Development of V-Cr-Ti Type Alloys with Small Additives for Advanced Fusion Applications

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Abstract. Advanced approach to develop a practically tough material was demonstrated in recent research activity of low activation vanadium alloys for fusion applications. Results on development of V-4Cr-4Ti alloy as a reference composition showed feasibility of vanadium alloys as fusion blanket structural materials. It was also shown that modification by small addition of yttrium to the V-4Cr-4Ti alloy improved integrity of their material performance including post-irradiation mechanical properties.

1. Introduction

Vanadium alloy has been considered as a blanket structure material for fusion reactor applications because of their promising properties such as low induced radioactivity, high-heat-loading capability and compatibility with coolant materials like lithium. The critical issues to use vanadium alloys as blanket structure material in lithium self-cooled and breeding system include development of insulator coating for reducing magneto-hydrodynamic (MHD) pressure drop and filling up material performance database of the vanadium alloys. Significant progress has been made in development of the coating[1-4] and material database of vanadium alloys[5,6]. Gaseous impurities such as oxygen in vanadium alloy affect hardening very much especially when radiation induced defects exist. Initial impurity levels were successfully reduced by modification of melting process. A large heat program of purified V-4Cr-4Ti alloy (NIFS-heat) by National Institute for Fusion Science in Japan have demonstrated improvement in the material properties including workability, high temperature strength, ductility and weldability[7-9]. It has been shown that the impurity levels of the V-Cr-Ti alloys can be controlled by small additives such as yttrium by means of their scavenging effect. Tensile properties after neutron irradiation of the modified V-Cr-Ti alloys have been shown remarkable performance [10]. In this paper, successful development of the vanadium alloys by means of advanced melting process and their material performance database are described.

2. Experimental Procedures

2.1. Material Preparation

Raw materials of vanadium, chromium and titanium were same grade as the one used for the NIFS-heat. Gaseous impurities carbon, nitrogen and oxygen levels in yttrium raw material were 210, 380 and 823 wppm, respectively. Yttrium addition will reduce oxygen level by oxide slug formation on the melting ingot surface. Two possible mechanisms of the reduction were proposed, that is, suppression of oxygen penetration into molten metal at the surface and removal of oxygen from inside by forming Y_2O_3[11]. As shown in fig.1, about 0.15wt.% of yttrium is enough to obtain adequately low level of oxygen with assumption that all of the oxygen in the alloy form Y_2O_3. A 15 kg V-4Cr-4Ti-0.15Y ingot was melted in flowing argon gas (O_2: 0.62 ppm, N_2: 0.59 ppm) using a levitation furnace with induction heating of 450kW and 15 kHz for about 30 min.

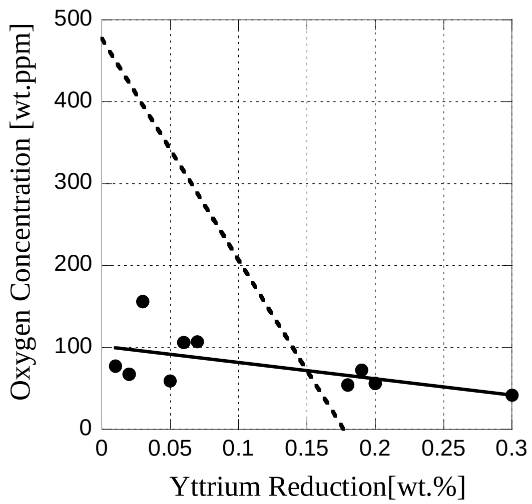


FIG.1. Correlation between oxygen concentration and amount of reduced yttrium in the V-4Cr-4Ti-Y alloys fabricated by levitation melting process. Dashed line represents calculated oxygen concentration when all of oxygen in the alloy removed as Y_2O_3 *slug formation. Initial oxygen concentration set same as in the V-4Cr-4Ti alloy without yttrium addition (480wt.ppm).*

