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Grain boundary chemistry and heat treatment effects on the ductile-to-brittle transition behavior of vanadium alloys

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Abstract

The ductile-to-brittle transition (DBTT) behavior of vanadium alloys currently being developed for fusion power systems is sensitive to thermo-mechanical processing variables and history. Factors which contribute to this sensitivity are (1) pickup of interstitial impurities such as oxygen, nitrogen and carbon during heat treatments and elevated temperature forming operations, (2) the final grain size achieved, (3) removal of impurities from solid solution due to precipitation reactions, and (4) segregation of impurities to grain boundaries. Previous work on a V–5Cr–5Ti (Heat No. 832394) alloy suggested that sulfur segregation or precipitation during final mill annealing may play a role in determining DBTT behavior. The effect of heat treatment on grain boundary chemistry and Charpy impact behavior was investigated using a production-scale heat of V–4Cr–4Ti (Heat No. 832665). Specimens were examined with Auger electron spectroscopy to characterize grain boundary microchemistry for correlation with Charpy impact test results obtained from one-third size specimens.

1. Introduction

It has been shown that the fracture toughness and Charpy impact properties of vanadium alloys being considered for fusion power system applications are sensitive to heat treatment variations [1–7]. In an earlier study, heat treatment of V–5Cr–5Ti from Heat No. 832394 at 1125°C for 1 h gave a fracture toughness of about 52 kJ/m^2 when tested at room temperature (RT) and a ductile-to-brittle transition (DBTT) of 80°C, Fig. 1 [4]. Fracture surfaces exhibited a mixture of intergranular and cleavage fracture features. When some specimens were given an additional heat treatment at 890°C for 24 h, they became ductile at RT and fractured by microvoid coalescence [4]. The fracture toughness for material in this condition was very high (~1100 kJ/m^2) and the DBTT decreased to −145°C, Fig. 1.

The reasons for this behavior are not completely understood. Based on Auger analyses sulfur concentrations on grain boundaries were higher [2,4] and precipitate densities appeared to be lower for the 1125°C/1 h heat treatment relative to the 1125°C/1 h + 890°C/24 h treatment [4,5]. Transmission electron microscopy was performed to provide microstructural and microchemical information. Detailed microstructural comparisons showed distinct differences in precipitation behavior between the two heat treatments [6]. Following heat treatment at 1125°C, only Si was found as a minor impurity in large particles, but S could be identified at grain boundaries, which were coated with a fine distribution of precipitates. After the additional heat treatment at 890°C more precipitation consisting of (Ti,V)O and containing Si, S, and P was observed. It was concluded that embrittlement of V–5Cr–5Ti was probably due to a combination of interstitial solid solution hardening and grain boundary impurity segregation since both intergranular and transgranular failure modes were found.

The objective of the present study is to perform the same set of heat treatments on a production-scale heat (No. 832665) of V–4Cr–4Ti to determine if similar variations in grain boundary chemistry and Charpy impact properties are observed. Grain boundary chemistry is characterized by Auger electron spectroscopy

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and initial microstructural evaluation is by optical microscopy.

2. Experimental procedure

The material used in this study was V–4Cr–4Ti (Heat No. 832665) produced by Wah Chang of Albany, Oregon. Material chemistry and fabrication details have been reported previously [8]. A 3.8 mm thick plate was obtained from Argonne National Laboratory in the warm rolled condition. One-third scale Charpy specimens were machined from the plate with dimensions 23.6 mm × 3.33 mm × 3.33 mm. A 30°, 0.51 mm deep notch was used with a 0.030 mm root radius. Charpy specimens were taken from the plate in the T–L orientation. After machining, specimens were heat treated in a vacuum of $\leqslant 1.33 \times 10^{-5}$ Pa. Three different heat treatments were investigated.

(1) HT1: 1000°C for 1 h, furnace cool.
(2) HT2: 1125°C for 1 h, furnace cool.
(3) HT3: HT2+890°C for 24 h, furnace cool.

Charpy impact testing was performed at Oak Ridge National Laboratory using an instrumented system. The hammer was dropped from a low-blow position with a potential energy of 70 J at an impact velocity of ~2.3 m/s. Fracture surfaces of selected specimens were examined in a scanning electron microscope.

