Processing and Fabrication of Experimental Vanadium Alloys for HFIR RB-17J Experiment

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OBJECTIVE

Process 12 experimental heats of vanadium alloys and fabricate into small plates to investigate the effects of composition, precipitation, and the presence of He on the microstructure during neutron irradiation in the HFIR RB-17J experiment.

SUMMARY

A proposed plan was formulated to make 12 experimental heats of vanadium alloys (HR1-HR12) to investigate the effects of composition, precipitation, and the presence of He on the microstructure and mechanical properties of vanadium during neutron irradiation in the HFIR RB-17J experiment. The main objectives for controlling the substitutional and interstitial solute concentrations in the alloys were achieved in this study. All of the alloys except the high N alloy (HR9) were successfully rolled into plates, which were suitable for machining flat sheet tensile (SS-J1 and SS-J2), TEM disks, and pre-cracked bend bars (PCBB) specimens. The alloys were processed with two (three for HR11) thermo-mechanical processes (TMP) in order to develop microstructures containing different precipitate and grain structures for the unirradiated annealing and neutron irradiation experiments.

PROGRESS AND STATUS

Experimental Procedure

In November 2002, participants of the Fusion Energy Program from ORNL, PNNL, and UCSB initiated weekly conference calls to finalize the specimen matrix and to coordinate activities for capsule assembly and insertion in the HFIR RB17J irradiation experiment. Early discussions addressed the finalization of the specimen matrix, which led to a conclusion that a series of small heats (~300g) of vanadium alloys were needed to investigate the effects of precipitate structure, grain size, He generation, and composition on the fracture and mechanical properties of vanadium alloys. A proposed plan was then formulated for making 12 small experimental heats of vanadium alloys, which are designated HR1 to HR12. Each processed alloy was fabricated into a small plate following one or two (three in the case of HR11) thermo-mechanical processing (TMP) procedures. Depending on the research objectives, specimens were then machined from the plates for investigation of microstructural changes and tensile and fracture properties resulting from exposure to the neutron irradiation conditions.

The Proposed Alloys

The compositions of the 12 vanadium-based alloys that were proposed based on research and processing objectives are listed in Table 1. The objective for making HR1-5 was to investigate higher Cr and Ti solute concentrations while keeping the interstitial C, N, and O concentrations the same in each alloy and close to the levels usually contained in the 832665 heat of V-4Cr-4Ti. HR1 is the reference alloy for the HR2-5 and HR11 alloys. For HR6-9, a 1:1 stoichiometric ratio between Ti, or Zr in HR7, and the interstitial C, N, and O atoms was the primary goal. However, it was also important to keep the C, N, and O concentrations the same in these alloys with the exception of the higher C level in HR8 and N level in HR9. HR10 is the reference alloy for HR8 and HR9 since it contains nearly the same Ti content but does not have the high C or N levels. The primary goal for HR11 and HR12 was to add 100 wppm B to V-4Cr-4Ti (HR11) and unalloyed V (HR12).

The primary goal for preparing HR1-HR5 was to explore higher substitutional Cr and Ti solute regimes as a basis for improving creep resistance while maintaining acceptable fracture behavior at 450ºC. This investigation will also address radiation phase stability, particularly the issue of two phase regime with higher Ti. In parallel with the irradiation experiment, these alloys will also form the basis of studies on thermal creep and phase stability. The objective for processing these alloys was to vary the Ti and Cr

concentration while maintaining a constant interstitial concentration and a nearly constant grain size. The thermo-mechanical processing (TMP) of these alloys consists of a solutionizing treatment at 1300ºC and a final anneal at 1000ºC to produce a random dispersion of coarse globular-shaped TiCON particles in the BCC matrix. The specimens prepared from these alloys include TEM, SS-J1 tensile, and fracture toughness specimens. There will be TEM and SS-J1 specimens at all three irradiation temperatures. However, fracture toughness specimens will only be included at 450ºC since this pertains to the upper temperature range for irradiation hardening in V-Cr-Ti alloys.

