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Creep of V–4Cr–4Ti in a lithium environment

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Abstract

Biaxial creep specimens of V–4Cr–4Ti were exposed to liquid lithium at 665 and 765 °C to complement similar tests in a vacuum environment. Although the Li tests are at an early stage, results are consistent with those of the vacuum tests. At 765 °C, exposures of nearly 2000 h have been reached, and at 665 °C, 1100 h have been attained. There is only a brief period of steady-state creep, a power law stress dependence is observed, and temperature dependence is described by an activation energy slightly lower than that of self-diffusion, 2.8 eV. At this stage, even the vacuum tests had little increase in oxygen so that the similarity is not unexpected. No creep failures have been observed. This is expected based upon comparison with vacuum tests on similar specimens and with uniaxial tests with specimens of the same heat of V–4Cr–4Ti.

1. Introduction

A study of creep in V–4Cr–4Ti was initiated in order to determine thermal creep behavior in an environment that does not increase the interstitial oxygen concentration during the creep test. This investigation complements a similar study of the same alloy, and same heat, using an ultra-high vacuum environment [1].

It is of primary importance to control interstitial impurities since they have a profound hardening and embrittling effect on vanadium and its alloys [2]. Since oxygen is absorbed readily under all attainable pressures and diffuses more rapidly than nitrogen, it is expected to increase during high temperature testing, and this has been observed [1,3]. In creep testing, Schirra observed that oxygen had a marked effect on creep behavior at low Ti levels but only a mild effect in vanadium alloys with 20% Ti [4]. However, carbon and nitrogen had little effect on creep in an investigation by Bohm and Schirra, at least for levels below about 600 ppm [5].

The present experiments use an environment of liquid Li at temperatures in the range of 665–800 °C. Under these conditions, oxygen is removed from vanadium and ultimately forms Li_2O. Nitrogen and carbon can be transferred to the vanadium from the Li [6], but in light of the results of Bohm and Shirra, this is not likely to be a problem. However, the expectations about the effect of oxygen have been confirmed in pure vanadium by Shirra who observed a decrease in creep rate of five orders of magnitude at 650 °C by increasing oxygen concentration from 220 to 750 ppm [4]. A smaller but still large extension of creep rupture life due to increased oxygen was observed in V–Ti alloys [4]. A Li environment not only serves to prevent oxygen contamination but is also relevant to fusion devices using vanadium first wall and blanket structures cooled by Li [7,8].

2. Experimental methods

Pressurized tubes were chosen as the specimens since they permit testing a large number of specimens covering a wide range of stresses. All specimens at a given temperature can be tested in a single container and furnace. Specimens were fabricated from drawn tubing of V–4Cr–4Ti from Teledyne Wah Chang Heat 832665 [9,10]. End caps of the same alloy were electron-beam welded in place, after which the tubes received an anneal at 1000 °C/1 h. The tubes initially had a grain size of 10 μm, but following the heat treatment the grain size was expected

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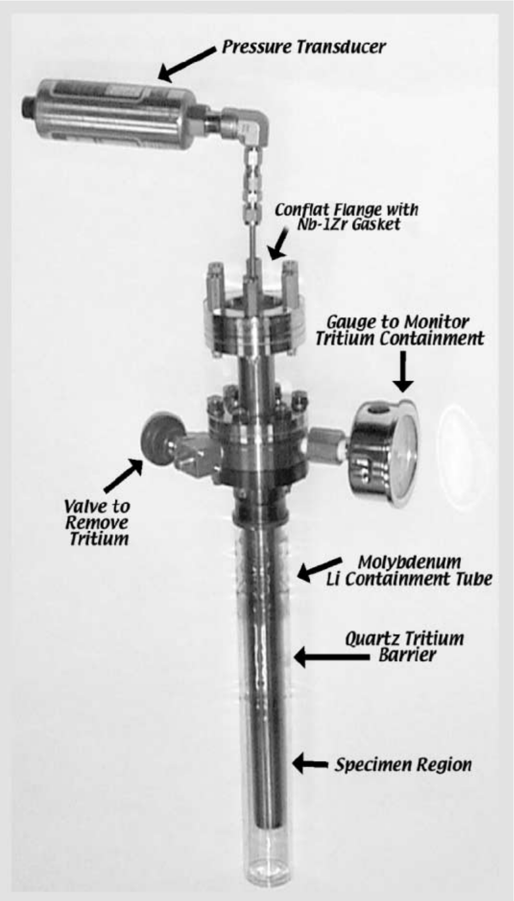

Fig. 1. Refractory metal retort for lithium tests.

to double [1]. The internal pressure was attained by sealing a small hole in one end cap with a laser welder while the specimen was in a pressure chamber at the desired pressure of He. The tubes were 25.4 mm in length by 4.57 mm in diameter and 0.25 mm wall thickness.

