FABRICATION OF CREEP TUBING FROM THE US AND NIFS HEATS OF V-4Cr-4Ti—A. F. Rowcliffe, D. T. Hoelzer, and M. L. Grossbeck (Oak Ridge National Laboratory)

OBJECTIVE

Utilize commercial-scale processing to fabricate small-diameter, thin-wall tubing from plate stock of V-4Cr-4Ti for both the US program heat no.832665 and the NIFS-HEAT-2 and produce sufficient tubing to meet the programmatic needs for investigating creep behavior in both lithium and vacuum environments and for carrying out irradiation creep measurements.

SUMMARY

Previous attempts at commercial–scale processing to fabricate thin-wall tubing from the V-4Cr-4Ti alloy resulted in extensive surface cracking and a doubling of the oxygen content during multiple intermediate anneals in a vacuum of 1-4 x 10^{-4} torr. An improved procedure was developed to fabricate tubing from both the US program heat and the NIFS-HEAT-2. Although the intermediate vacuum was improved by an order-of-magnitude, the oxidation rate was increased by a factor of ~3, resulting in an unacceptably high oxygen level of ~1700 wppm in the finished tubing. It is shown that under the poorer vacuum conditions, oxygen diffusion to the interior is inhibited by the formation of an oxide film whereas under the improved vacuum conditions, oxygen diffuses rapidly into the tube wall unimpeded by an oxide film .Internal oxidation proceeds by the formation of an oxygen-rich globular Ti(CON) phase. This process is reversed during exposure to liquid lithium at 800-1000ºC. A two–stage heat treatment in liquid lithium was developed which lowered the oxygen content to ~700 wppm and resulted in a uniform grain size distribution with 12-15 grains across the tube wall. This technique was used to produce a set of creep tubes from both heats to be used in the HFIR-RB-17J irradiation experiment.

PROGRESS AND STATUS

Introduction

Determination of the thermal and irradiation creep properties of the heats of V-4Cr-4Ti procured in both the US and in Japan is carried out utilizing a pressurized creep tube specimen measuring 25.4mm long, with a 4.57mm outside diameter and a wall thickness of 0.25mm. Because of the high solubility and rapid mobility of oxygen in this material, maintaining the desired chemical and microstructural characteristics of the alloy during the fabrication of thin sections presents a difficult technological challenge. In 1995, the US fusion program procured some 6 meters of tubing of the US heat No. 832665 with Century Tubes Inc. of San Diego as the primary sub-contractor [1].This effort (Batch A), met with mixed success since a large fraction of the tubing developed cracks at both surfaces which were frequently linked through the wall via a band of severe macroscopic deformation. In addition to the cracking problems the levels of interstitials were also increased significantly during processing; carbon increased from 80 to 300 wppm, oxygen increased from 310 to 700 wppm, (nitrogen remained fairly constant). Relatively crack-free sections of tubing were selected by visual inspection and were used for a series of creep tests in both in vacuum and liquid Li environments [2] and also used to develop irradiation creep data in experiments conducted in the ATR [1], and in the HFIR [3].

Two small heats of V-4Cr-4Ti with low levels of interstitials (~350wppm) were produced in Japan under the direction of the National Institute for Fusion Sciences (NIFS). A limited quantity of creep tubing was prepared from the NIFS-HEAT-2 material using a three-directional rolling process [4]. The problems encountered with surface cracking and interstitial pick-up were somewhat less severe than those experienced with Batch A of the US heat. Based upon the experience with these two tubing campaigns, a new procedure was developed and applied to the production of ~10meters of finished tubing from both the US heat and the NIFS-HEAT-2 materials.

