique through point scanning (Figure 4.b) and map scanning (Figure 5). The validation of alloying, by EDS analysis, showed that the aluminothermy-produced alloy consisted of both Al and V and present in the form of Al_3V and Al_8V_5 intermetallic phases. The mass ratio distribution of Al and V of the grey phases in the following spectrums 89 and 97 were 75.0 at. % and 25.0 at.%; and 74.9 at.% and 25.1 at.% respectively. Furthermore, the EDS map scanning revealed the average proportion of Al and V as approximatively 77.81 at % and 22.19 at. % respectively (Table 3), the phase equilibria being the Al_3V as also determined in [15]. The chemical composition found to be 65 ± 0.03 and 35 ± 0.03 wt.% Al and V respectively. Although the starting materials were in the right proportions, the final alloy of 65A-35V is close to the theoretical elemental composition of the 60Al-40V master. This indicates that the composition of atoms is close to 3:1 (Al: V), and Al_3V is the most expected compound. Hence, the phase constitutions which were determined by XRD conform to EDS results.

5. Conclusion

The aluminothermy process was adopted in this experiment to produce the intermetallic 60Al-40V master alloy. The microstructural characterization of the 60Al-40V master alloy produced was carried out. According to the XRD analysis, coupled with SEM-EDX technique, the following conclusions were drawn:

- The alloy consisted of both Al and V elements with the elemental chemical composition was 65 wt. % and 35 wt. % respectively.
- Two intermetallic phases namely Al_3V and the Al_8V_5 were formed in the final product as predicted by Thermo-Calc.
- The aluminothermic process can be used to produce the 60Al-40V master alloy to produce the famous Ti-6Al-4V alloy.

6. References

[1]   Y. M. Ahmed, K. Salleh, M. Sahari, M. Ishak, and B. A. Khidhir, "Titanium and its Alloy," no. October 2014.

[2]   A. Kostov and D. Zivkovi, "Thermodynamic analysis of alloys Ti-Al, Ti – V, Al – V and Ti-Al – V ˇ," vol. 460, pp. 164–171, 2008.

[3]   M. A. Masikane, "Investigation into the microstructure and tensile properties of unalloyed titanium and Ti-6Al-4V alloy produced by powder metallurgy, casting and layered manufacturing," 2015.

[4]   E. Gock and B. Friedrich, "ALUMINOTHERMIC PRODUCTION OF TITANIUM ALLOYS (PART 2): IMPACT OF ACTIVATED RUTILE ON PROCESS SUSTAINABILITY," 2015.

[5]   A. Oxide, "A thermite reaction (sometimes called a "," vol. 3, no. Iii,

[6]   M. K. G. Vermaak, "Vanadium recovery in the electro-aluminothermic production of ferrovanadium," University of Pretoria, 2000.

[7]   T. Division, "1. Introduction," vol. 143, pp. 1117–1124, 1986.

[8]   D. D. Akerkar, "Physico Chemical Aspects Of Alumino-Thermic Reduction In The Production Of Low Carbon Ferro-Alloys by," in *4th Refresher Course on Ferro Alloys*, 1994, p. 7.

[9]   ASTM International, "ASTM E3-11(2017) Preparation of Metallographic Specimens 1," *Area*, vol. 03, no. July, pp. 1–17, 2001.

[10]   B. Lindahl, X. L. Liu, Z. Liu, and M. Selleby, "CALPHAD : Computer Coupling of Phase Diagrams and Thermochemistry A thermodynamic re-assessment of Al – V toward an assessment of the ternary Al – Ti – V system," vol. 51, pp. 75–88, 2015.

[11]   A. Kroupa, M. Mazalová, and K. W. Richter, "CALPHAD : Computer Coupling of Phase Diagrams and The reassessment of the Al-V system and new assessment of the Al-Si-V system," vol. 59, no. July, pp. 47–60, 2017.

[12]   H. Okamoto, "Al-V (Aluminum-Vanadium)," *J. Phase Equilibria Diffus.*, vol. 33, no. 6, p. 491, 2012.

[13]   K. W. Richter and H. Ipser, "Al-V phase diagram between 0 and 50 atomic percent vanadium,"

Zeitschrift fuer Met. Res. Adv. Tech., 2000.

[14]   V. Raghavan, "Al-Ti-V (aluminium-titanium-vanadium)," *J. Phase Equilibria Diffus.*, vol. 26, no. 3, pp. 276–279, 2005.

[15]   Q. Luo, K. Li, and Q. Li, "Thermodynamic investigation of phase equilibria in Al-Si–V system," *J. Mater. Sci. Technol.*, 2018.