

GRAIN BOUNDARY CHEMISTRY AND HEAT TREATMENT EFFECTS ON THE DUCTILE-TO-BRITTLE TRANSITION BEHAVIOR OF VANADIUM ALLOYS -

R. J. Kurtz, M. L. Hamilton, and H. Li (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this work is to determine the effect of different heat treatments on the grain boundary chemistry and Charpy impact properties of the production-scale heat of V-4Cr-4Ti (Heat No. 832665) for comparison with results generated previously on V-5Cr-5Ti (Heat No. 832394).

SUMMARY

One-third scale Charpy impact specimens of V-4Cr-4Ti were given the same heat treatments applied to equivalent specimens of V-5Cr-5Ti. Auger specimens of V-4Cr-4Ti were also heat treated with the Charpy specimens to enable grain boundary chemistry measurements. The microstructural, microchemical and Charpy impact response of V-4Cr-4Ti displayed trends similar to those observed for V-5Cr-5Ti. The results show that grain size plays an important role in determining the ductile-to-brittle transition temperature (DBTT) of these materials and that a threshold level of grain boundary segregant appears to be required to cause grain boundary embrittlement and intergranular fracture.

PROGRESS AND STATUS

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 fracture toughness of about 52 kJ/m² when tested at room temperature (RT) and a DBTT of 80°C, Figure 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/m²) and the DBTT decreased to -145°C, Figure 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/1h heat treatment relative to the 1125°C/1h + 890°C/24h 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

*Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

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.

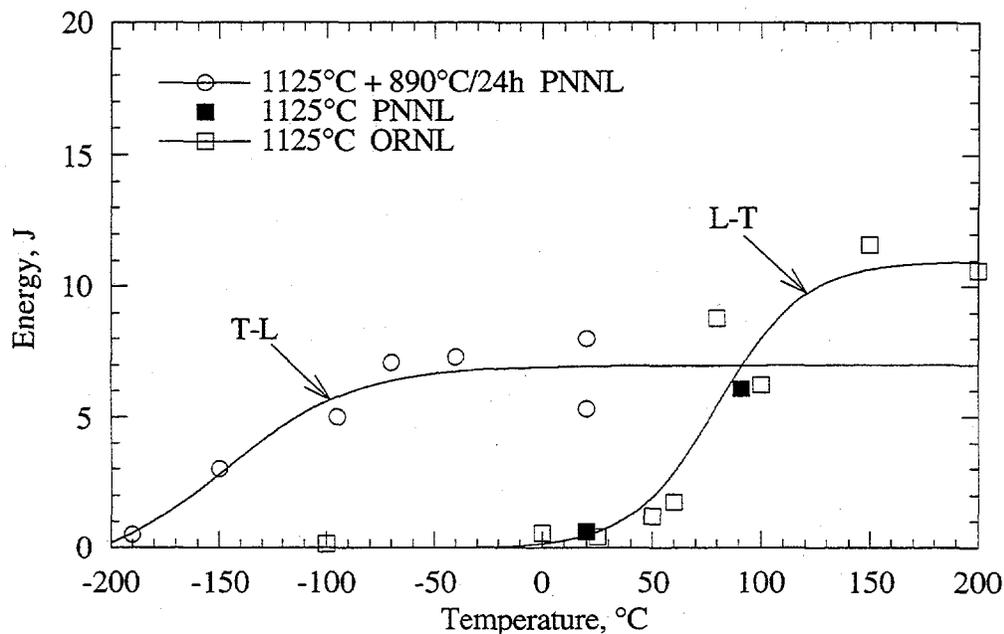


Figure 1. Unirradiated Charpy impact properties for V-5Cr-5Ti (Heat No. 832394) following heat treatments at 1125°C for 1 h [4,5,7] and 1125°C for 1 h + 890°C for 24 h [4,5].

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 and initial microstructural evaluation is by optical microscopy.

Experimental Procedure

The material used in this study was V-4Cr-4Ti (Heat No. 832665) produced by Wah Chang (formerly Teledyne 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 x 3.33 mm x 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 $\leq 1.33 \times 10^{-5}$ Pa. Three different heat treatments were investigated.

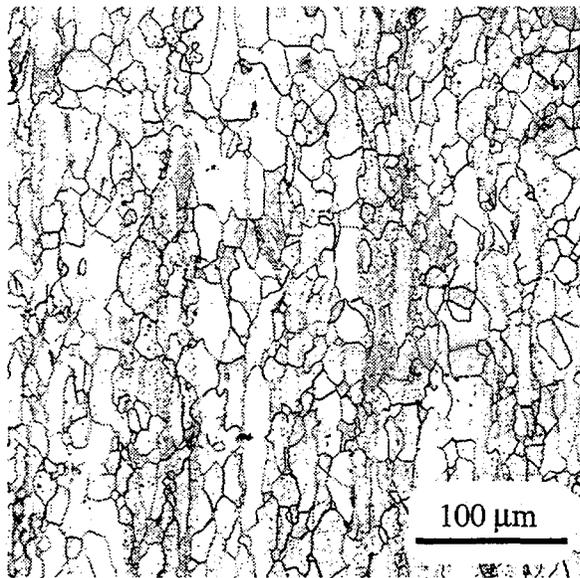
- 1) HT1: 1000°C for 1 h, furnace cool
- 2) HT2: 1125°C for 1 h, furnace cool
- 3) HT3: HT2 + 890°C for 24 h, furnace cool

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.