Grain boundary chemistry was determined by scanning Auger electron spectrometry (Perkin-Elmer Model 660). Auger specimens were hydrogen charged for 2 h prior to insertion into the Auger. Specimens were then cooled to liquid nitrogen temperature and fractured in the Auger system chamber in a vacuum of $\leqslant 1 \times 10^{-7}$ Pa. Auger spectra were taken at an accelerating voltage of 5 kV and an incident electron current of 200 nA.

3. Results

The microstructures resulting from the three heat treatments employed in this study are presented in Fig. 2. Fig. 2(a) gives the microstructure for the HT1 heat treatment. Heat treatment produces a partially recrystallized microstructure with a bimodal grain size distribution. The average grain diameter is 13 μm. In addition, there is evidence of the precipitation of secondary phases in this microstructure. The HT2 microstructure is shown in Fig. 2(b). The grain size in this microstructure is more equiaxed and is considerably larger (33 μm) than for the HT1 heat treatment. The precipitate volume fraction is much smaller compared to the HT1 condition. The microstructure for the HT3 heat treatment is displayed in Fig. 2(c). The grain shape and size (32 μm) is the same as for the HT2 microstructure but it is evident that a considerable amount of precipitation results from annealing at 890°C.

The Auger results for each heat treatment are collected in Table 1. Elemental measurements for intergranular facets are distinguished from cleavage facets in Table 1. Comparing the chemical information from cleavage facets to that from intergranular facets gives an indication of the degree to which various elements segregate to grain boundaries. Comparing intergranular to cleavage facets reveals that N, S, P and to a lesser extent C tend to segregate to grain boundaries for all heat treatments. There also appears to be a slight depletion of O at grain boundaries under all conditions. Comparing results for intergranular facets shows increased concentrations of S, C and Cr, and decreased levels of P for the HT2 specimens compared to HT1 and HT3 specimens. The grain boundary chemistries of the latter two heat treatments were similar to each other and distinct from the HT2 treatment. The grain boundary O levels were

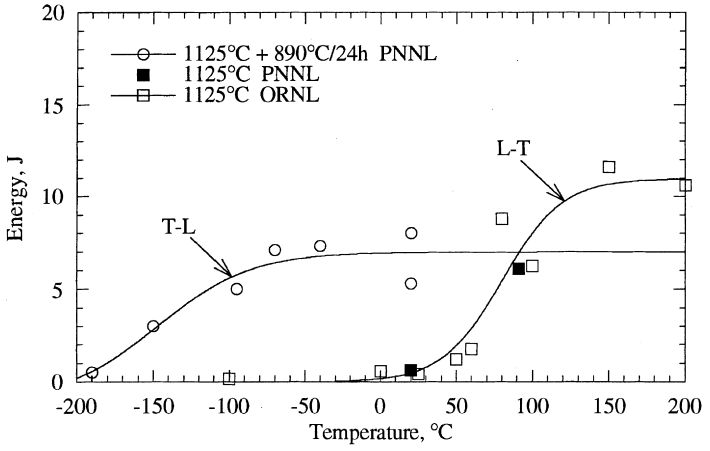

Fig. 1. Unirradiated Charpy impact properties for V–5Cr–5Ti (Heat No. 832394) following heat treatments at 1125°C for 1 h [4,5,7] and 1125°C for 1 h +890°C for 24 h [4,5].

