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Journal of Nuclear Materials 283–287 (2000) 711–715

journal of nuclear materials

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NIFS program for large ingot production of a V–Cr–Ti alloy

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Abstract

The National Institute for Fusion Science (NIFS), in collaboration with Japanese industry, has initiated a research program for vanadium alloys, which will be highlighted by the production of a large V–4Cr–4Ti ingot. In this program, the technology and underlying science associated with vanadium alloy fabrication will be enhanced. Effort has been focused on the control of interstitial impurities such as C, O and N. Purification of the present commercial metal vanadium was carried out by improvement of the processes. Medium size (30 kg), high purity V–4Cr–4Ti ingots have been produced, designated as NIFS-HEAT-1, and a large size (200 kg) ingot is planned. In this study, the technology for fabricating large V–Cr–Ti ingots with ~50 ppm C, ~180 ppm O and ~100 ppm N has been demonstrated.

1. Introduction

One of the key issues associated with the development of low-activation vanadium alloys is the absence of a large industrial production infrastructure. It is necessary to validate the fact that production of high-quality large alloy heats are possible with the present industrial base. The US DOE program efforts in the area of large heat production has contributed to enhancing this activity [1,2].

It is also important to promote the technologies and underlying science associated with large-scale vanadium alloy production. Control of interstitial impurities such as C, O and N is particularly important because increased levels of those impurities are known to result in loss of workability [3,4] and weldability [5,6]. Recent TEM analysis has suggested that radiation-induced loss of ductility of V–Cr–Ti alloys at <700 K may be attributed to fine precipitates containing C, O and N [7,8]. Thus, the reduction of these impurities is expected to improve the radiation resistance of the alloys. Observed improvement in the ductility of irradiated V–Cr–Ti alloys by addition of Si, Al and Y, which act as scavengers of these impurities, also supports this idea [9]. Existence of a different opinion [10], in which the loss of ductility is considered to be due to flow localization induced by easily shearable defect clusters, shows the need for further investigation, however.

The National Institute for Fusion Science (NIFS), in collaboration with Japanese industry, has initiated a program to fabricate a large ingot of V–4Cr–4Ti alloy. The objectives of this program are summarized as follows.

1. To determine the feasibility of large vanadium alloy heat production by the present Japanese industrial base.
2. To determine fundamental understanding of impurity pick-up during vanadium alloy fabrication.
3. To utilize the resulting ingots for research such as workability tests, full-size mechanical property tests and welding tests.

In this program, particular attention has been paid to the pick-up and transport of interstitial impurities. It is intended, in this program, to reduce the impurity levels in the ingots as low as possible within a reasonable

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PII: S0022-3115(00)00281-6

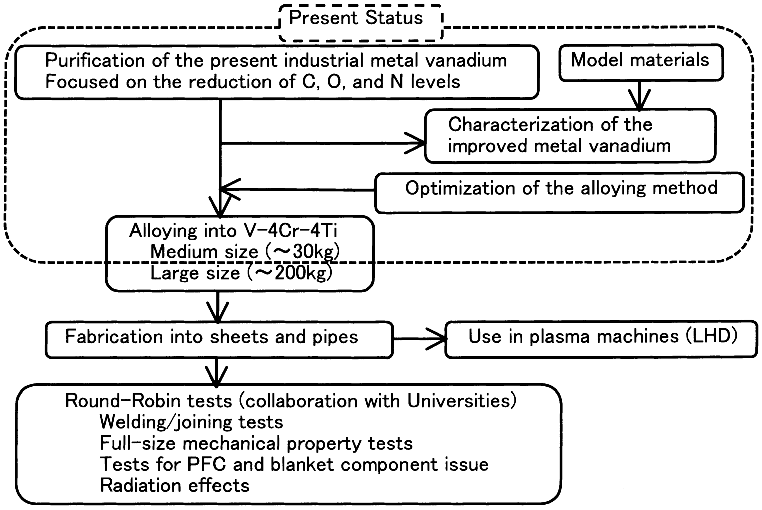

Fig. 1. Structure and present status of the program.

increment of cost. With reduced impurity levels, it may be possible to further enhance the properties of vanadium alloys. Interstitial impurities are, on the other hand, useful for maintaining the high temperature creep strength of vanadium alloys. Thus, alloying to compensate for this loss of creep strength may be necessary for high-purity vanadium alloys. It is thus expected that an optimum alloy composition with lower impurity levels may be found, which may be different from the present leading candidate (V–4Cr–4Ti).