Revisions to Fabrication Procedure

A number of changes were made to the Batch A procedure [5] which may be summarized as follows;

a) The intermediate heat treatments for Batch A were carried out by a commercial vendor (Vendor A), using a tube furnace operating with a vacuum in the range 1-4 x 10^{-4} torr. For Batch B a different vendor was specified (Vendor B) operating a large oven furnace with a vacuum in the range1-10 x 10^{-6} torr.

b) It was conjectured that the surface cracking encountered with the Batch A tubing resulted from a combination of high surface oxygen levels picked up during the annealing cycle and the high stresses imposed by the relatively large reductions in area (>40%) imposed during the draw cycle. Accordingly for Batch B, it was specified that the reduction in area (R/A) per cycle should not exceed 30% for the final 6 stages. Because of this change, it was necessary to utilize 12 drawing and annealing cycles followed by a final 26% R/A to reach final dimensions compared with the 9 drawing and annealing cycles followed by a final 45% R/A to final dimensions used for Batch A.

c) A more rigorous cleaning operation was introduced for the removal of the die lubricant prior to annealing. Following this cleaning, a less aggressive acid cleaning was adopted consisting of a 30 sec. treatment with 20%HNO_3 + 10%HF + 70% H_2O compared with the 5 min treatment with 20% HNO_3 + 20% HF + 60% H_2O used during Batch A processing.

d) Problems were encountered with the bonding of the Ti wrap to the tubing surface during Batch A. For Batch B, gettering was achieved using a tent consisting of multiple layers of clean Ta foil.

These procedures and the modifications are fully documented in Refs [5,6].

Characterization of Batch B Tubing

<u>Interstitial pick-up</u>

Archive samples for chemical analysis and metallography were obtained after each draw cycle and after each anneal. (For Batch A only the initial and final interstitial analyses were obtained).The interstitial analyses for Batch B are summarized for both heats in Table 1.

Table 1. Chemical analyses (wppm) for Batch B tubing

Anneal No.	Wall (mm)	U.S. Heat			NIFS Heat		
		C	O	N	C	O	N
BLANK	4.87	119	331	88	59	130	156
1	4.87	134	346	93	63	152	132
2	4.32						
3	3.50						
4	2.85						
5	2.13	169	403	92	85	219	140
6	1.52	119	511	94			
7	1.22	155	494	101	90	378	148
8	0.99	179	637				
9	0.81						
10	0.64				223	741	210
11	0.48	264	994	133	253	879	206
12	0.38						
13	0.31	457	1745	170	390	1675	211

Because of the order-of –magnitude improvement in the vacuum conditions it was expected that the level of interstitial pick-up would be lower for Batch B than for Batch A. Contrary to these expectations, the pick-up of oxygen accelerated rapidly during the final stages and eventually exceeded the final oxygen content of Batch A tubing by more than a factor of two. During the last two anneals the oxygen content of both heats approximately doubled to reach 1745 wppm for the US heat and 1675 wppm for the NIFS heat. Significant increases also occurred in carbon and nitrogen levels. The oxygen analysis data for each anneal cycle closely tracked the increasing surface area:volume ratio (SAV) of the tubing as shown in Fig. 1 for the US heat. (For tubing, the SAV=2/t, where t is the wall thickness). The NIFS heat showed identical behavior [6].

Microstructure

During the early stages of processing the recrystallized microstructures were uniform across the tube wall. The recrystallized grain size of the NIFS heat was ~50 microns whereas the US heat contained a much higher fraction of small grains (5-10 microns) and an average grain size of ~28 microns. These grain size differences were probably related to differences in the number density and distribution of Ti(CON) particles in the initial plate materials. A more detailed discussion of the microstructural differences between the two heats and details of the type and frequency of surface defects may be found in [5,6].

As the number of anneals increased, a near-surface zone developed which etched differently and was characterized by very fine irregularly-shaped grains. After the tenth anneal, when the oxygen concentrations had increased to 950 and 741wppm in the US and NIFS heats respectively, the surface zones were 40-50 microns thick. After a final draw of ~26% R/A, tubing samples were recrystallized in a laboratory furnace at 1000ºC in a vacuum of $<10^{-6}$ torr. The recrystallized microstructures for both heats were very similar with an inhomogeneous irregular grain structure, due to extensive grain boundary pinning during recrystallization, and with surface zones characterized by very fine grains extending 60-70 microns in from the OD surface and 30-40 microns in from the ID surface. In spite of the high oxygen concentrations, there was no generalized surface cracking.

