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Oxidation behavior of a V–4Cr–4Ti alloy during the commercial processing of thin-wall tubing

A.F. Rowcliffe [a,*], D.T. Hoelzer [a], R.J. Kurtz [b], C.M. Young [c]

[a] *Oak Ridge National Laboratory, Metals and Ceramics Division, MS 6136, Oak Ridge, TN 37830, USA*
[b] *Pacific Northwest National Laboratory, Richland, WA 9935, USA*
[c] *Century Tubes Inc., 7910 Dunbrook Road, San Diego, CA 9212, USA*

Abstract

Because of the high solubility and mobility of oxygen in vanadium, composition control during the fabrication of thin (0.25 mm) wall tubing from vanadium alloys by cold drawing and annealing, presents a technological challenge. During intermediate annealing at 1000 °C in the 10^{-4} Torr vacuum regime, oxygen penetration into the tube wall is controlled by the development of a semi-protective surface oxide (linear-parabolic oxidation conditions); oxygen-hardened surface layers lead to a high incidence of surface cracking during the final stages of cold drawing. In the 10^{-5} Torr regime, under linear kinetic oxidation conditions, rapid oxygen penetration results in unacceptably high levels of oxygen pick-up (~1500 wppm). In the 10^{-7} Torr vacuum regime, molecular impingement rates are reduced to the point where overall oxygen pick-up is reduced to <100 wppm. Improved cleaning/gettering procedures also restrict carbon and nitrogen pick-up to very low levels.
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1. Introduction

The determination of the thermal and irradiation creep properties of V–4Cr–4Ti using the pressurized tube technique requires a supply of 4.57 mm outside diameter tubing with a wall thickness of 0.250 mm. 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 wall tubing presents a difficult technological challenge. In 1995, the US fusion program procured some 6 m of tubing, using the US heat No. 832665, utilizing commercial vendors [1]. This effort, (Batch A), met with mixed success since a large fraction of the tubing developed cracks at both surfaces and during processing, the carbon concentration increased from 80 to 300 wppm, oxygen increased from 310 to 700 wppm, while nitrogen remained fairly constant. During the intermediate annealing cycles at 1000 °C for this batch the furnace vacuum was maintained in the 10^{-4} Torr range. In an effort to control oxygen pick-up during the intermediate annealing heat treatments, further processing of thin-wall tubing has been undertaken utilizing vacuum conditions in the 10^{-5} Torr regime and in the 10^{-7} Torr regime.

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[*] Corresponding author. Tel.: +1 410 708 9426; fax: +1 410 745 4304.
E-mail address: afr@goeaston.net (A.F. Rowcliffe).

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2. Processing conditions for batches A and B

The intermediate heat treatments of 1 h at 1000 °C for Batch A were carried out in a ∼170 l tube furnace operating with a vacuum in the 10^{-4} Torr range. During the nine drawing and annealing cycles, the average oxygen content increased from an initial ∼300 wppm up to ∼700 wppm [1]. Cracks developed at both surfaces which were frequently linked across the tube wall via a band of severe macroscopic deformation; this cracking was probably related to the high surface oxygen levels picked up during the annealing cycle combined with the high stresses imposed by the relatively large reductions in area (>40%) imposed during the final drawing stages [2]. 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 [3] and also used to develop irradiation creep data in experiments conducted in the ATR [1], and in the HFIR [4].

In a subsequent fabrication effort, two small heats of V–4Cr–4Ti with low levels of interstitials (∼350 wppm) were produced in Japan under the direction of the National Institute for Fusion Sciences (NIFS). A limited quantity of creep tubing was prepared in Japan from the NIFS-HEAT-2 material using a three-directional rolling process [5] and the problems encountered with surface cracking and interstitial pick-up were less severe than those experienced with Batch A of the US heat.

