



Synthesis of V-Ti-Cr alloys by aluminothermy co-reduction of its oxides

Sanjay Kumar*, Nagaiyar Krishnamurthy

Fusion Reactor Materials Section, Bhabha Atomic Research Centre Mumbai, 400085, India

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Abstract

Synthesis of V-Ti-Cr solid solution alloy by co-reduction of V_2O_5 , Cr_2O_3 and TiO_2 with aluminium in an open bomb reactor was investigated. The reduction of V_2O_5 and Cr_2O_3 was highly exothermic while reduction of TiO_2 was not sufficiently exothermic for self-sustaining reaction. A range of composition of V_2O_5 , Cr_2O_3 and TiO_2 mixture was chosen to make overall process sufficiently exothermic to sustain the reaction in a controlled manner. After the co-reduction, V-Ti-Cr-Al solid solution was obtained. As-obtained solid solution was refined by electron beam melting (EB) to remove the aluminium and residual oxygen. EB melted V-Ti-Cr thus obtained contains substantially less amount of aluminium (~0.081%). Throughout the synthesis process the prepared products were analyzed using scanning electron microscope (SEM), energy dispersive X-ray fluorescence (EDAX), chemical analysis, gravimetric analysis and X-ray diffraction.

Keywords: exothermic, V-Ti-Cr alloy, aluminothermy, intermetallic

1. Introduction

Metallic vanadium (V) is one of the few refractory metals that can absorb hydrogen even at low temperature and ambient pressure. Vanadium based alloys have shown very good properties of hydrogen absorption and hydrogen permeation. Vanadium-titanium-chromium (V-Ti-Cr) alloy with substantially varying composition of Ti and Cr is potential candidate material for hydrogen storage due to its high volumetric hydrogen absorption properties [1] compared to the existing hydrogen storage materials. The V-Ti-Cr alloys with high vanadium contents possess also good cyclic properties [2,3]. Therefore, V-Ti-Cr alloys are candidates for hydrogen storage medium. Vanadium based alloy V-4Cr-4Ti was considered as first wall structural material for fusion [4] reactor due to many advantages, including low long term activation, high temperature strength, high irradiation resistance properties, high temperature stress resistance and liquid metal compatibility.

Vacuum arc-melting of the constituent alloying components in high pure metallic form is the most conventional route for the synthesis of alloys and intermetallic compounds including V-Ti-Cr alloy [5]. Key issues in

this synthesis process are the production cost, due to the use of the expensive highly pure metals, and inhomogeneity, due to the insufficient mixing during arc melting. Another synthesis process of V-Ti-Cr alloy reported earlier was from oxide mixture in $CaCl_2$, similar to FFC Cambridge process [6,7].

Aluminothermy has been commercially used for the synthesis of pure vanadium and chromium metals [8,9]. Synthesis of V-Al, V-Ti, V-Cr and many other alloys of vanadium by thermite process has been reported by Krishnamurthy *et al.* [8]. Recently, synthesis of orthopaedic and dental implant material, Ti-6Al-14V, by thermite process was reported [10]. The critical issues associated with the synthesis of V-Ti-Cr alloys by the thermite process are: i) unpredictable loading of alloying components in the vanadium matrix, particularly titanium, because of less exothermicity of TiO_2 -Al reduction, ii) possibility of refinement of the thermite [11–14], iii) V-Ti-Cr-Al-O alloy to V-Ti-Cr alloy change-over with reproducible composition by electron beam melting and iv) yield of the product, because of evaporation of the product alloying components in metallic as well as sub-oxide form (all the components are prone to evaporation in sub-oxide form). In spite of these issues, better product homogeneity, single step synthesis and use of unexpensive oxides make thermite process

* Corresponding author: tel: +91 22 2559 0489
fax: +91 22 2550 5151, e-mail: sanjay.barc@gmail.com