An alternative approach to development of creep resistant microstructures and control of helium based on uniformly dispersed TiCON particles and control of grain boundary structure was proposed for preparing HR6-HR10. The investigation of these alloys includes the effects of interstitial concentration on the development of damage structure, radiation hardening and deformation behavior including dynamic strain aging (DSA) investigation of the effect of varying Ti: interstitial ratios on interstitial partitioning between matrix and precipitated phases; investigation of C, O and N solubilities; determination of regimes of phase stability (globular and plate morphologies); and investigation of relative effectiveness of Ti and Zr as interstitial getters. The objective for processing these alloys was to produce two different starting microstructures for the irradiation experiment. The TMP steps include a solutionizing treatment at 1300ºC and final annealing treatments to produce (a) randomly distributed globular-shaped TiCON particles and a 20-30 μm grain size in the matrix and (b) uniformly distributed nano-size plate-shaped TiCON particles and a large matrix grain size. Thermal aging and phase stability studies will be carried out in parallel with the irradiation experiments with the goal of eventually developing multi-phase microstructures with improved thermal creep resistance. The specimens consist of thicker SS-J2 tensile specimens for DSA measurements and TEM specimens for microstructural analysis.

An investigation of helium mobility and trapping in V-4Cr-4Ti and pure V was the primary goal for preparing HR11 and HR12, respectively. The investigation includes using boron doping to produce 100 appm helium and will be coupled with post–irradiation annealing with and without applied stress. The V-4Cr-4Ti (HR11) alloy will be processed to develop a range of microstructures to provide information on the effectiveness of various microstructural constituents as helium traps. Following the homogenization at 1300ºC, cold rolling and annealing at 1000ºC. Several TMT steps will be used to produce

Table 1. Heat designation and specified nominal compositions.

Alloy Number	V (wt.%)	Cr (wt.%)	Ti (wt.%)	Zr (wt.%)	C (wppm)	O (wppm)	N (wppm)	Comment
HR1	Bal.	4	4		140	350	85	Re-melt V-4Cr-4Ti
HR2	Bal.	10	4		140	350	85	Add Cr to V-4Cr-4Ti
HR3	Bal.	15	4		140	350	85	Add Cr to V-4Cr-4Ti
HR4	Bal.	4	10		140	350	85	Add Ti to V-4Cr-4Ti
HR5	Bal.	4	15		140	350	85	Add Ti to V-4Cr-4Ti
HR6	Bal.	4	0.195	-	70	330	200	Add Ti, Cr to V
HR7	Bal.	4	-	0.375	70	330	200	Add Zr, Cr to V
HR8	Bal.	4	0.57	-	1000	330	200	Add Ti, Cr, TiC to V
HR9	Bal.	4	0.48	-	70	330	1000	Add Ti, Cr, TiN to V
HR10	Bal.	4	0.50	-	70	330	200	Add Ti, Cr to V
HR11	Bal.	4	4	-	140	350	85	Add B to V-4Cr-4Ti
HR12	Bal.	-	-	-	25	210	150	Add B to V

microstructures containing, (a) uniformly dispersed globular TiCONs, (b) dispersion of plate morphology TiCON (~950ºC), and c) uniformly dispersed nano–size TiCON plates. Pure V will be processed to produce fine and coarse grain size microstructures.

Processing of the HR Alloys

The approach for making the HR alloys consisted of arc melting material from either the V-4Cr-4Ti plate (832665 heat) or unalloyed V ingot (820645 heat) with additional material to obtain the proposed alloy composition. HR1 consisted of material from the 1 in thick V-4Cr-4Ti plate (832665 heat) that was simply arc melted. HR2 and HR3 were made by arc melting material from the V-4Cr-4Ti plate with 99.999% pure Cr, in the form of -4/+7 mesh granules. HR4 and HR5 were made in a similar manner with 99.995% pure Ti, in the form of 0.125 in diameter x 0.25 in long slug. HR6, HR7, and HR10 were made by arc melting material from the V ingot with 99.999% pure Cr granules and either 99.995% pure Ti slug (HR6 and HR10) or 99.5% pure Zr slug (HR7). HR8 and HR9 were made in a similar manner as HR6 except that an additional amount of 99.5% pure TiC powder and 99.8% pure TiN powder was also arc melted to obtain the 1000 wppm C level in HR8 and 1000 wppm N level in HR9, respectively. The equivalent of 100 wppm natural B was arc melted with material from the V-4Cr-4Ti plate to make HR11 and with the V ingot to make HR12. All of the alloy samples were arc melted four times and then drop-cast into ~300 gram rectangular-shaped billets with dimensions of 1 in wide x 0.5 in thick x 5 in long.

The results of the chemical analyses of the HR alloys are shown in Table 2. Most of the processing objectives were achieved in making the alloys. Table 3 shows the average and total interstitial C, N, and

Table 2. Chemical analyses of V-4Cr-4Ti (832665), unalloyed V (820645), and HR alloys. The concentration for all elements are in wppm except for Ti, V, and Cr, which are in weight percent.