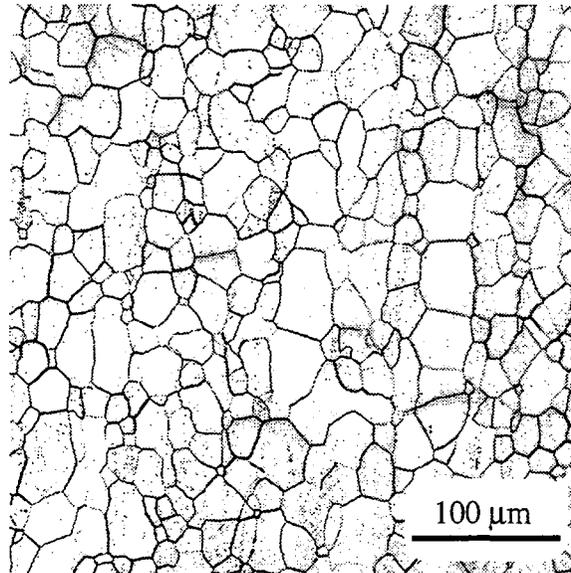
Grain boundary chemistry was determined by scanning Auger electron spectrometry (Perkin-Elmer Model 660). Auger specimens were hydrogen charged for 2 h prior to insertion into the Auger. Specimens were then cooled to liquid nitrogen temperature and fractured in the Auger system chamber in a vacuum of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

Results

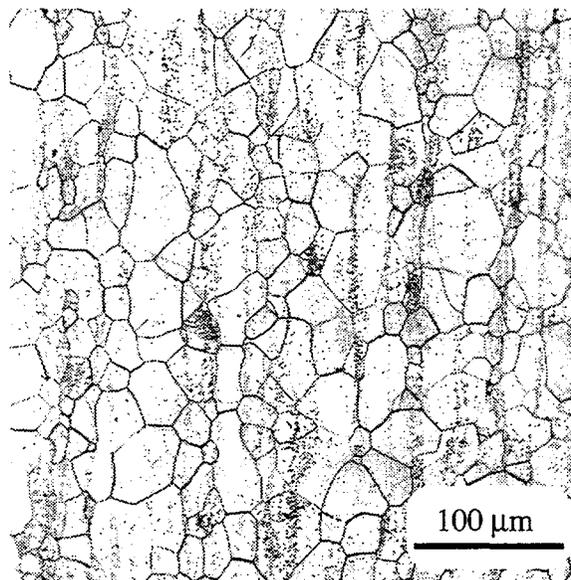
The microstructures resulting from the three heat treatments employed in this study are presented in Figure 2. Figure 2a gives the microstructure for the HT1 heat treatment. Heat treatment produces a partially recrystallized microstructure with a bimodal grain size distribution. The average grain diameter is 13 μm . In addition, there is evidence of the precipitation of secondary phases in this microstructure. The HT2 microstructure is shown in Figure 2b. 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 Figure 2c. 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.



(a)



(b)



(c)

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

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 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.

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

Element	Heat Treatment Conditions					
	1000°C/1h		1125°C/1h		1125°C/1h + 890°C/24h	
	IF*	CF**	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

*IF = Intergranular Facet

**CF = Cleavage Facet

The Charpy impact results are plotted in Figure 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 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.