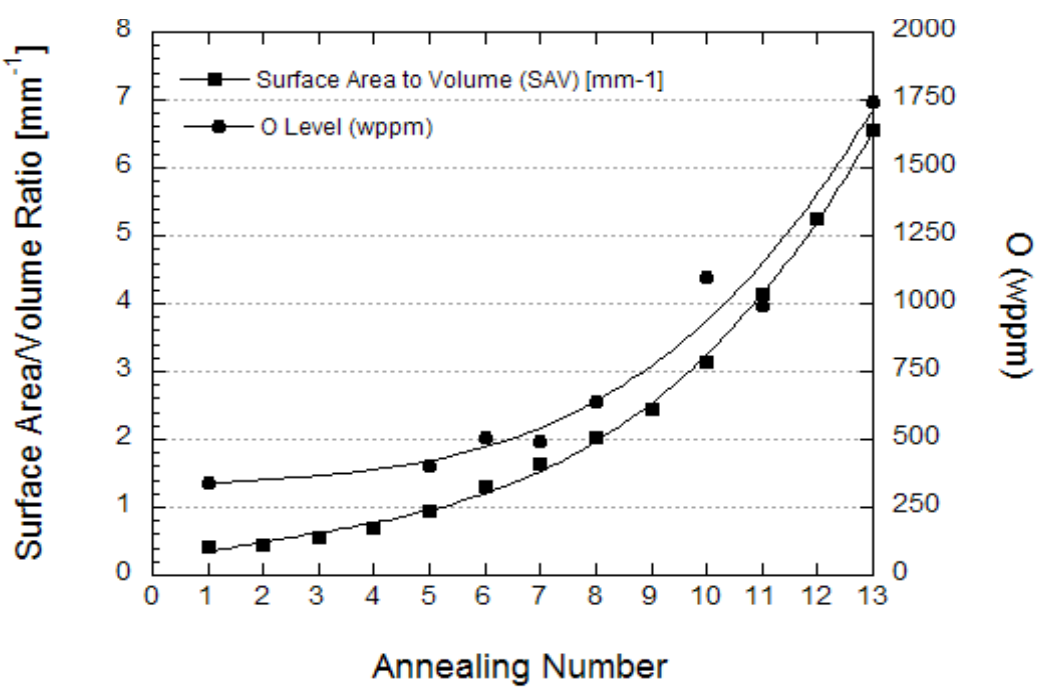

Fig. 1. Oxygen concentration and SAV ratio versus annealing cycle for Batch B (US Heat).

The nature of the surface oxidation zones was examined further using a scanning-Auger system. The results indicated that a process of internal oxidation was occurring with the formation of Ti(CON) particles with sizes in the range 0.1-0.5 microns, with the number density of particles increasing towards the surfaces. Grain growth in the surface zone was severely restricted due to grain boundary pinning by the particles (Fig. 2). Auger analyses showed that the preponderance of oxygen was associated with the particles and that there were no significant differences between the oxygen concentrations in matrix regions located near the center of the tube wall and the matrix regions near the surfaces.

(a) (b)