Element	V-4Cr-4Ti (832665)*	Pure V (820645)*	HR1	HR2	HR3	HR4	HR5	HR6	HR7	HR8	HR9	HR10	HR11	HR12
B	<7	<5	9	-	-	-	-	-	-	-	-	-	80	70
C	79	24	110	110	150	120	100	30	30	980	60	60	140	60
N	85	113	100	90	130	80	110	170	190	780	1210	180	90	180
O	310	313	380	360	380	350	370	290	290	530	320	330	360	290
Al	158	243	210	200	210	230	190	170	200	230	200	200	210	150
Si	783	173	570	620	660	570	530	20	30	<20	20	30	650	170
P	<30	<30	130	<20	<20	<20	<20	40	60	<20	<20	<20	110	<20
S	<10	<10	10	10	20	20	10	20	20	20	20	20	20	20
Cl	<2	-	<10	10	10	10	<10	<10	20	<10	<10	<10	<10	10
Ca	<10	<5	<20	10	40	<10	<10	<20	<20	30	<20	<20	<20	<20
Ti (%)	3.91	-	3.58	3.75	3.67	9.77	14.73	2100	30	5700	5000	5100	4.01	-
V (%)	Bal.	Bal.	92.87	86.33	81.47	86.47	81.66	95.56	95.38	95.05	95.11	95.26	92.00	99.88
Cr (%)	3.77	-	3.35	9.71	14.65	3.56	3.43	4.10	4.14	4.09	4.19	4.12	3.78	-
Fe	223	147	20	140	70	60	40	60	50	40	30	40	30	60
Ni	-	-	<20	20	20	70	30	20	<20	<20	<20	<20	<20	<20
As	-	-	<20	30	<20	<20	<20	100	<20	110	20	100	<20	40
Zr	-	-	<20	20	20	20	<20	<20	3700	<20	<20	<20	20	<20
Nb	<60	40	50	100	<20	100	30	180	20	40	<20	<20	<20	30
Mo	320	<50	280	300	290	290	270	50	50	70	60	60	310	50

* average of 3 positions.

O solute concentrations that were measured in HR1 to HR5. The results indicate that the total interstitial concentration did not change significantly for these alloys and was 588 ± 43 wppm. In addition, the individual C, N, and O concentrations were also nearly constant. Therefore, this series of alloys met the primary goal of changing only the substitutional Cr or Ti levels while maintaining a constant interstitial concentration. Maintaining an exact stoichiometric ration between Ti or Zr and the total interstitial C, N, and O concentration in the HR6 to HR10 alloys was more difficult in achieving. Table 4 shows the measured levels of Ti to interstitial C, N, and O solutes and the Ti:OCN ratio for HR6-HR10. Most of the alloys show a Ti:OCN ratio close to 1 or slightly larger, i.e. HR6 and HR7. However, HR8 showed a Ti:OCN ratio <1, which was due to a larger pick up of O and N than was observed in the other alloys. This may be attributed to a greater amount of impurities present in the TiC powder that was used to make the HR8 alloy. HR10 had a Ti:OCN ratio of 2.77. This alloy was designed to have a similar Ti level as in HR8 and HR9 and the lower total interstitial O, C, and N level observed in HR6. In the HR11 and HR12 alloys, the measured B level was slightly lower than the desired level of ~100 wppm.

Table 3. Average interstitial C, N, and O concentrations in the HR1-HR5.

Element	Average (wppm)
C	$\bar{x}$ = 118 ± 19
N	$\bar{x}$ = 102 ± 19
O	$\bar{x}$ = 368 ± 13
C, N, O (Total)	$\bar{x}$ = 588 ± 43

Table 4. Stoichiometric ratio between Ti or Zr and interstitial C, N, and O in HR6-HR10.

Heat	Ti:OCN (appm)	Ti/OCN Ratio
HR6	2232:1668	1.34
HR7	2068:1743	1.19
HR8	6025:8628	0.70
HR9	5298:5653	0.94
HR10	5418:1958	2.77

Fabrication of the HR alloys

The fabrication histories of the HR alloys are shown in Table 5. Each cast billet was cut into two sections. One section from each alloy was then rolled from ~0.50 to ~0.25 in thickness (50% reduction) at room temperature. All of the alloys were rolled without any evidence of cracking except for HR2, HR3, HR8, and HR9. This was not too surprising since these alloys were expected to have high strength properties resulting from the high Cr levels in HR2 and HR3 and high C and N levels in HR8 and HR9, respectively. The samples that were successfully cold rolled (CR) to 50% were cut into two sections that were to be used for different thermo-mechanical processing (TMP) conditions, i.e. TMP1 and TMP2 (plus a TMP3 for HR11) designations. For the HR2, HR3, HR8, and HR9 alloys, the remaining second section cut from the billet was cut into two sections and each section was then warm rolled (WR) at 400ºC from ~0.50 to ~0.25 in thickness (50% reduction). Only HR9, which contained the high N level, experienced cracking using this WR condition. Therefore, further work with HR9 was stopped in order to proceed with the fabrication of the remaining 11 HR alloys.

