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

T O Mapoli1, a, K A Annan1, C W Siyasiya1 and Kalenda Mutombo2

1 University of Pretoria, Department of Material Science and Metallurgical Engineering, Lynnwood Road, Hatfield, Pretoria 0002, South Africa.

2 Light Metals, Materials Science & Manufacturing, Council for Science and Industrial Research, Meiring Naude Road, Brummeria, Pretoria 0185, South Africa.

E-mail: atresormapoli@gmail.com

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. V2O5 (Vanadium pentoxide) and Al metal were mixed in the proportion of producing 60Al-40V and Al2O3 (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 Al3V phase and some peaks of slightly homogenized Al8V5 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, V2O5 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 V2O5 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 V₂O₅ 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. V₂O₅, 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 V₂O₅ to V by Al is thermodynamically favourable, equation 1.

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3V_2O_5 + 16Al \rightarrow 6AlV + 5Al_2O_3 + \text{heat} \quad \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.

| Phase names | Other names | Weight range | strukterbericht | Space group | Pearson symbol | Model |
|-------------|-------------|--------------|-----------------|-------------|---------------|-------|
| liquid      | (Al)        | fcc          | 0-0.05V         | A1          | Fm-3m         | (Al, V) |
| Al₁₂V₂     | Al₁₀V       | 8.7-4.9      | Fd-3m           | cF184       | (Al)₁₀(V)    |       |
| Al₈V₅     | Al₇V        | 16.1V        | C2/m            | Mc104       | (Al)₇(V)₅    |       |
| Al₁₂V₄     | 21-24V      | P63/mmm      | hP54            | (Al)₁₂(V)₄ |               |       |
| Al₃V       | 24-38V      | D022         | I₄/mmm          | tI₈         | (Al)₃(V)₈    |       |
| Al₈V₅     | 38V         | D82          | I₄-3m           | cI₂         | (Al)₈(V)₅    |       |
| (V)        | bcc         | 51.5-100V    | A2              | Im-3m       | (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 (Al₁₂V₂ and Al₈V₅). Figure 1. Shows the phase diagram corresponding to the Al-V binary system constructed and used in this work using Thermo-Calc.
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 $\text{Al}_23\text{V}_4$, $\text{Al}_3\text{V}$, and $\text{Al}_8\text{V}_5$ were obtained. The $\text{Al}_23\text{V}_4$ dissolve completely at a temperature of 800°C while the $\text{Al}_3\text{V}$ started to dissolve at a temperature of 800°C and ended at 1380°C. The high-temperature $\text{Al}_8\text{V}_5$ phase only existed between 1380°C to 1450°C. Therefore, for high applications two intermetallic phases, namely $\text{Al}_3\text{V}$, and $\text{Al}_8\text{V}_5$ 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$_3$V (illustrated by high-intensity diffraction peaks) and some peaks of the Al$_3$V$_5$. 
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.
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).

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 Al₃V and Al₅V₅ with the highest melting composition in Al-V to be the Al₅V₅ were obtained. It was therefore, observed that the melting reactions of peritectic type gave as transformation temperatures for Al₃V and Al₅V₅ of 1370°C and 1660°C respectively, while in their studies Richter gave peritectic temperatures of 1270°C and 1408°C for Al₃V and Al₅V₅ [13], and Massalki of 1360°C and 1670°C for Al₃V and Al₅V₅ 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 → Al₅V₅ 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 Al₃V and the Al₅V₅ intermetallic phases (Figure 3) with Al₃V (cubic I4/mmm Tl8) and the Al₅V₅ (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 Al₃V and Al₈V₅ 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 Al₃V 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 Al₃V 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 Al₃V and the Al₈V₅ 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

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