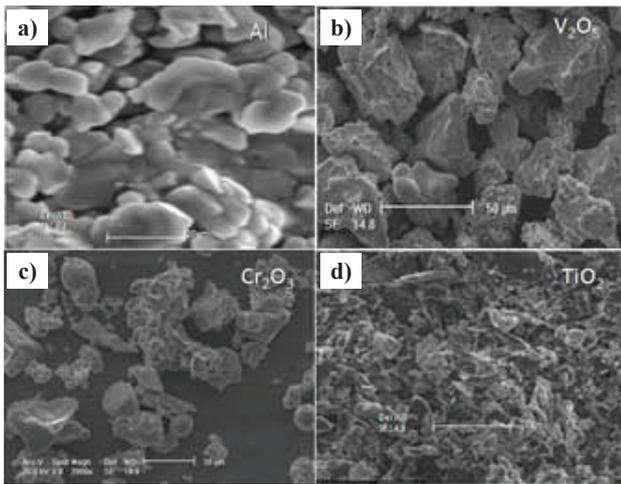


Figure 1. SEM micrographs of raw materials:
a) Al, b) V_2O_5 , c) Cr_2O_3 and d) TiO_2

attractive. The two important components for studying the process are therefore thermite making (loading of Cr&Ti) and refining (maintaining the alloy's composition). The percentage yield of the product could be substantially increased by the use of slag-metal separator/heat-sinker. The present paper deals with: loading pattern of the alloying elements (Cr and Ti), possibility of refinement process, removal of Al and oxygen by electron beam (EB) melting and effects of slag metal separators on the percentage yield.

II. Experimental

The starting materials used were V_2O_5 , TiO_2 , Cr_2O_3 , Al, CaO, CaF and $CaSiO_3$ in powdered form of 99.50, 99.90, 99.93, 99.97, 99.00, 99.00 and 98.90 % purity, respectively. All these raw materials were oven dried at $100^\circ C$ under rotary vacuum to remove moisture before use. Microstructural analysis obtained with scanning electron microscope SEM (AIS-2100 CERON) of V_2O_5 , TiO_2 , Cr_2O_3 and aluminium is presented in the

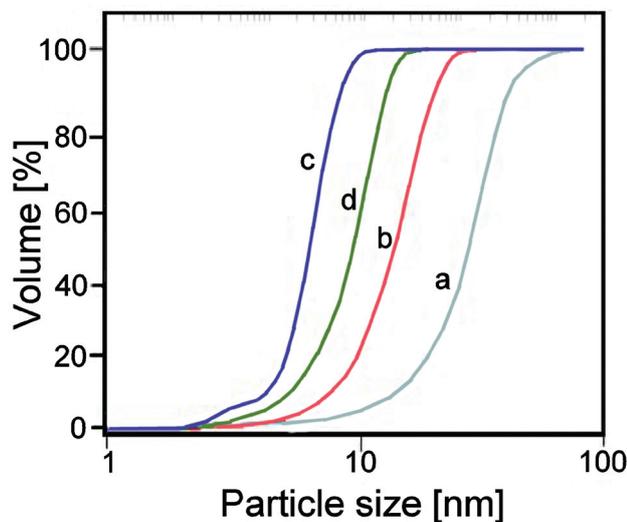
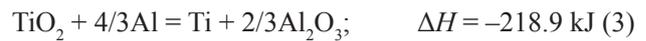
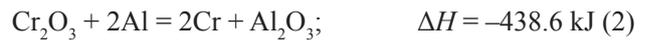


Figure 2. Particle size distribution of raw materials:
a) Al, b) V_2O_5 , c) Cr_2O_3 and d) TiO_2

Fig. 1. The size distribution of the particles was also analyzed by laser diffraction method (Particle Size Analyzer CILAS PSA 1064 L) and presented in Fig. 2. The XRD patterns (measured on Philips PW 1830) of these materials are shown in the Fig. 3.

The oxides of the vanadium, chromium and titanium along with aluminium in stoichiometric ratio were mixed thoroughly according to the reactions 1, 2 and 3:



