ELSEVIER

Journal of Nuclear Materials 258–263 (1998) 1425–1430

journal of nuclear materials

Fabrication of a 1200 kg ingot of V–4Cr–4Ti alloy for the DIII–D radiative divertor program

W.R. Johnson *, J.P. Smith [1]

General Atomics, P.O. Box 85608, San Diego, CA 92186-5608, USA

Abstract

Vanadium–chromium–titanium alloys are attractive materials for fusion reactors because of their high-temperature capability and their potential for low neutron activation and rapid activation decay. A V–4Cr–4Ti alloy has been selected in the US as the current leading candidate vanadium alloy for future use in fusion reactor structural applications. General Atomics (GA), in conjunction with the Department of Energy's (DOE) DIII–D Program, is carrying out a plan for the utilization of this vanadium alloy in the DIII–D tokamak. The plan will culminate in the fabrication, installation, and operation of a V–4Cr–4Ti alloy structure in the DIII–D Radiative Divertor (RD) upgrade. The deployment of this vanadium alloy will provide a meaningful step in the development and technology acceptance of this advanced material for future fusion power devices. Under a GA contract and material specification, an industrial scale 1200 kg heat (ingot) of a V–4Cr–4Ti alloy has been produced and converted into product forms by Wah Chang of Albany, Oregon (WCA). To assure the proper control of minor and trace impurities which affect the mechanical and activation behavior of this vanadium alloy, selected lots of raw vanadium base metal were processed by aluminothermic reduction of high purity vanadium oxide, and were then electron beam melted into two high purity vanadium ingots. The ingots were then consolidated with high purity Cr and Ti, and double vacuum-arc melted to obtain a 1200 kg V–4Cr–4Ti alloy ingot. Several billets were extruded from the ingot, and were then fabricated into plate, sheet, and rod at WCA. Tubing was subsequently processed from plate material. The chemistry and fabrication procedures for the product forms were specified on the basis of experience and knowledge gained from DOE Fusion Materials Program studies on previous laboratory-scale heats and a large scale ingot (500 kg) of V–4Cr–4Ti alloy produced by WCA for Argonne National Laboratory (ANL). Charpy V-Notch (CVN) impact tests have been conducted on sheet material from the 1200-kg heat. The values are compared to data obtained on previous heats of the alloy.

1. Introduction

General Atomics (GA), along with Argonne National Laboratory (ANL), Oak Ridge National Laboratory (ORNL), and Pacific Northwest National Laboratory (PNNL), has developed a plan for the utilization of vanadium alloys in the DIII–D tokamak which will culminate in the fabrication, installation, and operation of a V–4Cr–4Ti alloy structure in the DIII–D RD upgrade [1,2]. The use of a vanadium alloy in this plan will provide a meaningful step towards developing advanced materials for fusion power applications by (1) demonstrating the in-service behavior of a vanadium alloy (V–4Cr–4Ti) in a typical tokamak environment, and (2) developing knowledge and experience on the design, processing, and fabrication of large-scale vanadium alloy components.

The program consists of three phases: first, small vanadium alloy coupons have, and are continuing to be exposed in DIII–D at positions in the vessel floor and behind the existing divertor structure (i.e., non-plasma-facing conditions). Post-exposure evaluation is being performed at ANL to determine the effects of the

---

* Corresponding author. Address: Los Alamos National Laboratory, TA-53, Sector R, Bldg. 3, Mail Stop H809, Los Alamos, NM 87545, USA. Tel.: +1 505 665 7891; fax: +1 505 667 2787; e-mail: bob.johnson@gat.com.

[1] Present Address: Ismeca, Carlsbad, California, USA.

0022-3115/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(98)00209-8

tokamak vacuum environment on the alloy [3]. Second, a V–4Cr–4Ti alloy demonstration component will be fabricated using candidate joining methods, and third, during the upcoming RD upgrade, a portion of the upper section of the double-null, slotted divertor will be fabricated from V–4Cr–4Ti alloy product forms. The plan is being carried out in conjunction with GA and the Fusion Materials Program of the Department of Energy's Office of Fusion Energy (DOE/OFE). The execution of the plan is a joint effort by GA, the DIII–D Program, and DOE Material Program participants, primarily ANL, ORNL, and PNNL.