2.2. Tensile Tests and Charpy Impact Tests

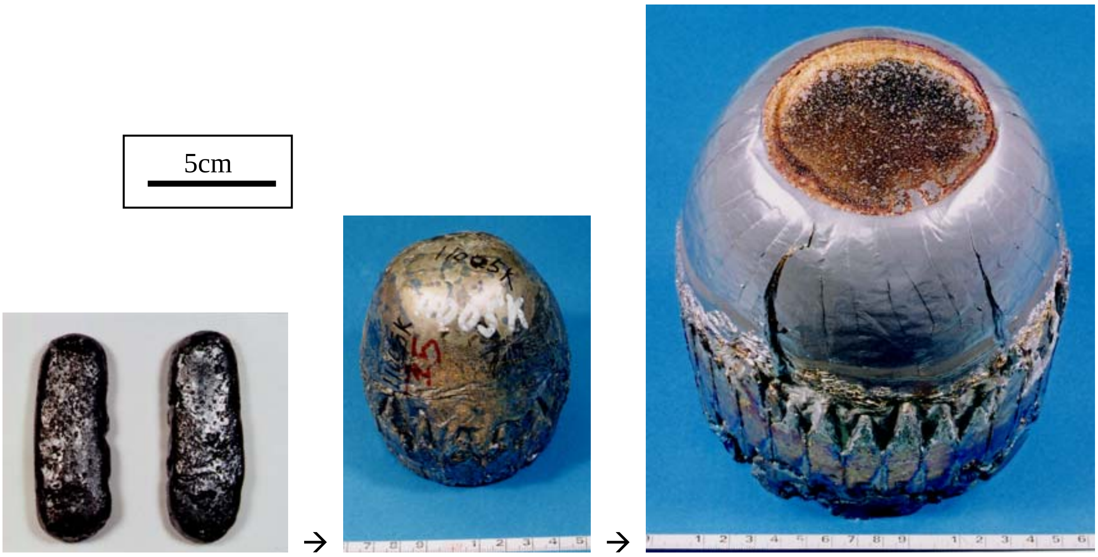
Mechanical properties of the series of V-4Cr-4Ti-Y type alloys were examined at various temperatures to see the effects of the small additives. The alloys used in the tests were V-4Cr-4Ti-0.1Y, V-4Cr-4Ti-0.2Y, V-4Cr-4Ti-0.3Y and V-4Cr-4Ti-0.5Y (nominal weight percentage) fabricated from 2kg-scale of levitation melting. Chemical analyses of the alloys are shown in table 1. Miniaturized specimens with a gauge section of 5x1.2x0.25mm were used after annealing at 950^{o}C for 3.6ks. Tensile tests were carried out using an INSTRON-type machine with an external cooling bath at strain rates of 6.7x10^{-4} to x10^{-2}s^{-1}. Charpy impact tests were carried out using notched specimens of 1.5x1.5x20mm at the Oarai Branch, Institute for Materials Research, Tohoku University. Test temperatures were from ambient and to liquid nitrogen temperature. The head speed was approximately 5m/s. After these testing, specimens were examined by scanning electron microscopy in order to characterize the fracture surface.

2.3. Oxidation Tests

Even though vanadium alloy in the blanket system will be used in a reduction atmosphere, e.g. in lithium, the oxidation-resistance properties make the alloy practically tough material. Oxidation behavior of the alloys was investigated in following helium gas atmosphere with controlled oxygen partial pressure. Oxidation heat treatment of the V-4Cr-4Ti-Y alloys was done at 600^{o}C up to 100h in helium gas flow of 12cm^{3}/min with 330 ppmO_2. Weight gain measurement and hardness test and tensile test were carried out after oxidation treatment. Indentation fracture toughness of the oxidation layer on the alloy was evaluated.

2.4. Neutron Irradiation and Post-Irradiation Experiment

Neutron irradiation was conducted in various fission reactors including JMTR (Japan Material Test Reactor, Japan), JOYO (Japan) and HFIR (High Flux Isotope Reactor, USA). The alloys that show the results in this paper were V-4Cr-4Ti-0.1Si-0.1Al-0.1Y alloy and V-4Cr-4Ti-0.1Si-0.1Al-0.3Y alloy and V-4Cr-4Ti alloy (NIFS-heat). Miniaturized tensile specimens annealed at 900^{o}C for 3.6ks were used. Tensile tests at ambient temperature were carried out with strain rate of 6.7x10^{-4}s^{-1} at the Oarai Branch, Institute for Materials Research, Tohoku University. The specimens were irradiated in MNTR capsules with purified sodium bond at JOYO. Irradiation temperature was 450°C. Neutron fluences were 2.5 x 10^{21}n/cm^2 and 1.1 x10^{22} n/cm^2 corresponding to 1.7 and 7.4 dpa(displacements per atom) for vanadium, respectively.