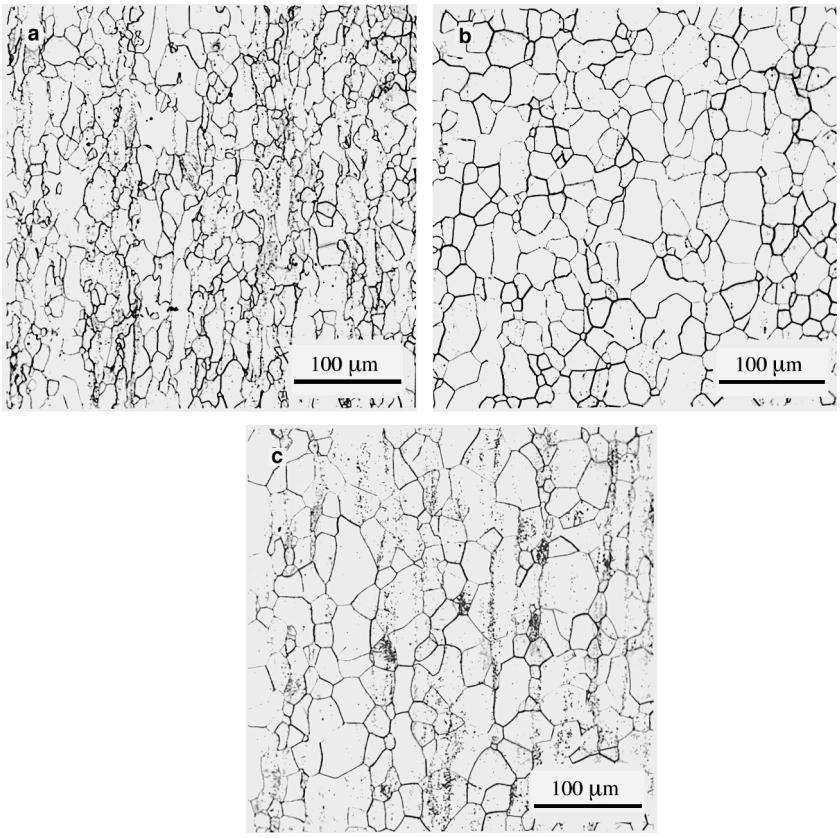

Fig. 2. Optical micrographs showing microstructures of V–4Cr–4Ti resulting from various heat treatments: (a) HT1, (b) HT2 (c) HT3.

the same for all three heat treatments. Little variation in grain boundary N level was found, with the highest level occurring in specimens given the HT3 heat treatment.

The Charpy impact results are plotted in Fig. 3. The data for the HT2 and HT3 specimens were fitted to a hyperbolic tangent function to aid identification of the DBTT. The data for the HT1 heat treated material shows that no DBTT was observed down to −196°C. The trend of the data is increasing absorbed energy with decreasing test temperature, which is consistent with flow stress controlled deformation. Crack initiation and arrest was observed for HT1 specimens tested at −150°C and −196°C, but no crack initiation was seen for specimens tested at higher temperatures. The HT2 annealed material exhibited a DBTT of about −125°C. The HT3 specimens also gave a DBTT of about −125°C, but the

Table 1
Auger electron spectroscopy results (at.%) for V–4Cr–4Ti (Heat No. 832665)

Element	Heat treatment conditions					
	1000°C/1 h		1125°C/1 h		1125°C/1 h + 890°C/24 h	
	IF [a]	CF [b]	IF	CF	IF	CF
Cr	4.1	5.3	5.6	8.0	4.5	6.0
Ti	5.9	6.1	5.6	5.9	8.7	5.7
C	3.3	2.8	7.3	3.5	4.7	2.3
O	17	20	17	23	17	21
N	19	3.7	20	3.1	25	3.6
S	1.4	0.2	3.2	0.3	0.9	0.2
P	4.1	0.7	2.4	0.6	4.3	0.6

[a] IF = Intergranular facet.
[b] CF = Cleavage facet.

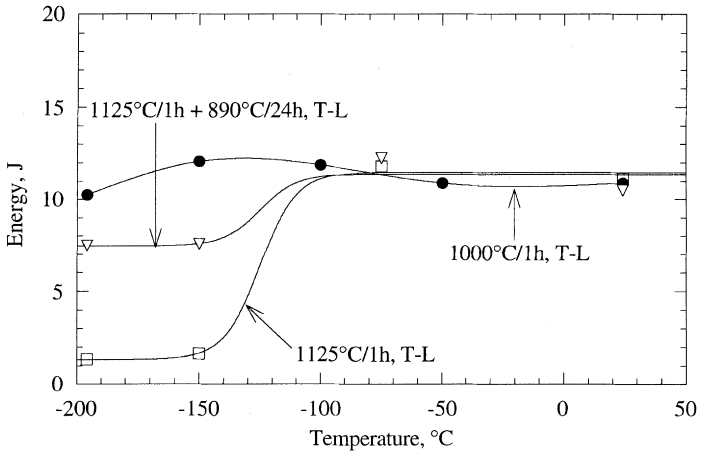

Fig. 3. Unirradiated Charpy impact properties for V–4Cr–4Ti (Heat No. 832665) following heat treatments at 1000°C for 1 h, 1125°C for 1 h and 1125°C for 1 h +890°C for 24 h.

lower shelf energies were significantly greater than the HT2 specimens demonstrating the beneficial effect of the 890°C heat treatment. Similar to the HT1 specimens crack initiation and arrest occurred for HT2 and HT3 specimens tested at the two lowest test temperatures, but not for the two highest temperatures. For HT2 and HT3 specimens, once a crack initiated it propagated almost entirely through the initial uncracked ligament.