2. Fabrication of product forms for the radiative divertor

On the basis of the excellent properties that have been determined for both laboratory-scale and production-scale heats (produced at WCA), V–4Cr–4Ti alloy has been identified as the most promising vanadium-based candidate alloy for application in fusion reactor structural components [4–6]. This alloy was selected by GA for procurement from WCA in product forms applicable for the manufacture of a portion of the DIII–D RD upgrade.

The production campaign included: (1) ingot production and conversion to product forms by wrought processes; (2) analyses of chemical composition, after different stages of processing; and (3) charpy V-notch (CVN) impact testing to determine the ductile–brittle transition temperature (DBTT) of the alloy. A large-scale (1200 kg) V–4Cr–4Ti alloy ingot was produced by electron beam melting of unalloyed vanadium ingots and then alloying the vanadium with high purity Cr and Ti using vacuum-arc melting (two times). The alloyed vanadium ingot was extruded into rectangular bars and warm-rolled into plate. Subsequent conversions by warm- or cold-working, and intermediate heat treatments were used to produce sheet, rod, and tubing.

2.1. Specification of chemical composition

The specification for the chemical composition of the alloy was developed by GA to reflect the valuable experience and knowledge gained from fabrication, testing, and microstructural examination of laboratory-scale heats of V–Ti and V–Cr–Ti alloys, and a relatively large heat (500 kg) of a V–4Cr–4Ti alloy [4–6]. Particular attention was given to the control of impurities to meet the immediate goals for the RD program and also future goals for further deployment of vanadium alloys in advanced fusion systems. This effort included the minimization of Nb, Mo, and Ag for low neutron activation; the optimization of Si (400–1000 ppm) to suppress neutron-induced swelling and the limitation of other minor impurities (e.g., O, N, S, P, etc.) to avoid grain boundary segregation and precipitation of vanadium-based embrittling phases (oxycarbochlorides, vanadates, and borides) [5]. The final specification requirements for unalloyed and alloyed vanadium chemical composition for the V–4Cr–4Ti alloy procurement are listed in Table 1.

2.2. Screening of raw materials

The major sources of intrinsic impurities for the V–4Cr–4Ti alloy are entrained in the raw vanadium, raw chromium, and raw titanium base metal stocks used in processing the ingot material [5].

Raw vanadium, in the form of ~100 kg lots, was prepared from high purity vanadium oxide by aluminothermic reduction. This process generally produces material with lower impurities compared to other typical reduction processes (e.g., calcium-reduction process) [5]. Chemical analysis of ~30 processed lots revealed that all of the lots contained only 100–200 wppm Si, less than the Si (400–1000 wppm) specified. This variation observed in processed raw vanadium is due to the varying levels of Si typically found in the starting material, vanadium oxide. Approximately half of the vanadium lots contained ~40 wppm Nb; the other half contained substantially higher levels (several hundred wppm). Variations in other elements were also noted; most elements were within specification limits for all of the lots. The primary source of the Nb was attributed to contamination of equipment which is also utilized by WCA for processing raw Nb.

The raw vanadium lots were divided into two groups. Ingots of 395 mm diameter vanadium, one weighing ~900 kg and the other ~2200 kg, were processed by electron beam melting. Chemical analysis of the resulting ingots indicated that both were generally within specification limits except for Nb, which was above specification (see Table 2). One ingot (~900 kg, Ht.#820645) had a Nb level which averaged 40 wppm: the larger ingot (~2200 kg, Ht.#820642) averaged 226 wppm. A combination of the two ingots was required for producing a sufficient quantity of the vanadium alloy. A decision was made to blend the lower-Nb ingot and part of the higher-Nb containing ingot to produce the V–4Cr–4Ti alloy heat (Ht.#832864). Measurements of Ca, Na, K, Mg, and Ag were conducted but with insufficient sensitivity (see Table 2). As a further check on the vanadium ingot impurities, samples were excised from the surfaces of the two ingots at their midlengths to provide material for CVN toughness tests. Toughness is a property which is extremely sensitive to impurities in vanadium [5]. The excised ingot material was first processed further by cold rolling and annealing at ORNL, machined into CVN specimens, and then tested at ANL at temperatures of −196°C and above. Both vanadium ingot materials exhibited ductile behavior and had