Plasma arc melting(0.1kg) Levitation melting(2kg) Levitation melting(15kg)

FIG.2. Scale-up of melting ingot of V-Cr-Ti-Si-Al-Y type alloys. Optimum procedure of melting procedures and chemical compositions were identified so far from various mechanical and compositional investigations.

3. Results and Discussion

3.1. Chemical Composition of Prepared Materials

As shown in fig.2, a high-purity 15kg-ingot of V-4Cr-4Ti-0.15Y alloy was made by a levitation melting method. It is demonstrated that the melting process successfully completed. Concentration of interstitial impurities in the ingot reached adequately low levels (O: 108, N:129, C: 113 in wt.ppm)[12]. Precipitation behavior of the alloy indicated that oxygen was successfully removed from the ingot during process. Breakdown process to make final products such as plate, rod and tube has been developed.

TABLE 1 Chemical analysis of the V-4Cr-4Ti-Si-Al-Y type alloys in weight percentage.(O, N,C in wt.ppm). All of the alloys were melted in levitation furnaces, except for V-4Cr-4Ti(NIFS).

	Cr	Ti	Si	Al	Y	O	N	C	V
V-4Cr-4Ti (NIFS)	4.03	3.73	-	-	-	114	122	50	Bal.
V-4Cr-4Ti-0.15Y	4.52	4.65	-	-	0.09	108	129	113	Bal.
V-4Cr-4Ti	4.39	4.48	0.02	0.029	<0.01	496	174	64	Bal.
V-4Cr-4Ti-0.1Y	4.35	4.54	0.01	<0.002	0.04	106	220	110	Bal.
V-4Cr-4Ti-0.2Y	4.32	4.35	0.01	<0.002	0.24	47	85	70	Bal.
V-4Cr-4Ti-0.3Y	4.38	4.69	0.02	0.014	0.28	67	108	77	Bal.
V-4Cr-4Ti-0.5Y	3.97	4.49	-	-	0.32	54	388	72	Bal.
V-4Cr-4Ti-0.1SiAlY	4.31	4.54	0.13	0.13	0.07	112	94	86	Bal.
V-4Cr-4Ti-0.1SiAl-0.3Y	4.41	4.81	0.14	0.13	0.25	80	103	64	Bal.

3.2. Mechanical Properties

Tensile Properties: The alloys showed fairly good ductility and tensile strength even in liquid nitrogen temperature. Little dependence of the levels of yttrium contents on the tensile properties was shown. The only difference was reduction in area became the smallest and the size of dimples observed in the fracture surface became the largest in the V-4Cr-4Ti-0.5Y alloy tested with strain rate of $6.7 \times 10^{-2} s^{-1}$ at liquid nitrogen temperature. From these results with higher strain rate deformation at low temperature, yttrium oxide that perhaps existed as inclusions might be starting point of the fracture.

Charpy Impact Properties: Figure 3 shows the test temperature dependence of absorbed energy for the V-4Cr-4Ti-Y alloys measured by instrumented Charpy impact test. Absorbed energy, E, was normalized by size parameter of the specimen using a following equation:

$$E = E_{obs.} / Bb^2,$$

where $E_{obs.}$ is the observed value of absorbed energy, B is the width and b is the ligament size (= thickness - notch depth) of the specimen, respectively. The DBTTs of the alloys are as low as -150°C. The alloys of V-4Cr-4Ti-0.1Y and V-4Cr-4Ti-0.2Y show higher upper shelf energy (USE) compared to the alloys V-4Cr-4Ti-0.3Y and V-4Cr-4Ti-0.5Y. The NIFS-heat showed slightly higher USE than the V-4Cr-4Ti-0.1Y alloy as 0.5 Jmm^{-3} at -196°C. The dependence on the levels of yttrium contents of the USE may indicate heterogeneous distribution of yttrium as precipitates. To clarify and to control the distribution of yttrium is a key issue to understand the properties of the alloys even though the most of them considered to be distributed as nano-size precipitates.