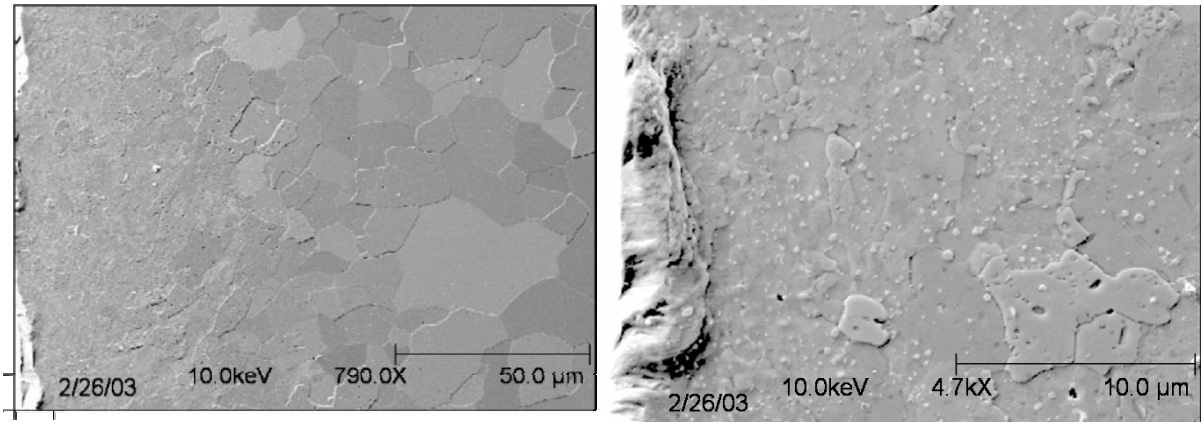

Fig. 2. SEM micrographs of the US heat of tubing following the tenth anneal showing (a) the changes in grain size from surface to the interior of the tube wall and (b) the increase in number density of TiCON particles near the surface region

Oxygen Removal

The high oxygen content and inhomogeneous microstructure of the finished tubing made it unacceptable for the fabrication of specimens for irradiation creep experiments and it was decided to lower the oxygen content by exposing the creep specimens prior to pressurization to a liquid Li environment at 800ºC-1000ºC. Based upon a series of trial exposures [6], a double treatment was defined in which the cold-worked tubing was exposed initially to Li at 800ºC for 168 hrs. During this treatment, dissolution of the surface zone Ti(CON) particles occurred as oxygen transferred to the Li and the overall oxygen content was reduced to ~1100 wppm. At this temperature, which is below the recrystallization temperature, recovery was impeded by the relatively high concentration of oxygen. The temperature was then increased to 1000ºC for a further 1 hour to further reduce the oxygen concentration. Sufficient stored energy was retained following the 800ºC treatment to effect full recrystallization during the 1000ºC treatment. Because of the reduction in the concentration of surface zone Ti(CON) particles which occurred at 800ºC, the final grain size distribution was uniform with approximately 12-15 grains across the tube wall (Fig 3). The double treatment was effective in reducing the oxygen concentrations to acceptable levels of ~700wppm for both heats. Fig. 4 shows the interstitial concentrations measured in the creep specimens of the U.S. Heat following the various conditions of exposure in Li.

Fabrication of Pressurized Creep Tubes for HFIR-RB-17J

<u>Test matrix</u>

The HFIR-RB-17J test matrix for the pressurized creep tube (PCT) specimens is shown in Table 2. It consists of a total of 28 PCT specimens of V-4Cr-4Ti; 14 specimens were fabricated from the U.S. Heat 832665 and the Japanese NIFS-1 Heat. Two subcapsules containing 7 PCT specimens from both heats will be irradiated at 450ºC and 600ºC.