Table 1
Chemical composition requirements and goals for unalloyed and alloyed vanadium (V–4Cr–4Ti)

Material	Content, maximum, parts/million by weight (wppm)																					
	Cr [a]	Ti [a]	Si	H	O	N	C	Al	Fe	Cu	Mo	Nb	Cl	Ga	Ca	Na	K	Mg	P	S	B	Ag
Vanadium ingot	–	–	400–1000	10	400	200	200	200	300	50	50[b]	20[b]	3	10	1[b]	1[b]	1[b]	1[b]	30	30	5	1
V–4Cr–4Ti ingot and extrusion	3.5–4.5	3.5–4.5	400–1000	10	400	200	200	200	300	50	50[b]	20[b]	3	10	1[b]	1[b]	1[b]	1[b]	30	30	5	1
V–4Cr–4Ti sheet and rod				10	400	200	200															

[a] wt%

[b] Desired values: <5 ppm Mo, <1 ppm Nb, <1 ppm total Ca + Na + K + Mg.

impact toughness (ductility) values similar to that obtained by ANL for the pure vanadium ingot material for a previous 500 kg V–4Cr–4Ti alloy heat [7]. These results confirmed the purity of the vanadium ingots and the absence of embrittling precipitates.

The major source of the undesired impurities, Cl, K, and Na, observed previously in V–Cr–Ti alloys, is now known to be from low-quality sponge Ti stock, which is normally produced by the Kroll process. Therefore, to preclude these impurities the use of double- or triple-vacuum-melted Ti was mandated in the alloy ingot specification. High purity chromium was also specified.

2.3. Specification of secondary fabrication and conversion

The procedures for extrusion, secondary fabrication, and conversion to finished product forms were specified to closely reproduce the procedures used by WCA in fabricating the previous large scale (500 kg) heat of V–4Cr–4Ti alloy for ANL (plate, sheet, and rod) [5]. Conversion procedures for tubing were based on prior experience in fabricating tubes from extruded material from this heat [8].

2.4. Alloy melting and hot processing (extrusion)

The two vanadium ingots were machined into large chips and consolidated with high purity Cr and Ti (double vacuum-melted Ti chips), and a 1200 kg ingot was produced by double vacuum-arc melting (Fig. 1). The ingot was 34.9 cm in diameter by 210.8 cm in length. Chemical analysis of the ingot (Table 2) indicated that it was generally within preferred specification limits for all elements except for the Nb, Ca, Na, K, and Mg impurities. The ingot chemistry was also determined to be homogeneous, a major accomplishment for an ingot of this size, and was therefore accepted for continued processing.

The diameter of the ingot was machined to 32.1 cm and the ingot was sectioned into two ~85 cm lengths. Each section was then encapsulated in a stainless steel can fabricated from rolled and seam-welded ~4.8 mm thick sheet; the cans were evacuated to $\sim 4 \times 10^{-3}$ Pa and seal welded. The canned sections were heated for several hours in a slightly reducing, gas-fired furnace to a temperature of ~1140°C and extruded in a 49 MN capacity press to form rectangular billets of ~11.4 cm × ~24.1 cm cross-sections (extrusion ratio of ~3). Chemical analyses of the billet ends verified that no additional pickup of impurities occurred during the extrusion process (Table 2).