In our experiment, approximately 8–20 wt.% excess aluminium was used because the reaction was carried out in an open bomb reactor and 8–14 wt.% of Al loading in the thermite was required for the subsequent refining process. The reduction was carried out in an open top end magnesia lined steel reactor. The reaction was vigorous and completed within few minutes. The reduction processes were illustrated schematically in the Fig. 4. The product was allowed to cool down overnight and removed by inverting the reactor and gentle tapping; followed by separation of solidified slag from the alloy ingot readily. The yield of the experiment was calculated by using the theoretical 100% yield obtained after complete recovery of the metallic value in the used oxides. Many experiments were carried out along with CaO, $CaSiO_3$ and CaF (20–30% of total weight) as a fluidizers/slag metal separator/heat sinker and the yield was calculated. The alloys thus obtained were alloys of V-Ti-Cr-Al along with residual oxygen and nitrogen (Table 1). The morphology and composition of the crude thermite product was analysed by scanning electron microscope (SEM AIS-2100 CERON), energy dispersive analysis (EDAX, SEM AIS-2100 CERON) and wet chemical analysis. The products thus obtained were refined by electron beam melting under high vacuum condition to remove excess aluminium and residual oxygen up to the possible extent.

III. Results and discussion

3.1 Theoretical aspects

The free energy changes with temperature of the reactions (1-3) are shown in the Fig. 5 and it indicates the feasibility of the reaction at low temperature, although heat of reaction is a key parameter to decide about the self-sustainability of the reaction. The exothermicity of the reaction, represented as the ratio of the heat of the reaction and the sum of the molecular weights of the products, is calculated. The value needed is in the range between 2.25 kJ/g and 4.50 kJ/g for the reaction to develop in a controlled manner, resulting in melting of both the reduced metal and the slag, and to retain them

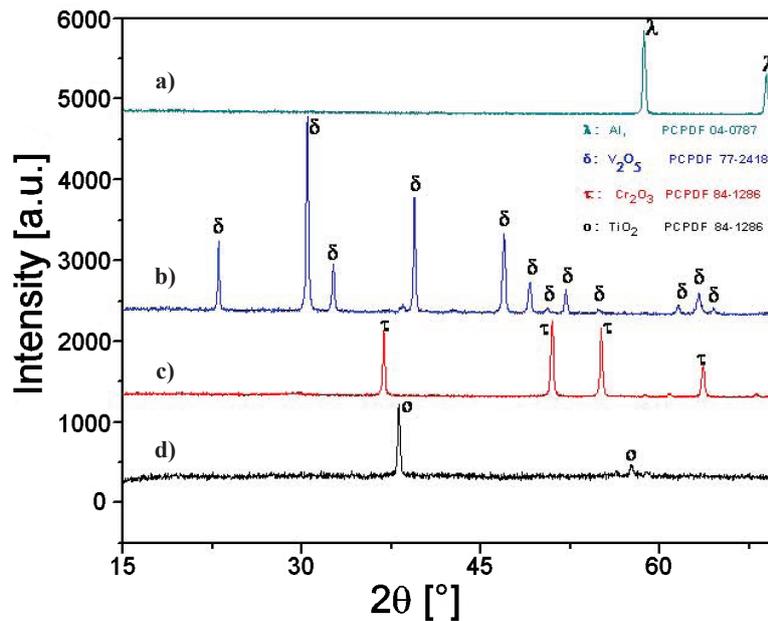


Figure 3. XRD of raw materials (rotary vacuum oven dried at 100°C) used in the synthesis: a) Al, b) V₂O₅, c) Cr₂O₃ and d) TiO₂

in the fluid condition long enough for good slag metal separation [15]. The heat of aluminothermy reduction of TiO₂ is very low and heat booster is essential in general. The ternary alloy V-Ti-Cr was made by aluminothermy reduction of mixed oxides of V₂O₅, TiO₂ and Cr₂O₃. The reduction of V₂O₅ and Cr₂O₃ with Al are highly exothermic which overcome the shortfall of the heat required for self sustaining of TiO₂ reduction by Al.

3.2 Effect of slag fluidizer on yield

Table 2 illustrates that the yield of the thermite reaction without any additive was substantially lower. Alumina, as a slag formed during the thermite reaction, is the highest melting point component in the system and its fusion point was lowered by making eutectic with additive like CaO/CaSiO₃/CaF. The use of slag flux/fluidizer substantially decreases the melting point of alumina