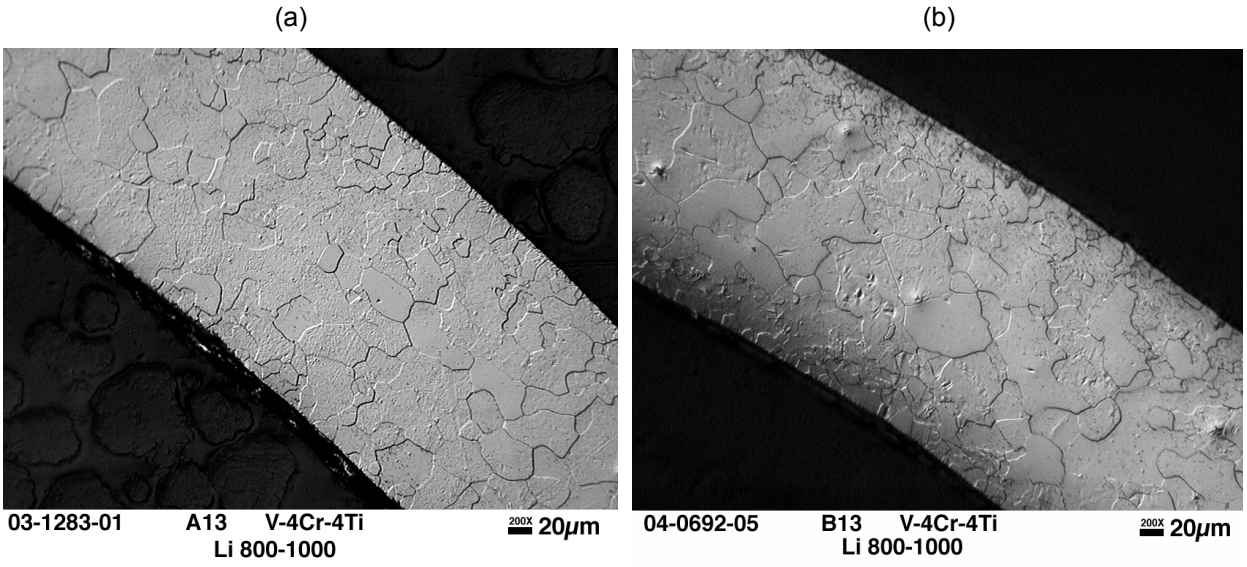

Fig. 3. Light micrographs showing the microstructure of the creep tube specimens of the: (a) U.S. Heat and (b) NIFS Heat after the double exposure to Li at 800ºC for 168 hrs followed by 1 hr at 1000ºC.

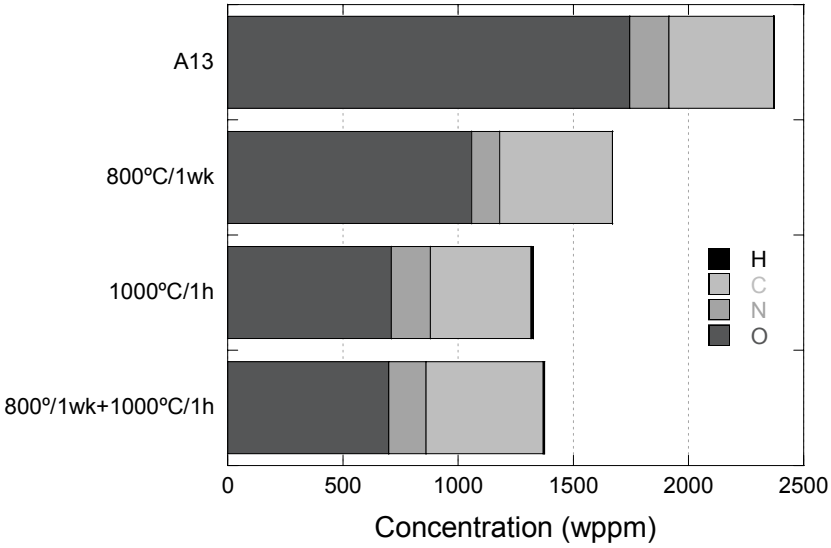

Fig. 4. A summary of the interstitial concentrations measured in the Batch B tube (US Heat) following various conditions of exposure to molten Li.

Li treatments

Twenty-three creep tube specimens were machined from the Batch B drawn tubing of V-4Cr-4Ti from the U.S. Heat 832665 and the Japanese NIFS-1 Heat. These specimens were 25.4 mm in length and were exposed to molten Li for lowering the oxygen concentration. The specimens were placed in liquid Li in a TZM alloy retort, located inside a glove box with high purity Ar atmosphere. The moisture, oxygen, and nitrogen levels are below 1 ppm in the glove box using a continuously operating molecular sieve/copper purification system and Ti-sponge column that is heated to 850ºC. The creep tubes were placed in the retort at a temperature of ~200ºC and then sealed using a Nb-1Zr gasket between mating knife-edge

Table 2. Test matrix of PCT specimens in HFIR-RB-17J irradiation experiment

Material	Temperature	
	450ºC	600ºC
U.S. Heat	7	7
NIFS-1 Heat	7	7

flanges. The temperature of the retort was then raised to 800ºC and the creep tubes were held for 168 hrs. Following this treatment, the temperature was raised to 1000ºC and the tubes were held for 1 hour, and then subsequently removed from the Li.