The billets were then rough machined (to remove the stainless steel cans) and finish ground into sheet bars of dimensions of 10 × 23 cm by lengths of 245 and 107 cm. The sheet bars were then acid pickled in a solution of 50

Table 2
Chemical composition of unalloyed vanadium ingots and alloyed vanadium (V–4Cr–4Ti) ingot, extrusion, and product forms

Material	Content, parts/million by weight (wppm)																					
	Cr [a]	Ti [a]	Si	H	O	N	C	Al	Fe	Cu	Mo	Nb	Cl	Ga	Ca	Na	K	Mg	P	S	B	Ag
Vanadium ingot 1 [b]	–	–	173	<3	313	113	24	243	147	<50	<50	44	–	<5	<10	<5	<5	<10	<30	<10	<5	<50
Vanadium ingot 2 [b]	–	–	137	<3	213	153	25	167	135	<50	<50	226	–	<5	16	<5	<5	<10	<30	<10	<5	<5
V–4Cr–4Ti ingot [b]	3.8	3.8	273	<3	357	130	37	193	228	<50	<50	106	<3	<1	4	<2	2	<1	<30	<10	<5	<1
V–4Cr–4Ti extrusion A [c]	3.8	4.1	335	4	360	130	46	170	215	<50	<50	87	<3	<1	52	<2	3	<10	<30	15	<5	<3
V–4Cr–4Ti extrusion B1 [c]	3.8	3.9	330	<3	380	130	44	195	225	<50	<50	89	<3	<1	<5	<2	3	<10	<30	15	<5	<3
V–4Cr–4Ti sheet [d]				<3	379	115	47															
V–4Cr–4Ti rod [e]				<3	337	160	51															

[a] wt%.

[b] Average of three measurements from top, middle, and bottom (Ht#s. 820645, 820642, and 832864, respectively, for vanadium ingots 1 and 2 and the V–4Cr–4Ti alloy).

[c] Average of measurements from both ends.

[d] Average of measurements for ten sheets.

[e] Average of measurements for three rods.

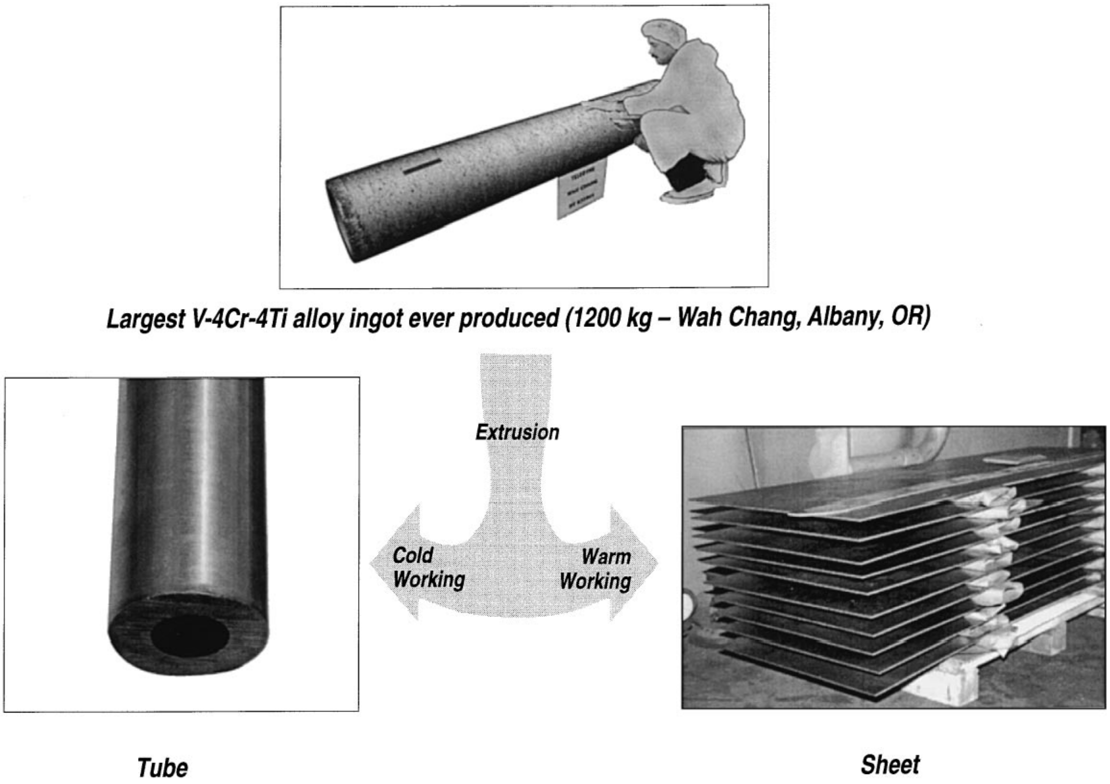

Fig. 1. Fabrication of product forms from 1200 kg V–4Cr–4Ti alloy ingot.