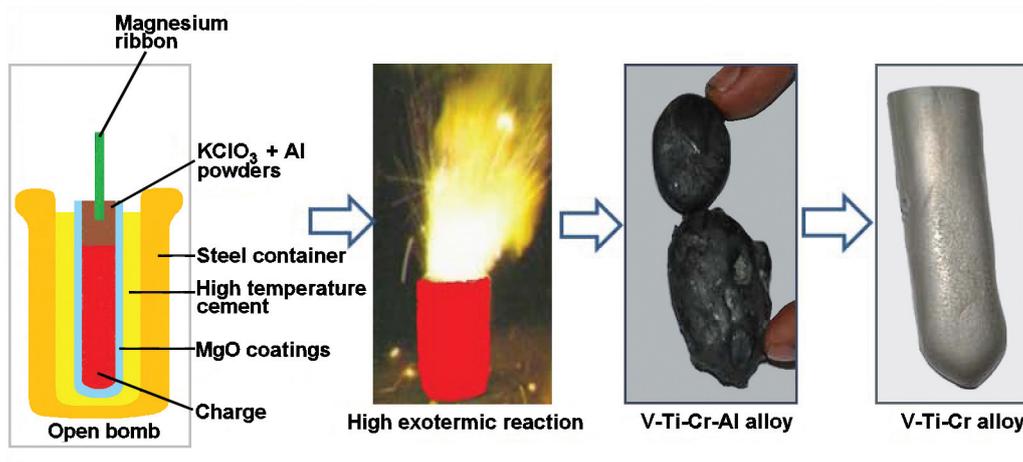


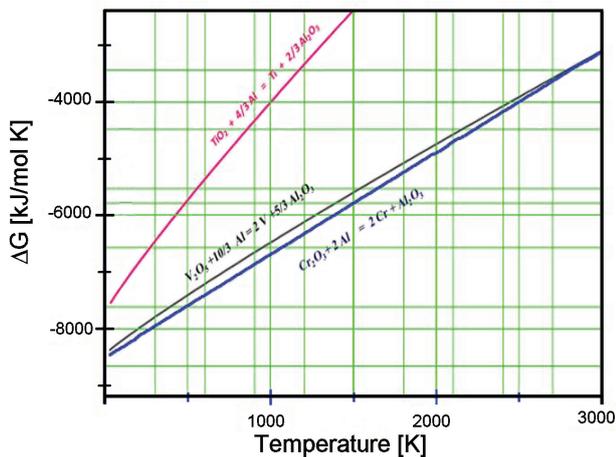
Figure 4. Flow sheet of highly exothermic thermite process

Table 1 Wet chemical / inert gas fusion technique and EDAX analysis of the crude thermite and the EB melted samples

Sample	V	Ti	Cr	Al	O	N
(a) EDAX analysis						
Crude thermite	Balance	5.81	10.31	5.80	-	-
EB melted	Balance	5.31	10.02	-	-	-
(b) Chemical analysis						
Crude thermite	Balance	5.891	10.531	5.791	0.075	0.025
EB melted	Balance	5.322	10.125	0.081	0.003	0.022

Table 2. Effects of slag fluidizer on yield

Charge	Sample I	Sample II	Sample III	Sample IV
Size of charge [g]	302	301	302	307
CaO [wt.% of total charge]	-	-	-	20
CaSiO ₃ [wt.% of total charge]	-	20	-	-
CaF [wt.% of total charge]	-	-	20	-
Yield [wt.%]	79	92	80	86
Excess Al in the product [wt.%]	16	9	15	12