A cleaning procedure was used to remove the residual Li that solidified on the surface of the creep tubes. The first step consisted of removing the tubes from the glove box and soaking them in a beaker containing liquid anhydrous ammonia until most of the Li was removed. The tubes were then soaked in ethanol, followed by water. This procedure minimized the contamination of the tubes by hydrogen, which was confirmed by chemical analysis (Fig. 4).

Specimen Assembly and Dimensions

The creep tube specimens were individually fitted to end caps that were machined from the U.S. Heat of V-4Cr-4Ti and engraved with specimen identification codes. The wall thickness of each tube was measured in three azimuthal locations at approximately 6 mm from both ends using a tube wall micrometer. Table 3 shows the measured average wall thickness and standard deviation for the creep tubes. The end caps were electron-beam welded to the creep tubes, followed by annealing at 1000ºC for 1 hr in vacuum. The creep tube specimens were then measured using a laser profilometer. A total of 500 measurements were made in a helical pattern near the central 12.7 mm of the tubes to a precision of ±250nm. The average tube diameter was calculated from the central 300 measurements. Two measurements were recorded for each specimen.

Fill Pressures

The creep tube specimens were pressurized with He to several different pressures for the HFIR-RB-17J experiment. The specimens were placed in a pressure chamber, which was then pressurized at the desired pressure of He. A 0.20 mm diameter hole was machined into one endcap welded on the tube that allowed the internal pressure of the creep tube to equilibrate with the external pressure in the chamber. A 0.127 mm diameter wire of vanadium was inserted in the end cap hole and sealed with a laser welder. The pressurized creep tubes were leak tested using a helium leak detector and then measured using the laser profilometry, making three measurements on each tube. Table 4 shows the fill pressures of specimens that were included in HFIR-RB-17J experiment.

Discussion of Oxidation Behavior During Processing

The increase in oxygen for each annealing stage for Batch B tubing may be estimated from Fig 1 and plotted against the SAV ratio of the tubing at each stage, (Fig 5). For Batch A tubing only the initial and final oxygen analyses are known. Assuming that the oxygen content followed the same curve as the increasing SAV ratio as it did for Batch B, then we can estimate the incremental change in oxygen for each anneal and also plot these data in Fig 5. A comparison of the slopes of the two lines indicates that the oxygen pick-up rate was approximately three times more rapid for Batch B when the measured vacuum in the furnace chamber ranged from10^{-5} to 10^{-6} torr, than it was for Batch A (1 - 4 x 10^{-4} torr.)

A number of possible differences between the two batches were eliminated as being significant factors in this surprising result. The surface condition of the tubing was similar for both batches since the tubes

Table 3. Wall thickness measurements of un-pressurized creep tube specimens

U.S. Heat			Japanese NIFS-1 Heat		
Specimen I.D.	Average (mm)	Standard Deviation	Specimen I.D.	Average (mm)	Standard Deviation
UB00	0.259	0.005	UN00	0.247	0.010
UB01	0.241	0.002	UN01	0.256	0.008
UB02	0.253	0.003	UN02	0.246	0.004
UB03	0.224	0.006	UN03	0.246	0.004
UB04	0.258	0.005	UN04	0.247	0.005
UB05	0.251	0.001	UN05	0.247	0.002
UB06	0.255	0.003	UN06	0.250	0.003
UB07	0.259	0.004	UN07	0.250	0.001
UB08	0.251	0.004	UN08	0.249	0.003
UB09	0.257	0.012	UN09	0.248	0.003
UB10	0.247	0.004	UN10	0.247	0.003
UB11	0.254	0.007	UN11	0.244	0.004
UB12	0.252	0.007	UN12	0.248	0.007
UB13	0.249	0.004	UN13	0.246	0.003
UB14	0.254	0.004	UN14	0.246	0.004
UB15	0.252	0.003	UN15	0.252	0.002
UB16	0.258	0.004	UN16	0.246	0.005
UB17	0.262	0.002	UN17	0.247	0.003
UB18	0.252	0.004	UN18	0.239	0.003
UB19	0.257	0.003	UN19	0.243	0.003
UB20	0.263	0.008	UN20	0.241	0.003
UB21	0.257	0.004	UN21	0.243	0.001
UB22	0.258	0.003	UN22	0.250	0.005

were drawn by the same vendor. Batch A utilized a Ti getter-wrap whereas Ta was used for Batch B. However trial anneals at Vendor B with US heat tubing using Ta or Ti produced essentially the same level of oxygen pick-up. Differences in vacuum measurement techniques and furnace geometry between the two vendors were also discounted.