vol% water +30 vol% nitric acid +20 vol% hydrofluoric acid. They were then annealed at 1050°C for 2 h in a $\leqslant 4 \times 10^{-4}$ Pa vacuum in preparation for longitudinal rolling into plate product form.

2.5. Final products

Plate: The sheet bars were heated in air to 400°C and longitudinally rolled into 4.7 cm thick × 23 cm wide plate (~540 and ~240 cm lengths, plates A and B1, respectively). Plate A was cut into seven 60 cm long sections, one 67 cm long section, and one 40 cm long section. Plate B1 was cut into three 60 cm long sections and one 44 cm long section.

Sheet: The ten 60 cm long sections from both aforementioned plates were cross-rolled, after heating in air to 400°C, and successively reduced to sheet 0.48 cm thick × 65 cm wide by 185 cm long. Several 400°C rolling cycles of 50 ± 15% total cross-section reduction, were performed, using no more than 15% thickness reductions per rolling pass. After each rolling cycle, vacuum anneals were conducted for 2 h at ~1050°C and a vacuum pressure of $\leqslant 4 \times 10^{-4}$ Pa. The sheets were trimmed to 59 cm wide × 178 cm long and roller leveled after heating to 315°C. Finally, the sheets were cleaned, acid pickled, and annealed in vacuum ($\leqslant 4 \times 10^{-4}$ Pa) for 2 h at 1000°C. A metallographic analysis of samples taken from both ends of a sheet indicated 98% recrystallization of the material and an equiaxed grain size of ~25 μm. Quantitative chemical analyses for H, O, N, and C, performed on samples taken from each of the finished sheets, indicated levels within specification limits (Table 2).

CVN tests were conducted at ANL on miniature specimens excised from sheet material to characterize the fracture behavior. Tests conducted between −196°C and +25°C (no pre-crack, 0.076 mm root radius, 0.61 mm depth, 30° notch) indicated ductile behavior for all temperatures. As a result, the 1200 kg heat was characterized as having a ductile/brittle transition (DBTT) temperature below −196°C and an upper shelf CVN energy of ~10 J. The DBTT of the heat is similar to that obtained for previously-processed V–4Cr–4Ti and V–5Cr–5Ti alloy heats. However, the 10 J shelf is slightly lower than the reported 12–16 J upper shelf energy for these previous heats [9].

Rod: The 67 cm long section from Plate A, taken from the middle of the sheet bar, was cut into several $4.7 \times 4.7 \times 67$ cm^3 long sections, and machined to a diameter of ~4 cm. This material was swaged after heating to 400°C in air and successively reduced to 11 mm diameter rod in several 400°C swaging cycles. No more than 15% cross-section reductions per swaging pass were used, and intermediate vacuum anneals for 2 h at ~1050°C and $\leqslant 4 \times 10^{-4}$ Pa were performed after 50 ± 15% total cross-section reduction. The rods were cut into fifteen 180 cm lengths, straightened and centerless ground to 10.1 mm diameter. They were then cleaned, acid pickled, and final annealed in vacuum ($\leqslant 4 \times 10^{-4}$ Pa) for 2 h at 1000°C. Metallographic analysis of samples taken from the ends of one representative production-annealed rod length indicated 95–98% recrys-tallization of the material and an equiaxed grain size of ~50 μm. Chemical analyses for H, O, N, and C, determined on samples taken from three representative finished rod lengths, indicated levels within specification limits (Table 2).