Fig. 1 shows the structure and the present status of the program. Purification of the present industrial vanadium metal was carried out first. Efforts were focused on the reduction of C, O and N impurities. Chemical analyses of the intermediate products as well as the final vanadium metal products were performed for studying impurity transport during fabrication.

Characterization of the improved vanadium metal was carried out, including comparative studies with conventional commercial vanadium metal and model vanadium metal doped with controlled amounts of N and O. Details of the study are reported in another paper of these proceedings [11].

2. Improvement of metal vanadium

Table 1 defines the impurity levels of the present commercial vanadium metal in Japan, the raw vanadium ingot of the US DOE program [2] and the goal for this program. Efforts are focused on the reduction of N levels, which are presently much higher than those of vanadium metal produced by the US DOE program [1,2]. As explained in a previous review paper [12], special care must be taken in eliminating N from the products.

For low activation purposes, Mo, Nb and Al levels should be low. According to a recent estimation [13], concentration limits for Mo, Nb and Al are 20, 0.12 and 353 wppm, respectively, for recycling purposes. The Nb source for the US-produced V–4Cr–4Ti alloy heat was the contamination of equipment, which was also used for Nb production [2]. Since the equipment in this program is not used for fabricating Nb, Nb contamination is not likely. Mo is, in the present process, an inherent impurity because vanadium is extracted from spent catalysts used in the desulfurization of crude oil, which include Mo and some other metals.

Table 1
Impurity levels of the present commercial vanadium in Japan and the raw vanadium ingot produced by the US DOE program [2], and the goal of the present program (in wppm)

Element	C	N	O	Al	Mo	Nb
Commercial	60–300	300–800	50–200	40–600	5–80	<10
US DOE program						
900 kg	24	113	313	243	<50	44
2200 kg	25	153	213	167	<50	226
Goal of the present study	<100	<100	<100	<300	<20	<10

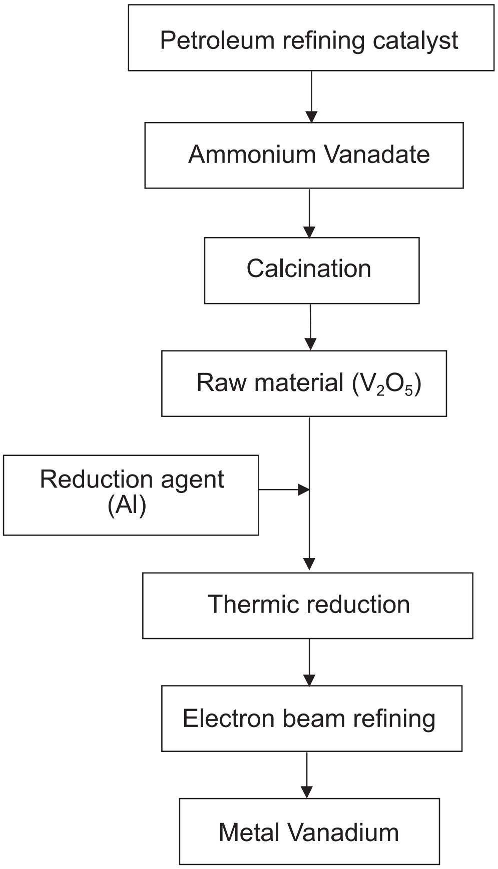

Fig. 2. Manufacturing process of the present commercial metal vanadium.

Fig. 2 defines the manufacturing process of metal vanadium. Based on chemical analysis of intermediate products, such as ammonium vanadate, raw material (V_2O_5) and aluminothermic reduction products (V–Al–O), two sources of N have been identified. They are (1) insufficient removal of N by oxidation during the calcination of ammonium vanadate and (2) interaction with the environment during the aluminothermic reduction process. The aluminium reduction agent was found to be the major source of carbon.

In the present program, the process was improved as follows.

1. The temperature monitoring and control system was improved for the calcination process. The temperature during calcination was precisely controlled so that ammonium was more efficiently removed. Also improved was a ventilation system to enhance the oxidation of V to V_2O_5.
2. The external aluminothermic reduction environment was changed from air to slow-flowing, pure Ar gas.
3. A higher purity aluminum agent was selected for the aluminothermic reduction process.