Since archive material from Batch A was not available, a section of the US heat tubing with a wall thickness 0.5mm was annealed at 1000ºC for 30min at Vendor A using the same furnace and vacuum conditions utilized during the earlier processing of Batch A (1-4 x 10^{-4} torr.) An identical sample, using the same wrap of Ta plus Ti foil was similarly annealed at Vendor B (1-2 x 10^{-5} torr.) The anneal carried out at the lower vacuum at Vendor A resulted in the formation of a visible oxide film whereas a visible oxide film did not form under the higher vacuum conditions at Vendor B It was found that this oxide film could be completely removed by subjecting the tubing to the 5 min acid cleaning procedure used for Batch A.

A possible explanation of the observed differences in the rate of increase in the bulk oxygen concentration between the two batches may be found in the work of Pint and DiStefano [7] who studied the oxidation kinetics of the US heat of V-4Cr-4Ti at 600-700ºC under partial pressures of oxygen in the range 10^{-3}-10^{-6} Pa (10^{-5}-10^{-8} torr). It was found that at 700ºC for example, oxidation followed linear kinetics at very low oxygen partial pressures (10^{-4}-10^{-6} Pa) without formation of a visible oxide film

Table 4. Helium pressurization data of creep tube specimens in the HFIR-RB-17J experiment

Tube		Irradiation	Hoop Stress	Fill Pressure
U.S. Heat	NIFS Heat	Temperature (ºC)	(MPa)	(Psig)
UB13	UN20	450	0	0
UB17	UN00	450	60	453
UB02	UN03	450	100	752
UB05	UN09	450	120	902
UB09	UN16	450	120	902
UB16	UN14	450	180	1350
UB04	UN07	450	200	1499
UB00	UN19	600	0	0
UB15	UN08	600	30	195
UB08	UN13	600	60	381
UB12	UN01	600	120	754
UB03	UN12	600	120	754
UB06	UN02	600	180	1126
UB10	UN11	600	200	1251

whereas at higher pressures, deviations from linearity were observed. The linear-parabolic behavior at 10^{-3} Pa was attributed to the formation of a surface oxide which inhibited oxygen diffusion into the substrate and under these conditions specimen surfaces became discolored by the formation of a visible oxide film. At 700ºC, the transition to an oxide film- limited oxidation regime occurred between 10^{-4} and10^{-3} Pa partial pressure of oxygen. Using tensile ductility measurements, it was shown that the surface oxide film formed a very effective barrier to the diffusion of oxygen into the interior.

Based on these observations, it is proposed that the origin of the unexpected increase in the overall oxygen pick-up rate which occurred under the improved vacuum conditions utilized for Batch B is related to a change in the oxidation mode. In the lower vacuum regime (Batch A), the formation of an oxide film inhibited internal oxidation and during subsequent prolonged acid cleaning, the oxide film, and hence a major fraction of the absorbed oxygen was removed prior to the next anneal. In contrast, the Batch B tubing was annealed in a regime where linear kinetics prevailed and the rate of internal oxidation was not inhibited by the formation of an oxide film. Further scanning–Auger analysis is in progress to quantify this hypothesis.

During commercial-scale processing of thick-sections of vanadium alloys, oxygen pick-up may be controlled satisfactorily by annealing in a sub-linear oxidation regime and removing the oxide film by acid cleaning at each stage. However for thin sections (< 0.5-0.8mm) this approach increases the risks of developing surface cracking. It is preferable to avoid the formation of surface oxide films and operate in the linear oxidation regime during intermediate anneals. However, since un-impeded oxygen diffusion into the bulk is rapid the furnace vacuum needs to be maintained in the 10^{-6}-10^{-7} torr regime.