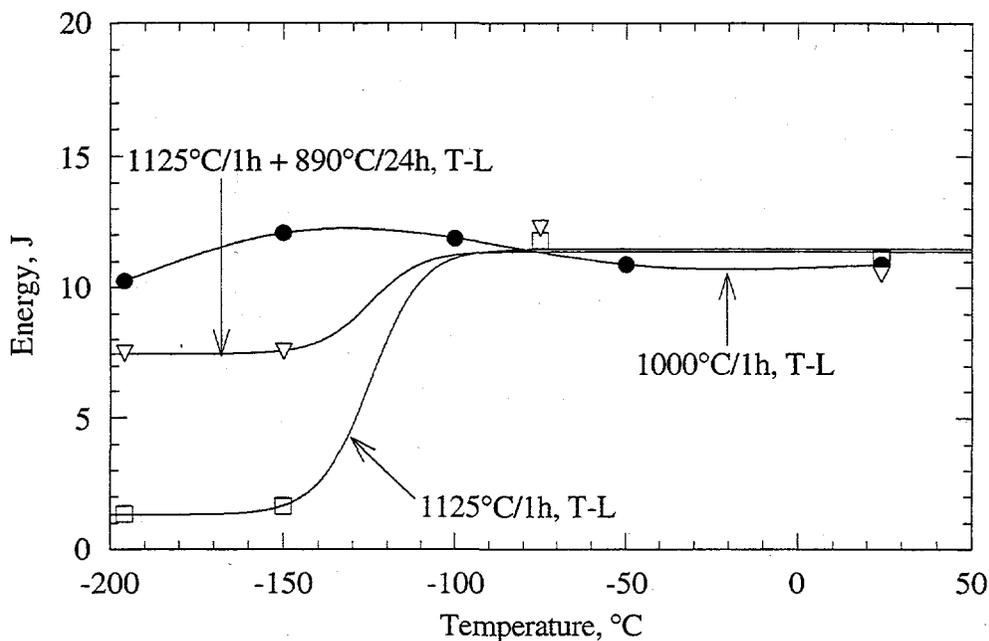


Figure 3. Unirradiated Charpy impact properties for V-4Cr-4Ti (Heat No. 832665) following heat treatments at 1000°C for 1 h, 1125°C for 1 h and 1125°C for 1 h + 890°C for 24 h.

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.

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 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 caused by 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.

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, $^{\circ}\text{C}$	Orientation	GB [S], at.%	Grain Size, μm	DBTT, $^{\circ}\text{C}$
V-5Cr-5Ti	832394	1125/1h	L-T	6.3	45	+80
"	"	1125/1h + 890/24h	T-L	1.1	45	-145
V-4Cr-4Ti	832665	1000/1h	T-L	1.4	13	<-196
"	"	1125/1h	T-L	3.2	33	-125
"	"	1125/1h + 890/24h	T-L	0.9	32	-125

CONCLUSIONS

The effect of heat treatment on the microstructure of V-4Cr-4Ti was similar to that observed for V-5Cr-5Ti. The increase in DBTT caused by 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 1h. Considerable toughness was recovered for V-4Cr-4Ti previously given the $1125^{\circ}\text{C}/1\text{h}$ heat treatment by aging at 890°C for 24 h. The aging heat treatment caused precipitation of phases which reduced grain boundary S levels and lowered 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.

FUTURE WORK

Transmission electron microscopy will be performed on heat treated V-4Cr-4Ti specimens for comparison with the earlier work on V-5Cr-5Ti. The objective shall be to characterize the precipitates formed during heat treatment.

ACKNOWLEDGEMENTS

We are indebted to Dr. David Alexander at Oak Ridge National Laboratory for performing the Charpy impact tests.

REFERENCES

1. H. M. Chung, J. Gazda, L. J. Nowicki, J. E. Sanecki and D. L. Smith, "Effects of Fabrication Variables on Impact Properties and Microstructure of V-Cr-Ti Alloys," Fusion Materials Semiannual Progress Report, DOE/ER-0313/15, 207.
2. M. L. Grossbeck, A. F. Rowcliffe and D. J. Alexander, "The Relationship Between Recrystallization Temperature, Grain Size, and the Charpy Impact Properties of V-Cr-Ti Alloys," Fusion Materials Semiannual Progress Report, DOE/ER-0313/16, 244.
3. D. N. Braski and M. L. Grossbeck, "Analysis of Grain Boundaries in a V-5Cr-5Ti Alloy Using Auger Electron Spectroscopy," Fusion Materials Semiannual Progress Report, DOE/ER-0313/16, 272.
4. H. Li., M. L. Hamilton and R. H. Jones, "Effect of Heat Treatment on Microstructure and Fracture Toughness of a V-5Cr-5Ti Alloy," Fusion Materials Semiannual Progress Report, DOE/ER-0313/17, 165.
5. H. Li., M. L. Hamilton and R. H. Jones, "Effect of Heat Treatment and Test Method on DBTT of a V-5Cr-5Ti Alloy," Fusion Materials Semiannual Progress Report, DOE/ER-0313/18, 215.
6. D. S. Gelles and H. Li, "Effect of Heat Treatment on Precipitation in V-5Cr-5Ti Heat BL-63," Fusion Materials Semiannual Progress Report, DOE/ER-0313/19, 22.
7. A. F. Rowcliffe and S. J. Zinkle, "Assessment of the Radiation-Induced Loss of Ductility in V-Cr-Ti Alloys," Fusion Materials Semiannual Progress Report, DOE/ER-0313/21, 63.
8. H. M. Chung, H.-C. Tsai, D. L. Smith, R. Peterson, C. Curtis, C. Wojcik and R. Kinney, "Fabrication of 500-kg Heat of V-4Cr-4Ti," Fusion Materials Semiannual Progress Report, DOE/ER-0313/17, 178.