The specimens were held at test temperature in a retort of Mo, TZM alloy, and Nb–1Zr in order to contain the high-temperature liquid Li. The retort, shown in Fig. 1, has a 25.4 mm diameter Mo tube with caps and flanges of Mo welded in place. The mating flange on the top uses a knife edge seal of the Conflat [1] design with a mating flange of Nb–1Zr for ease of welding the 4 mm Nb–1Zr tube leading to the pressure transducer. A gasket of Nb–1Zr was used for the flange seal. At a distance of about 120 mm from the top flange, where the temperature is below 100 °C, stainless steel tubing is used to attach to the pressure transducer which has a stainless steel diaphragm. No significant amount of lithium vapor is expected to reach the stainless steel. The retort serves an additional purpose as a prototype containment for a similar test with the addition of tritium to simulate the generation of helium by (n,α) reactions. For this purpose, a quartz tube was added to serve as a barrier to diffusion of tritium. A thermocouple was fastened to the quartz tube in the region of the specimens and the retort placed in a tube furnace. A calibration of the thermocouple was achieved by placing a shielded thermocouple directly into the molten Li through a hole in the cap for a short-term test.

The entire furnace was situated inside a glove box in a high-purity argon atmosphere. The glove box had a continuously operating molecular sieve/copper purification system to maintain moisture and oxygen below 1 ppm and a Ti-sponge column heated to 850 °C to maintain nitrogen below 1 ppm. This atmosphere enabled the specimens to be removed from the Li at a reduced temperature but still molten.

Pressure in the chamber was recorded at 120 s intervals to monitor rupture of the tube specimens. Since the retort was sealed, the increase in pressure from a leaking tube remained, producing a step change in internal pressure.

Following removal of the specimens from the Li and subsequently from the Ar atmosphere, the residual Li was removed with liquid anhydrous ammonia, followed by ethanol, followed by water. This sequence was used to prevent contamination by hydrogen [11]. The tubes were then measured by a non-contacting laser micrometer. A helical pattern of 500 measurements was made in the central 12.7 mm of the tubes to a precision of ±250 nm.

3. Results

At the present time, results are available for 765 °C at 200, 1064, and 1927 h and for 665 °C at 242 and 1105 h. The results are reported in Table 1 where effective uniaxial stress and strain are given [12]. For tubes that have leaked, no data are used since the time of failure is unknown, and negative values are to be considered possible measurement errors due to the very small strains observed.

It is an essential part of this investigation to compare data with the vacuum creep experiment conducted at Pacific Northwest National Laboratory as well as uniaxial experiment conducted at Argonne National Laboratory [13]. As longer test times are achieved, more data will be at strain levels where meaningful comparisons can be made. Fig. 2 shows data from all three investigations at stress levels in the range of 84–90 MPa. The ANL data show large primary creep as opposed to almost no primary creep in pressurized tubes, a phenomenon observed with irradiation creep in pressurized

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[1] Registered trademark of Varian Inc.

Table 1
Creep data in terms of effective stress and strain

Specimen	Effective stress (MPa)	Effective strain (%)		
		200 h	1064 h	1927 h
765 °C				
V5	25	−0.0037	−0.017	−0.016
V8	42	0.017	0.016	0.078
V3	59	0.027	0.039	0.38
V10	59	0.0007	−0.016	0.36
V7	75	0.033	0.13	2.5
V4	84	0.031	0.30	5.9
		242 h	1105 h	
665 °C				
V12	59	0.023	0.034	
V2	75	0.025	0.031	
V11	75	0.0074	0.0022	
V9	83	0.027	0.040	
V6	100	0.022	Leaked	
V1	117	−0.010	0.0044	
V13	133	0.014	Leaked	