Tubing: The starting material for tubing fabrication was saw cut, along the rolling direction, from one edge of a section of the 4.7 cm thick plate. Two pieces were gun-drilled and finished machined on the O.D. to a 4.57 cm diameter × 1 cm wall thickness. These tube blanks were then solvent cleaned, acid pickled, and annealed at 1000°C for 1 h in vacuum ($\leqslant 2 \times 10^{-4}$ Pa), and then cold drawn through a hardened steel die with a mandrel supporting the internal bore of the tube blank. During the first draw cycle, the cross-section was reduced in successive ~5% passes to achieve a total reduction of ~20%. During the second and the third draw cycles, the reduction per pass and total reduction, respectively, were successfully increased to between 10–15% per pass and between 30% and ~50% total reduction. A fourth draw cycle reduced the tubes to their final size of 26.7 mm diameter × 3.2 mm wall thickness by utilizing reductions of between 10–15% per pass. [Note: after each of the four draw cycles conducted, the tube blanks were solvent cleaned, acid pickled, and annealed in vacuum ($\leqslant 2 \times 10^{-4}$ Pa) at 1000°C for 1 h.]

3. Conclusion

The vanadium alloy V–4Cr–4Ti has been identified previously in the US as the primary vanadium-based candidate alloy for structure applications in fusion reactors. A heat of this alloy was successfully produced for the first time in a 1200 kg size which is a size large enough for production manufacturing of large scale components. The melt processing included: electron-beam melting of screened, high-quality vanadium; consolidation of the vanadium with high-purity titanium and chromium; and double vacuum-arc melting of the V–4Cr–4Ti alloy ingot. The ingot was converted by extrusion into flat bar; warm and cold working processes were used to fabricate plate, sheet, rod, and tubular product forms. The alloy chemical composition, of the ingot and of material after secondary fabrication, was found to be satisfactory. Results of CVN tests showed that the fracture properties of this large-scale heat were approximately the same as those obtained on previous smaller heats. This overall accomplishment demonstrates the fabrication methods used will be reliable for the production of industrial-scale ingots and wrought product forms of the V–4Cr–4Ti alloy.

Acknowledgements

This is a report of work supported by the US Department of Energy under Contract DE-AC03-89ER 51114 and by General Atomics under internal R&D funding.

References

[1] J.P. Smith, W.R. Johnson, R.D. Stambaugh, P.W. Trester, D. Smith, E. Bloom, Proceedings 16th IEEE/NPSS Symposium Fusion Engineering, 1995, p. 858.

[2] J.P. Smith, W.R. Johnson, R.D. Stambaugh, P.W. Trester, D. Smith, E. Bloom, J. Nucl. Mater. 233–237 (1996) 421.

[3] H. Tsai, D.L. Smith, W.R. Johnson, J.P. Smith, Fusion Reactor Mater. Semiann. Prog. Rep. DOE/ER-0313/21, 1997, p. 10.

[4] D.L. Smith, H.M. Chung, B.A. Loomis, H. Matsui, S. Votinov, W. Van Witzenburg, Fusion Eng. Des. 29 (1995) 399.

[5] H.M. Chung, H.-C. Tsai, D.L. Smith, R. Peterson, C. Curtis, C. Wojcik, R. Kinney, Fusion Reactor Mater. Semiann. Prog. Rep. DOE/ER-0313/17, 1995, p. 178.

[6] W.R. Johnson, J.P. Smith, K. Richardson, Adv. Mater. Proc. 151 (6) (1997) 25.

[7] Private communication with H.M. Chung, ANL, 25 January 1996, work not yet published.

[8] C.B. Reed, R.F. Mattas, D.L. Smith, H.M. Chung, H-C. Tsai, G.D. Morgan, G.W. Wille, W.R. Johnson, C. Young, Proceedings of the 12th Top. Mtg. on Tech. of Fusion Energy, 1996, in press.

[9] D.L. Smith, H.M. Chung, H. Matsui, A.F. Rowcliffe, Proceedings of the Fourth International Symposium Fusion Nuclear Technology, 1997, in press.