Conclusions

1. Changes to the procedure for commercial-scale processing of thin-wall tubing of V-4Cr-4Ti were effective in reducing the incidence of surface cracking; however the rate of internal oxidation of the tubing increased by a factor of ~3 in spite of the improvement to the vacuum conditions by an order-of-magnitude.

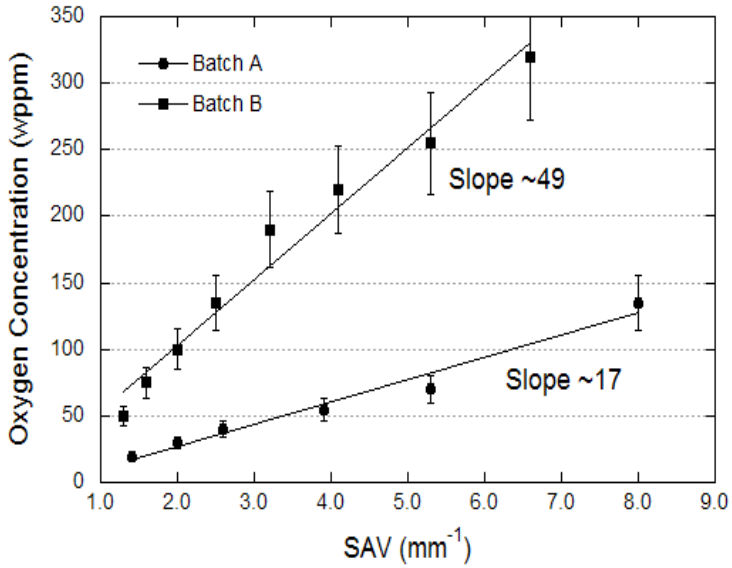

Fig. 5. Incremental oxygen increase for Batch A and Batch B tubing

2. Under the improved intermediate annealing vacuum conditions, the evidence suggests that oxygen diffusion was un-impeded by a surface oxide film and rapid internal oxidation occurred. Under the previously used lower vacuum conditions, oxygen diffusion into the bulk was limited by the formation of a visible oxide film; this oxide film was removed after each anneal by aggressive acid cleaning and as a result, the effective rate of oxygen pick-up was lower by a factor of ~3.

3 The internal oxidation process involved the formation of an oxygen-rich phase of the globular type of Ti(CON) phase; this process was reversed by exposure to liquid lithium at 800ºC and 1000ºC.

4. A two stage heat treatment in liquid lithium was developed which lowered the oxygen content in the final cold drawn tubing for both heats from ~1700wppm to ~700wppm and simultaneously produced a uniform recrystallized microstructure with 12-15 grains across the tube wall. This procedure was used to prepare the specimens for the irradiation creep test matrix in the HFIR-RB-17J experiment

Acknowledgements

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References

[1] H. Tsai, M. C. Billone, R. V. Strain, and D. L. Smith, Fusion Materials semi-Annual Report DOE/ER-0310/23 (December 1997) 149.

[2] M. L. Grossbeck, R. J. Kurtz, L. T. Gibson, and M. J. Gardner, Fusion Semi-Annual Progress Report DOE/ER-0310/32 (June 2002) 26.

[3] H. Tsai, M. C. Billone, T. S. Bray, and D. L. Smith, Fusion Materials Semi-Annual Progress Report DOE/ER-0310/27 (December 1999) 65.

[4] T. Nagasaka, T. Muroga, and T. Iikbo, Development of Tubing Technique for High-Purity Low Activation Vanadium Alloys, ANS Winter Meeting, Washington DC (November 2002).

[5] A. F. Rowcliffe, W. R. Johnson, and D. T. Hoelzer, Fusion Materials Semi-Annual Progress Report DOE/ER-0310/ 33 (December 2002) 7-21.

[6] A. F. Rowcliffe, D. T. Hoelzer, W. R.Johnson, and C. Young, Fusion Materials Semi-Annual Progress Report DOE-0310/34 (June 2003) 6-21.

[7] B. A. Pint and J. R. Distefano, Oxygen Embrittlement of Vanadium Alloys With and Without Surface Oxide Formation, J. Nucl. Mater 307-311 (2002) 560-565.