In an attempt to reduce the rate of oxygen pick-up and to eliminate the surface cracking which occurred in Batch A, several changes were made in the drawing and annealing procedure; these changes in part benefited from the experience gained with the NIFS heat [5]. The cleaning procedure to remove the die lubricant was revised and problems associated with the bonding of the Ti wrap to the tubing surface during Batch A annealing were eliminated by using a tent consisting of multiple layers of clean Ta foil. Using a large volume (1760 l) oven furnace, (Vendor B), intermediate annealing was carried out in a vacuum in the 10^{-5} Torr regime. These procedural changes are fully documented elsewhere [2,6].

3. Characterization of batch B tubing

3.1. Interstitial pick-up

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.

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 (Table 1). 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 $\text{SAV} = 2/t$, where t is the wall thickness). The NIFS heat showed similar behavior.

3.2. Microstructure

Details of the initial microstructural differences between the two heats may be found in [5,6].

As the number of anneals increased, near-surface zones developed which were characterized by very fine irregularly-shaped grains. After the tenth anneal, when the oxygen concentrations had increased to 950 and 741 wppm in the US and NIFS heats, respectively, the surface zones were 40–50 μm thick. After a final draw of ∼26% reduction in area, tubing samples were recrystallized in a laboratory furnace

Table 1
Chemical analyses (wppm) for Batch B tubing

Anneal no.	Wall (mm)	US 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

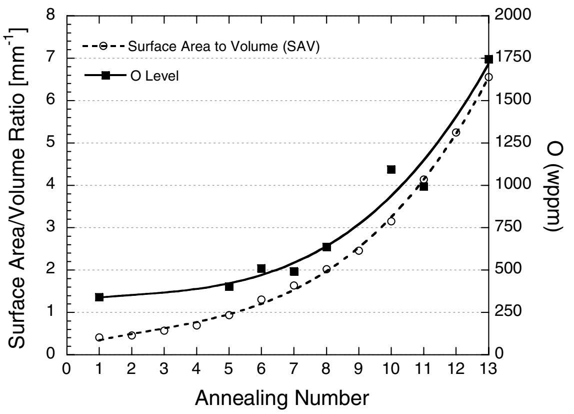

Fig. 1. Oxygen concentration and surface area:volume ratio as a function of annealing cycle for Batch B tubing from US heat no. 832665.

at 1000 °C 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 μm in from the OD surface and 30–40 μm in from the ID surface. However, in spite of the high oxygen concentrations, the incidence of surface cracking was very low.

The nature of the surface oxidation zones was examined further using a scanning-Auger system. The results indicated that internal oxidation had occurred via the formation of globular Ti(CON) particles in the size range 0.1–0.5 μm, 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. Auger analyses showed that the major fraction of the 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.

The high oxygen content and inhomogeneous microstructure of the finished tubing made it unacceptable for the fabrication of specimens for irradiation creep experiments. A double heat treatment at 800 °C and 1000 °C in contact with liquid Li was developed in which dissolution of the surface zone Ti(CON) particles occurred as oxygen transferred to the Li. The overall oxygen content was reduced to ~700 wppm and a uniform grain size developed with approximately 12–15 grains across the tube wall. A sufficient number of creep tube specimens were processed in this fashion to meet the requirements of the collaborative irradiation experiment HFIR-RB-17J [6]. Further work to elucidate the mechanisms of particle dissolution and oxygen removal is in progress.

4. Oxidation behavior of batches A and B

The increase in oxygen for each annealing stage for Batch B tubing, obtained from Fig. 1, is plotted against the SAV ratio of the tubing at each stage in Fig. 2. The observed linear dependence of gas absorption on specimen SAV ratio is in agreement with the following relationship described by Inouye [7] for conditions where absorption of the oxygen is not limited by the formation of a protective oxide film;

$$\Delta C_{\mathrm{m}} = Q_{\mathrm{a}} \cdot \Delta t \cdot A/\rho V,$$

where ΔC_{m} is the change in concentration, (g of gas/g of metal); Q_{a} is the absorption rate (g cm^{-2} s$^{-1)}$; Δt is the exposure time (s); A is the surface area (cm^2); ρ is the metal density (g cm^{-3}); V is the specimen volume (cm^{-3}).