**Figure 5. Gibbs free energy vs. temperature plot to confirm the feasibility of reactions**

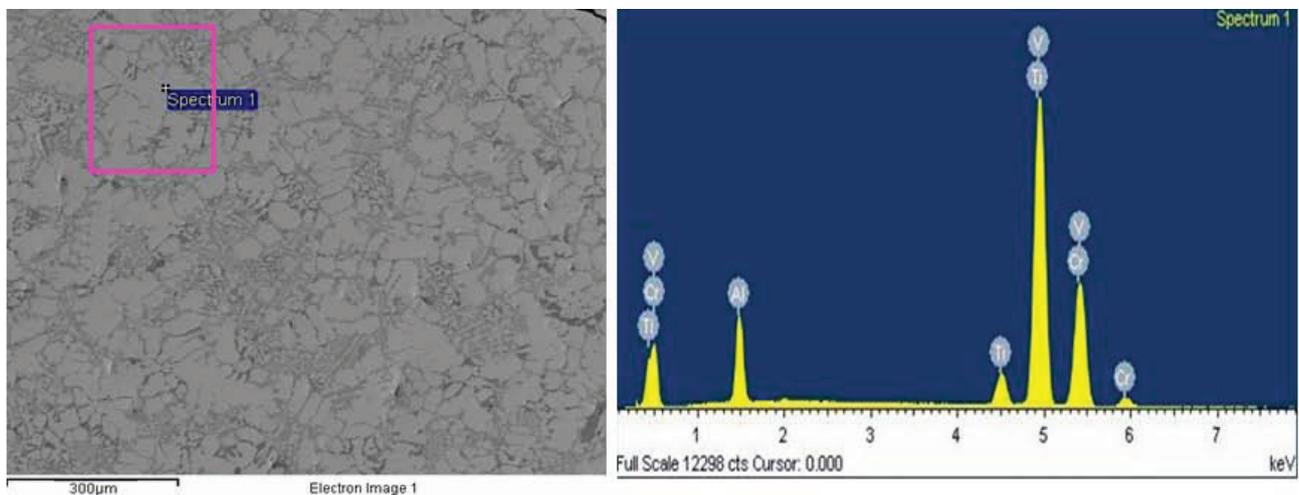
formed by making eutectic composition. The improvement in the yield is clearly visible in Table 2, by use of CaO, CaSiO₃ or CaF as slag-metal separators, which separate the metals from the slag by making it more fluidized and decrease the cooling period to prevent the metal loss due to evaporation. As indicated in Table 2, CaSiO₃ is better heat sinker than CaO or CaF and gives better slag metal separation to enhance the yield up to 92%. In the absence of slag fluidizer only about 20% titanium oxide ends up in the thermite. The loading of titanium was increased substantially by the use of fluidizers.

3.3 SEM-EDAX and chemical analysis

The microstructure of the crude thermite product, shown in the Fig. 6, was partially dendritic due to fast cooling. The presence of aluminium may be responsible for the dendritic structure, which became more grained structure after the EB melting as illustrated in Fig. 7. The SEM-EDAX and wet chemical analysis of the crude and EB melted samples are shown in Table 1. In the EDAX analysis, oxygen and nitrogen were not present. That could be due to low amount of oxygen (less than 500 ppm could not be recognized in EDAX analysis). The crude sample contains relatively high amount of aluminium (~5.8), which was confirmed by chemical and EDAX analysis. The product refined by electron beam melting shows substantial removal of aluminium as shown in the Table 1. Aluminium evaporates as elemental as well as sub-oxide form. The oxygen and nitrogen contents in the crude thermite as well as EB melted sample are shown in the Table 1. It is clear from the analysis that oxygen contents were substantially removed along with aluminium but the nitrogen remained in the product. However, the nitrogen and oxygen were below the solubility limit since no new phase (oxides or nitrides of vanadium) was observed in the XRD analysis.

3.4 XRD Analysis

The XRD analysis of the EB refined sample is shown in the Fig. 8. It is interesting to note that presence of titanium or chromium in any form was not detected. Also a