3.3. Oxidation Behavior

Results from oxidation experiments with controlled oxygen partial pressures in helium gas flow at elevated temperatures indicated that 0.2wt.% of yttrium addition to the V-4Cr-4Ti alloy decreased diffusion coefficient of oxygen an order of magnitude. Yttrium dissolved in solution of the alloy related to formation of a protective layer against oxidation. The results from indentation fracture toughness estimation showed that the oxidation layer of the V-4Cr-4Ti-0.2Y alloy had more than five times greater fracture toughness (K_{IC}) compared to that of the V-4Cr-4Ti alloy[13]. The depth profile of the hardness and weight change after

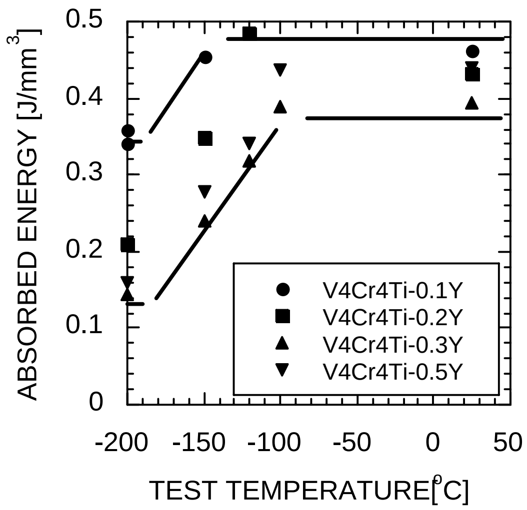


FIG.3. Charpy impact absorbed energy versus test temperature of V-4Cr-4Ti-Y alloys with various amounts of Y addition. Lower levels of yttrium addition shows higher absorbed energy at low temperatures.

oxidation indicated that the oxidation layer of the V-4Cr-4Ti-0.2Y alloy was denser and thinner than that of the V-4Cr-4Ti alloy. It is suggested that yttrium addition improves oxidation resistance of the alloy by means of reducing oxygen diffusion and forming tough protective layer. Improvement of compatibility with various environments including oxidation should lead to reduce effects of gaseous impurity pick-up during fabrication, thermo-mechanical treatment and reactor operations.

3.4. Irradiation Behavior

Figure 4 shows typical stress-strain curves of the specimens after irradiation. All of the specimen show fairly good ductility. In case of V-4Cr-4Ti-Si-Al-Y type alloys, the uniform elongation of the specimens irradiated to 1.7 and 7.4 dpa are 15 and 13.8 %, respectively. The yield stress of the V-4Cr-4Ti-Si-Al-Y type alloys is about 530MPa, while that of the V-4Cr-4Ti alloy is 625MPa at the lower fluence irradiation condition. Work hardening rate of the V-4Cr-4Ti-Si-Al-Y type alloys is larger than that of the V-4Cr-4Ti alloy. The differences probably represent the scavenging effects of the interstitial impurities by small amounts of the additives. The difference of the yield stress became negligible at the higher fluence condition. The ultimate tensile strength of the V-4Cr-4Ti-0.1Si-0.1Al-0.1Y alloy is the largest 730MPa, while the others are about 700MPa. It is possible that the differences correspond to microstructure evolution during irradiation, such as irradiation enhanced precipitates. The amount of yttrium contents had the optimum between 0.1 and 0.2 weight percents so far from