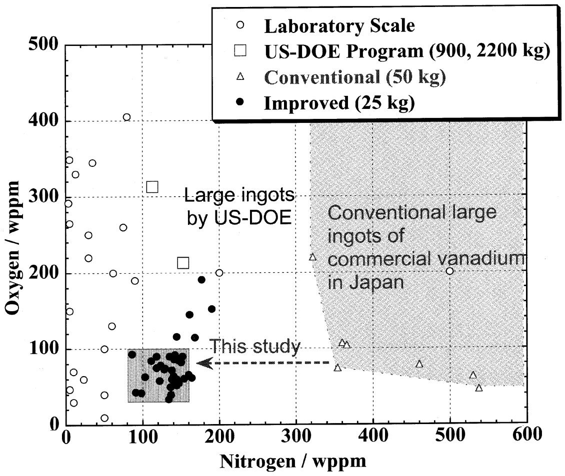

Fig. 3. Impurity level of conventional and improved metal vanadium in comparison with the large ingots produced by the US DOE program and other laboratory-scale melting [2,12,14–17].

The metal vanadium was produced in 25 kg ingots. The impurity levels are thus different in different ingots. Most of the ingots obtained in this study contained 40–90 wppm C, 40–100 wppm O, 60–160 wppm N and 100–330 wppm Al, nearly satisfying the goals shown in Table 1. O and N levels in the ingots produced after the improvement are shown in Fig. 3, compared with values obtained for other laboratory and large-scale production heats [2,12,14–17]. The figure shows that the vanadium metal ingots in this study have comparable levels of nitrogen, but much lower levels of oxygen impurity relative to that produced by the US DOE program [1,2].

Characterization of the improved vanadium metal was carried out in comparison with conventional vanadium metal. Vickers hardness of the conventional ingot materials as melted, as 90% cold worked and as annealed at 1373 K for an hour, were 138, 195 and 145, respectively, and those of the improved ingot materials were 76, 127 and 59, respectively. Thus, the improved vanadium metal was significantly softened by the improvement in impurity levels.

Vickers hardnesses of the improved and conventional vanadium metal cold rolled to 90% were also compared as a function of post-work heat treatment temperature. Conventional vanadium showed significant hardening at ~573 K, which is attributed to the decoration of dislocations by nitrogen, based on the result of previous post-irradiation heat treatment studies [18,19]. The hardening of the improved vanadium metal was much smaller than that observed for conventional vanadium metal. The details of this study are reported in another paper in these proceedings [11].

Table 2
Chemical composition of the 30 kg V–Cr–Ti ingot produced by EB–VAR (NIFS-HEAT-1). Chemical composition of the 30 kg ingot produced by EB side-feed is also shown for comparison (Ti, Cr in wt%, C, O, N, H in wppm)

Element	Cr	Ti	C	O	N	H
Top[a] center	4.33	4.18	54	189	97	6
Top *D*/4	4.35	4.22	57	185	108	6
Top surface[b]	4.31	4.01	48	192	96	6
Bottom[a] center	4.19	4.11	65	159	110	4
Bottom *D*/4	4.28	3.47	44	153	99	5
Bottom surface	3.25	3.81	34	184	104	5
Average	4.22	4.13	58	181	103	6
EB side-feed (average)	1.07	3.99	58	135	107	20

[a] Top/bottom: 20 mm from the top/bottom surface.
[b] Surface: 10 mm from the peripheral surface.

Since the interaction of impurities with defect clusters is considered to be one of the reasons for the loss of ductility of vanadium and vanadium alloys by irradiation [7–9], the improved vanadium metal and, hopefully, vanadium alloys produced with the improved vanadium metal will exhibit better resistance against radiation-induced embrittlement.

3. Alloying into V–4Cr–4Ti

Several alloying techniques were compared from impurity pick-up viewpoints. Vacuum refining and hydrogen refining have been explored for high-purity alloying. Both were, however, found to be ineffective. Melting in vacuum resulted in gradual increases in N levels. Hydrogen gas was shown to have no impurity reduction effects on vanadium. Hydrogen plasma effects are now being investigated.