**Figure 6. SEM-EDAX analysis of crude thermite**

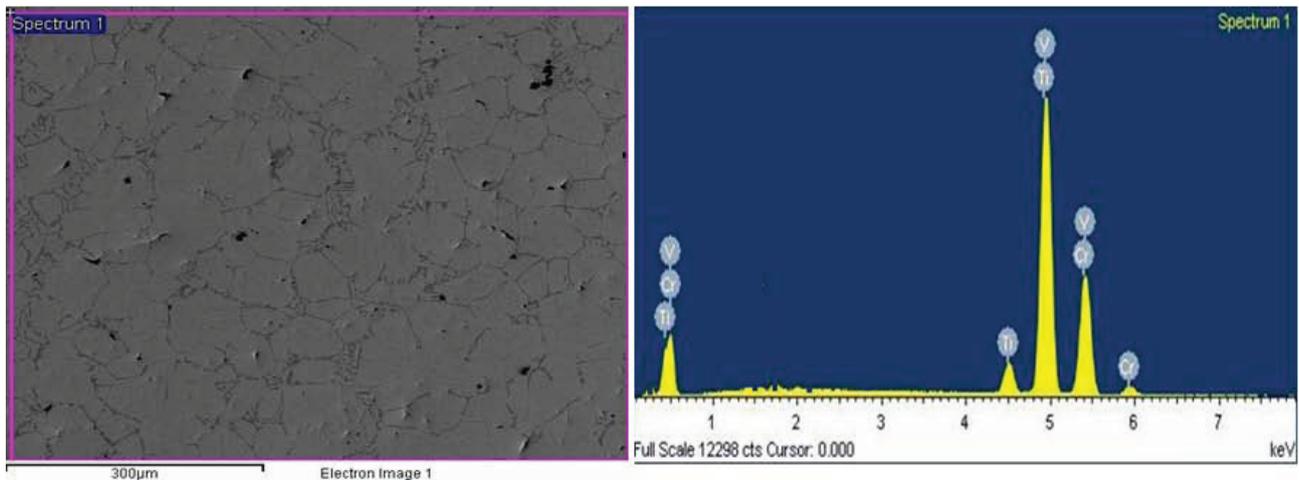


Figure 7. SEM-EDAX analysis of EB melted sample

positive shift of 2θ value by 0.1° with respect to vanadium matrix was observed. Essentially, these observations are indication of V-Ti-Cr solid solution formation. The composition of the Ti and Cr in the V-Ti-Cr alloy was within the solid solubility limit according to the V-Ti-Cr ternary phase diagram [16]. The volumetric size of titanium is larger than vanadium which is larger than chromium atom. As the alloy contains higher amount of Cr than Ti, the positive shift of 2θ for 0.1° can be explained with the fact that increase in 2θ value because of chromium is dominant over the decrease in 2θ value because of titanium.

Even though oxygen and nitrogen were present in the EB melted V-Cr-Ti solid solution no other phase was detected by XRD (Fig. 8). The observation thus confirms that the oxygen and nitrogen were below the solid solubility limit.

V. Conclusions

V-Ti-Cr master alloys were synthesized successfully by co-reduction of V_2O_5 , Cr_2O_3 and TiO_2 with alumin-

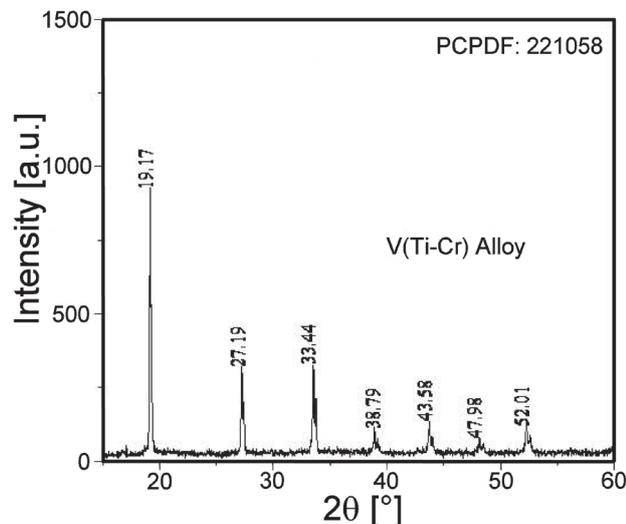


Figure 8. XRD analysis of V-Ti-Cr alloy after electron beam refining (all peaks are matching with the pure vanadium metals with positive shift of 0.1°)

ium in open bomb reactor. The reduction of V_2O_5 and Cr_2O_3 are highly exothermic and lead to self propagating type of reaction which results in self sustaining reduction of less exothermic TiO_2 by Al. A range of compositions of a mixture of V_2O_5 , TiO_2 and Cr_2O_3 can be chosen to make the overall reduction with aluminium sufficiently exothermic for a self-sustaining reaction. SEM-EDAX and chemical analysis confirmed that the co-reduction process lead to V-Ti-Cr-Al which refined to V-Ti-Cr alloy by EB melting. The excess aluminium was removed in metallic as well as sub-oxide form with the residual oxygen. The use of slag metal separator is beneficial to improve the percentage loading of titanium and chromium. The overall yield has been improved successfully using slag metal separator.

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