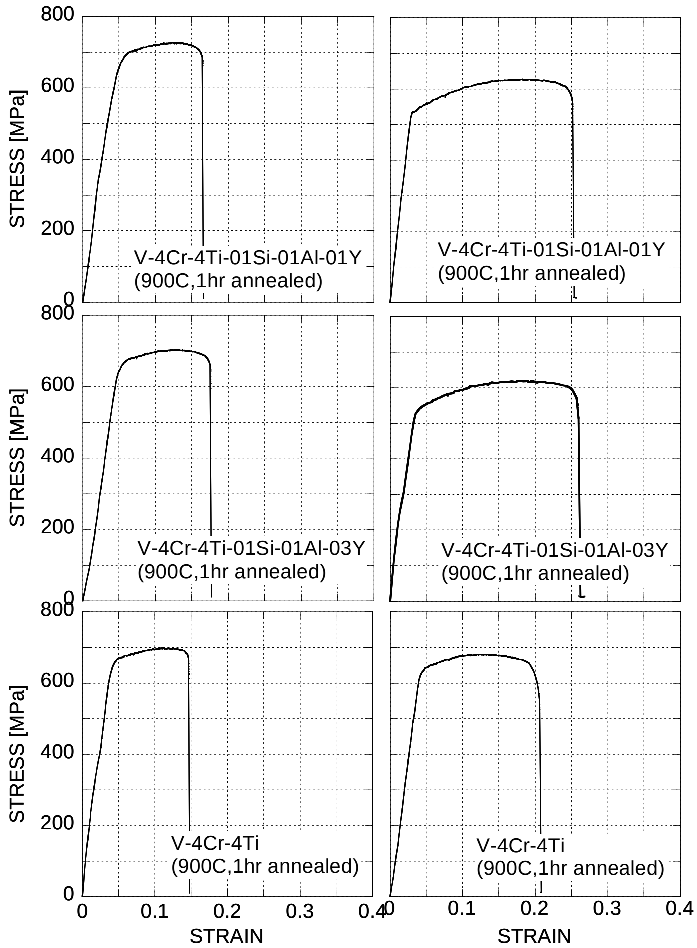


FIG. 4 Typical stress-strain curves for the V-4Cr-4Ti-type alloys after neutron irradiation at 450^{o}C to the fluences of 1.1x10^{22} (left column) and 2.5x10^{21} (right column) (n/cm^2, En>0.1MeV).

the Charpy impact properties before neutron irradiation. The present results of the irradiation behavior of the V-Cr-Ti type alloy may lead slightly different optimum composition from previously reported. More detailed examination including the Charpy impact test after neutron irradiation and microstructure observation will soon be carried out.

4. Summary

Advanced approach to develop a practically tough material was demonstrated in recent research activity of low activation vanadium alloys for fusion applications. Results on development of V-4Cr-4Ti alloy as a reference composition showed feasibility of vanadium alloys as fusion blanket structural materials. It was also shown that modification by small addition of yttrium to the V-4Cr-4Ti alloy improved integrity of their material performance including post-irradiation mechanical properties.
Results from tensile tests at temperature of liquid nitrogen with initial strain rate of 6.7×10^{-4} to 10^{-2}/s showed that yttrium addition up to 0.5wt.% affected neither flow stress nor elongation of the V-4Cr-4Ti-Y alloys but reduced their reduction in area depending on both of the amounts of yttrium additions and the strain rates. Results from Charpy impact tests show clear dependence on yttrium addition of the absorbed energy. Smaller level of yttrium addition to V-4Cr-4Ti alloy show higher absorbed energy. It was suggested from observation of fracture surface that small precipitates containing yttrium might become starting point of the fracture. The amount of yttrium contents has the optimum between 0.1 and 0.2 weight percents so far from the Charpy impact properties. The characterization of the alloys from other viewpoints such as irradiation behavior and weldability of the V-Cr-Ti type alloy with small addition of Si, Al and Y are under way compared to the NIFS-heats.

References

[1] PINT, B., et al., J. Nucl. Mater, **329-333** (2004) 119.
[2] KOCH, F., et al., J. Nucl. Mater. **329-333** (2004) 1403.
[3] SAWADA, A., et al., Fusion Engineering and Design, **75-79** (2005) 737.
[4] SAWADA, A., et al., “Long-term stability of erbium oxide coatings” (to be published).
[5] SAKAI, K., et al., J. Nucl. Mater. **329-333** (2004) 457-461.
[6] HINO, T., et al., “Effects of Si, Al and Y addition on neutron irradiation behavior of V-Cr-Ti type alloys”, (to be published).
[7] HEO, N.J., et al., Fusion Engineering and Design, **61-62** (2002) 749.
[8] NAGASAKA, T., et al., Fusion Science and Technology, **44** (2003) 465.
[9] FUKUMOTO, K., et al., J. Nucl. Mater. **335** (2004) 103.
[10] SATOU, M., et.al., J.Nucl. Mater., **283-287**, (2000) 367.
[11] CHUTO T., et.al., J.Nucl. Mater., **326** (2004) 1.
[12] NAGASAKA, T., et.al., “Impurity behavior in V-4Cr-4Ti-Y alloys produced by levitation melting” (to be published).
[13] TANIGUCHI, D., et al., “Oxidation behavior and mechanical properties of V-4Cr-4Ti-Y alloys in helium gas flow with controlled oxygen partial pressure” (to be published).