The fracture surfaces of HT2 and HT3 specimens were examined in a scanning electron microscope to determine the fracture mechanism. For HT2 specimens the fracture surfaces displayed predominantly cleavage fracture features with a minor amount (<10%) of intergranular fracture. A small amount of microvoid coalescence was noted in the HT2 specimen tested at −150°C. For HT3 specimens a mixture of ductile and brittle fracture mechanisms was found. The fracture surface of the HT3 specimen tested at −150°C showed largely microvoid coalescence features with isolated regions of cleavage fracture. The size of the cleavage fracture areas increased near the back face of the specimen. The fracture mechanism of the HT3 specimen tested at −196°C was ductile near the notch root and along the sides of the specimen, but cleavage fracture was observed in the middle of the specimen and toward the back face. It is interesting to note that the absorbed energies of the two HT3 specimens in which crack initiation occurred were nearly the same, but the pattern of ductile versus cleavage fracture features were somewhat different.

4. Discussion

Table 2 summarizes the pertinent microstructural, microchemical and Charpy impact data for the different heat treatments employed on V–(4–5)Cr–(4–5)Ti. In the previous investigations [4–6] of heat treatment effects on V–5Cr–5Ti it was concluded that the improved fracture properties seen in specimens aged at 890°C was probably due to two factors (1) a reduction in the grain boundary sulfur concentration and (2) a decrease in the interstitial impurity level resulting from precipitation reactions. Low energy fractures of V–5Cr–5Ti exhibited both intergranular and transgranular cleavage features suggesting that grain boundary embrittlement and interstitial hardening both played a role in reducing toughness. Specimens of V–5Cr–5Ti given the HT2 heat treatment yielded the highest DBTT and grain boundary S concentration. Following the HT3 heat treatment the

Table 2
Summary of microstructural, microchemical and Charpy impact data for various heat treatments of V–(4–5)Cr–(4–5)Ti

Alloy	Heat no.	Heat treatment (°C)	Orientation	GB [S] (at.%)	Grain size (μm)	DBTT (°C)
V–5Cr–5Ti	832394	1125/1 h	L–T	6.3	45	+80
		1125/1 h + 890/24 h	T–L	1.1	45	−145
V–4Cr–4Ti	832665	1000/1 h	T–L	1.4	13	<−196
		1125/1 h	T–L	3.2	33	−125
		1125/1 h + 890/24 h	T–L	0.9	32	−125

DBTT decreased to −145°C and the grain boundary S level to 1.1 at.% with no change in grain size relative to HT2 specimens.

In the present study some of the same effects were observed. The microstructures produced by the various heat treatments were similar to those found for V–5Cr–5Ti specimens. A high density of precipitates was evident in the HT3 microstructure and to a lesser extent the HT1 microstructure relative to the HT2 condition. Measurable increases in the grain boundary S concentration (and C) were noted following the HT2 heat treatment compared to the HT1 and HT3 anneals. Although the DBTT of the HT3 material was the same as the HT2 material the lower shelf energies were significantly greater. One important difference is that intergranular fracture of low toughness specimens was observed only to a very limited extent. This result suggests that a threshold level of grain boundary segregant is needed to produce grain boundary embrittlement. It also indicates that processes which remove interstitial impurities from the matrix are an important mechanism for improving toughness. It should also be noted that aging at 890°C improved the resistance of the matrix to cleavage fracture but did not recover all of the toughness lost by annealing at 1125°C. This is due to the much larger grain size produced at 1125°C compared to the 1000°C anneal. It is well known that the DBTT of refractory metals depends on grain size. All other factors remaining constant, the smaller the grain size, the lower the DBTT.

5. Conclusions

The effect of heat treatment on the microstructure of V–4Cr–4Ti was similar to that observed on V–5Cr–5Ti. An increased DBTT arising from heat treatment at 1125°C for 1 h was due to a larger grain size and reduced levels of precipitation compared to heat treatment at 1000°C for 1 h. Considerable toughness can be recovered for the 1125°C material by aging at 890°C for 24 h which causes precipitation of phases which reduce grain boundary S levels and lower the concentration of interstitials in solid solution. A threshold level of grain boundary segregant appears to be required to cause grain boundary embrittlement and intergranular fracture.

Acknowledgements

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