After the first rolling step, all of the samples were annealed in vacuum. The TMP1 and TMP3 samples were exposed to a solutionizing treatment by annealing at 1300ºC for 1h followed by removing the samples from the hot zone in the vacuum furnace. This treatment has been found to dissolve the globular Ti(CON) precipitate in the V-4Cr-4Ti alloy and then precipitate upon cooling a high number density of nano-size Ti(CON) plates in the matrix [1]. However, this heat treatment also produces a large grain size of several hundred microns. The TMP2 samples were annealed using the typical recrystallization treatment at 1000ºC for 2h followed by furnace cooling. This heat treatment has been shown to produce a grain size of typically 20-30μm and a low number density of sub-micron size globular Ti(CON) precipitates.

All of the samples were rolled a second time followed by a final heat treatment. A reduction in thickness of ~0.25 in to ~0.125 in (50%) was used for CR the HR1, HR4-HR7, and HR10-HR12 alloys and ~0.25 in to ~0.165 in (30%) for WR the HR2, HR3, and HR8 alloys. Only HR3 developed some cracks during the

second rolling operation. A final annealing was performed on all the samples, which consisted of annealing the TMP1 and TMP3 samples at 1000ºC for 2h followed by furnace cooling and the TMP2 samples at 1300ºC for 1h followed removing the samples from the hot zone in the furnace.

Table 5. Fabrication history of the HR alloys.

Alloy	TMP	1st Rolling Operation	1st HT	2nd Rolling Operation	Final HT
HR1	1	52% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	52% CR	1000ºC/2h	50% CR	1300ºC/2h
HR2	1	50% WR (at 400ºC)	1300ºC/1h	30% WR (at 400ºC)	1000ºC/2h
	2	50% WR (at 400ºC)	1000ºC/2h	30% WR (at 400ºC)	1300ºC/2h
HR3	1	50% WR (at 400ºC)	1300ºC/1h	30% WR (at 400ºC)	1000ºC/2h
	2	50% WR (at 400ºC)	1000ºC/2h	30% WR (at 400ºC)	1300ºC/2h
HR4	1	50% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	50% CR	1000ºC/2h	50% CR	1300ºC/2h
HR5	1	50% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	50% CR	1000ºC/2h	50% CR	1300ºC/2h
HR6	1	50% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	50% CR	1000ºC/2h	50% CR	1300ºC/2h
HR7	1	50% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	50% CR	1000ºC/2h	50% CR	1300ºC/2h
HR8	1	50% WR (at 400ºC)	1300ºC/1h	30% WR (at 400ºC)	1000ºC/2h
	2	50% WR (at 400ºC)	1300ºC/1h	30% WR (at 400ºC)	1300ºC/2h
HR9	1	Cracking occurred during 400ºC WR			
	2				
HR10	1	50% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	50% CR	1000ºC/2h	50% CR	1300ºC/2h
HR11	1	50% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	50% CR	1000ºC/1h	50% CR	1300ºC/2h
	3	50% CR	1300ºC/2h	50% CR	950ºC/2h
HR12	1	50% CR	1300ºC/1h	50% CR	1000ºC/2h
	2	50% CR	1000ºC/2h	50% CR	1300ºC/2h

Specimen Machining

A number of tensile (SS-J1 and SS-J2), TEM disks, and pre-cracked bend bar (PCBB) specimens were machined from the fabricated plates of the HR alloys and engraved with I.D. codes. These specimens will be used in the HFIR RB-17J experiment and a complete list of them will be published in the next semiannual. However, an unfortunate development that occurred during the fabrication of the alloys was that HR3 and HR8 samples were swapped during the first rolling operation. This was discovered during the resistivity measurements of the tensile specimens [2] and was confirmed by EDS on the XL30 SEM. This only affected the tensile and TEM specimens of these two alloys. Further details will be provided in the future semiannual which will describe the final specimen matrix for RB-17J.

References

[1] D.T. Hoelzer and J. Bentley, to be published in ICFRM-11, (2003).

[2] M. Li, D.T. Hoelzer and S.J. Zinkle, Electrical Resistivity Data of Vanadium Alloys in the RB-17J Experiment. This semiannual.