Using the analysed oxygen pick-up and the tubing SAV ratio during the final anneal, the oxidation rate under the Batch B vacuum conditions was estimated using this relationship to be $\sim 3 \times 10^{-2}$ mg/cm^2 h.

A number of procedural differences were examined as possible factors which could explain the higher rate of interstitial pick-up in Batch B compared to Batch A. The surface condition of the tubing was similar for both batches since the tubes were drawn by the same vendor. Batch A utilized a Ti

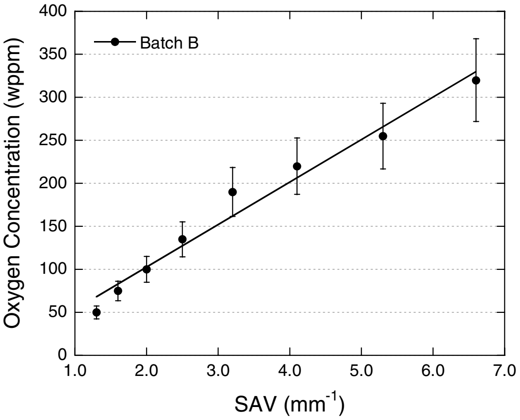

Fig. 2. Incremental oxygen increase as a function of tubing surface area:volume ratio during the processing of Batch B (10^{-5} Torr) from the US heat no. 832665.

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. Since archive material from Batch A was not available, a section of the US heat tubing with a wall thickness 0.5 mm was annealed at 1000 °C for 30 min at Vendor A using the same furnace and vacuum conditions utilized during the earlier processing of Batch A. This treatment 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 reasonable 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 [8] who studied the oxidation kinetics of the US heat of V–4Cr–4Ti at 600–700 °C under partial pressures of oxygen in the range 10^{-5}–10^{-8} Torr. It was found that at 700 °C for example, oxidation followed linear kinetics at very low oxygen partial pressures (10^{-6}–10^{-8} Torr) without formation of a visible oxide film whereas at higher pressures, deviations from linearity were observed. The linear-parabolic behavior at 10^{-5} Torr 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.

These observations suggest 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 were probably related to a change in the oxidation mode. In the 10^{-4} Torr 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 the 10^{-5} Torr vacuum regime where linear kinetics prevailed and the rate of internal oxidation was not inhibited by the formation of an oxide film.

5. Oxidation behavior of Batch D tubing

The above results indicated that at least an order-of-magnitude improvement in vacuum conditions would be required to maintain satisfactorily low oxidation rates during intermediate annealing at 1000 °C. Following an experimental Batch C, a further batch of tubing from the NIFS-2-HEAT (Batch D) was processed utilizing a 10 cm dia. tube furnace capable of maintaining a vacuum of $\sim 3 \times 10^{-7}$ Torr throughout the annealing cycle. Residual gas analyzer measurements indicated oxygen partial pressures of $< 2 \times 10^{-11}$ Torr. The annealing cycle was reduced to 30 min at 1000 °C which is sufficient to ensure full recrystallization following 25–30% cold work. An additional pre-annealing cleaning sequence was introduced using successive treatments with acetone, ultrasonic cleaning in ‘Microclean’ and de-ionized water and rinsing in methanol. Each tube was then individually wrapped in clean Ta foil and the package tented in clean Ti foil, the ends of the tent being pinched together to limit line-of-sight to the vacuum chamber.

The starting material for this batch was a tube, measuring 100 cm long × 0.81 cm OD × 0.10 cm wall thickness, which had been set aside following the eighth annealing cycle in the 10^{-5} Torr range during the production of Batch B. At this stage the oxygen concentration was 470 wppm. An initial surface sanding treatment to remove 50 μm from the wall resulted in a reduction of the average oxygen concentration to 380 wppm.