Based on this experience, two types of alloying methods were selected. The first step for both methods involved electron beam (EB) melting of ∼10 mm chips of the improved V, with commercial Ti (C:140, O:520, N:50 wppm, 30 × 30 × 5 mm^3 plates) and commercial Cr (C:80, O:140, N:30 wppm, 30 ∅× ∼ 50 mm) in a trough crucible. The second step involved either side-feed EB melting or vacuum arc remelting (VAR). Side-feed EB melting is a technique for melt alloy bars, produced by the first step, by inserting them horizontally into the beam focal position. Because side-feed EB melting is carried out in a vacuum of $\sim 10^{-5}$ Torr, control of Cr evaporation is difficult. In fact, the final level of Cr in the side-feed EB melted material was significantly different in different ingots. Therefore, this method is considered to be unsuitable for application in large-scale melting of V–4Cr–4Ti alloy. For EB–VAR, control of Cr level is much less serious. However, impurity pick-up is a greater concern because of the higher vacuum environment ($\sim 9\times 10^{-3}$ Torr) used in this process.

Table 2 shows the chemical composition at various positions in the 30 kg ingot (200 ∅ × 200 mm) produced by EB–VAR. The average composition of a 30 kg ingot produced by the EB side-feed process is also shown for comparison. Note that the Cr level of the EB side-feed material is only ∼1%, although 4% was the intended level. The alloy produced by EB–VAR was designated as NIFS-HEAT-1.

Glow discharge mass spectrometry of NIFS-HEAT-1 at the top *D*/4 and the bottom *D*/4 positions was carried out. The minor impurity levels detected ranged as follows (in wppm): B: 5–9, Na: 13–20, Al: 98–140, Si: 26–30, P: 13–19, S: 5–12, K: 7, Ca: 3, Fe: 68–92, Co: 1–3, Ni: 11–15, Cu: 2–6, Zr: 51–59, Nb: 6–7, Mo: 20–25 and

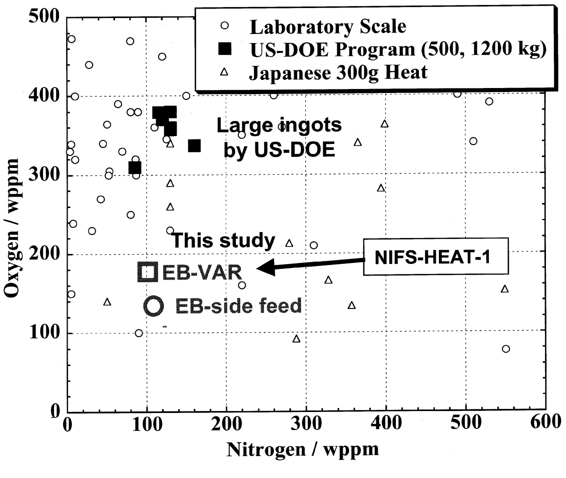

Fig. 4. Impurity level of V–Cr–Ti ingots produced in the present study in comparison with the large ingots produced by the US DOE program and other V alloys produced by laboratory-scale melting [2,12,14,15,17]. The ingot produce by the present EB–VAR is designated as NIFS-HEAT-1.

Ta: 47–68. The levels of the following elements were estimated to be 1 wppm or less: Mg, Cl, Mn, Zn, Ga, As, Se, Ag, Sn, Sb, Te and W.

Fig. 4 compares the O and N levels of V alloys produced in this study and previous Japanese and US efforts [1,2,14,15,17]. The nitrogen and oxygen levels of the ingots produced in the present study are comparable to and almost half of, respectively, those for the large ingots produced by the US DOE program.

4. Summary

A new program has been initiated at the NIFS for vanadium alloy development. For the purpose of fabricating large, high-quality ingots of V–4Cr–4Ti, fundamental mechanisms of impurity pick-up and transport during the fabrication process were investigated. As a result of improvements in the fabrication processes, additional purification of the present commercial vanadium metal was successfully achieved. A medium size (~30 kg) ingot of V–4Cr–4Ti was fabricated by EB and VAR methods, which was designated as NIFS-HEAT-1, and a 200 kg ingot is planned. In this study, the technology for fabricating large V–Cr–Ti ingots with ~60 ppm C, ~180 ppm O and ~100 ppm N has been demonstrated.

Acknowledgements

The authors are grateful to Dr M. Fujiwara, Director General of NIFS, for supporting the present research program.

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