Following a drawing sequence similar to that used for Batch B, this tube was reduced to a final wall thickness of 0.280 mm in five stages with intermediate anneals as described above; the chemical analyses results are shown in Table 2. Under these vacuum annealing conditions the total oxygen pick-up for the five anneals was limited to ~70 wppm. Within the uncertainty of the chemical analyses (±10%), there were no significant increases in the concentration of nitrogen or carbon. In Fig. 3, the oxygen analysis data for Batch D are compared with the earlier data for the NIFS-2-HEAT, during

Table 2
Chemical analyses (wppm) for Batch D tubing from the NIFS-2-HEAT

Anneal no.	Wall (mm)	Concentration		
		C	O	N
Batch B (Ann.8)	0.97	90	360	148
D1	0.81			
D2	0.66	87	325	175
D3	0.51	74	325	137
D4	0.37			
D5	0.28	128	432	151

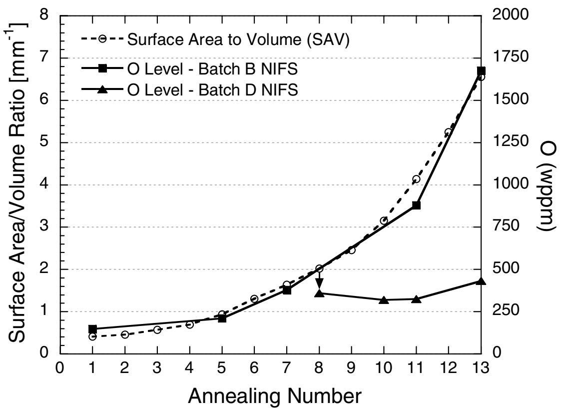

Fig. 3. Oxygen concentration and surface area: volume ratio as a function of annealing cycle for Batch B (10^{-5} Torr.) tubing from the NIFS-2-HEAT; following anneal no. 8, tubing from Batch B was surface-sanded to reduce surface oxygen concentration and used for Batch D processing (10^{-7} Torr).

the Batch B processing. The estimated oxidation rate under the Batch D vacuum annealing conditions was approximately 4×10^{-3} mg/cm^2 h which is a factor of ~7 lower than the estimated oxidation rate for the Batch B annealing conditions.

6. Conclusions

1. During intermediate annealing at 1000 °C in the 10^{-4} Torr vacuum regime, oxygen pick-up during fabrication of 0.250 mm wall tubing was limited by the formation of a semi-protective visible oxide film which was removed after each draw cycle by acid cleaning. Under these conditions, (Batch A), oxygen and carbon pick-up were ~400 wppm and ~220 wppm, respectively; however the frequency of surface cracking was unacceptably high.
2. With vacuum annealing conditions in the 10^{-5} Torr regime (Batch B tubing), rapid internal oxidation occurred via the formation of a globular-type of Ti(CON) phase. Under these conditions of linear oxidation kinetics, oxygen diffusion to the interior was un-impeded by the formation of a protective oxide film. Oxygen concentrations of tubing from both the US and the NIFS-2-HEAT increased by ~1500 wppm during processing, corresponding to an oxidation rate of ~3×10^{-2} mg/cm^2 h. However, the incidence of surface cracking was reduced.
3. Improving the vacuum annealing conditions into the 10^{-7} Torr regime resulted in a lowering of the oxidation rate at 1000 °C to ~4×10^{-3} mg/cm^2 h and the overall pick-up of oxygen was limited to ~70 wppm during the final five drawing/annealing cycles.
4. A combination of high vacuum conditions, rigorous cleaning and improved gettering techniques has been developed which limits oxygen pick-up to <100 wppm during the fabrication of thin-wall tubing from V–4Cr–4Ti; pick-up of carbon and nitrogen are also minimal. These procedures will probably be equally effective in controlling interstitial pick-up during the fabrication of thin-section products from the other GroupVa refractory metals and alloys.

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