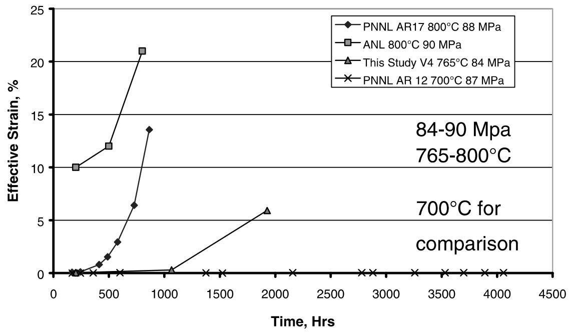

Fig. 2. Creep strain in V–4Cr–4Ti comparing temperature and stress state for 84–90 MPa.

tubes [14]. For the pressurized tube experiment, the creep strains exhibit a consistent trend with increasing temperature over the range of 700–800 °C.

A similar comparison for a stress range of 67–75 MPa shows similar behavior. Results for 665 °C show larger creep strains than observed at 700 °C in the vacuum environment. However, experimental scatter is rather large, especially for the 700 °C data. A more valid comparison awaits longer term tests now in progress. All specimens in the present study show little secondary creep.

The dependence upon stress is illustrated in Fig. 3 for 765 °C, where non-linear behavior is observed. Fitting the curves to a power law equation, $\dot{\varepsilon} = A\sigma^n$, where $\dot{\varepsilon}$ is strain rate, σ is the stress, and A and n are constants, yields values of n, the stress exponent, in the range of 1–5. The temperature dependence may be analyzed using an equation similar to the Dorn equation [15]:

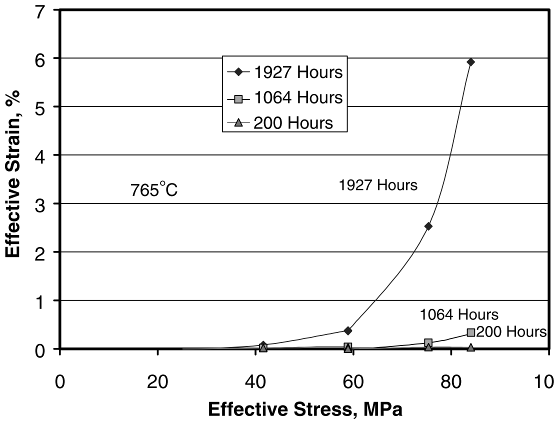

Fig. 3. Creep strain as a function of stress for Li-exposed V–4Cr–4Ti pressurized tubes.

$$\dot{\varepsilon} = \frac{A}{T}\sigma^n \mathrm{e}^{-\Delta H/kT}, \quad (1)$$

where T is the Kelvin temperature, ΔH is the activation energy, k is Boltzmann's constant, A and n are constants, and $\dot{\varepsilon}$ and σ are defined above. Using data for 765 °C and neglecting the weak $1/T$ dependence, an activation energy of 2.8 eV was obtained.

4. Discussion

An important part of this investigation is the comparison of the results with those from similar tests in a vacuum environment. Since oxygen increases slowly in the case of the vacuum environment, the oxygen concentrations in the lithium environment tests are not yet very different from those of the vacuum tests. An increase of 30% in oxygen was observed after 2812 h in a vacuum at 800 °C [1]. In light of the difference in temperature, and the few specimens that have shown significant creep, no conclusions can be drawn at this time from the comparison. However, after longer exposure times, more data will be available to make a valid comparison. More temperatures will also be explored to match the vacuum data more closely.

The leaking tubes indicated in Table 1 resulted from weld failures, not creep failures; however, the observation that most of the deformation is tertiary creep is a concern. The specimens will be destructively examined for uniformity of deformation when the testing is complete. No creep ruptures were observed at either of the two temperatures. To confirm consistency of this with existing data, an analysis was made using the concept of the Larson–Miller parameter,

$$P = T(\log t_r + 20)/1000, \qquad (2)$$

where T is the absolute temperature and t_r is the rupture time in hours [16]. Data from the vacuum tests conducted at PNNL and the uniaxial tests at ANL have been plotted by Kurtz and appear in Fig. 4 [1]. The data from the present study are also plotted in Fig. 4 as if the measurement time were the rupture time. This pseudo-Larson–Miller parameter plot shows that the specimens in the present experiment lie below the trend line of the actual creep rupture data, and that the tubes were not expected to rupture.

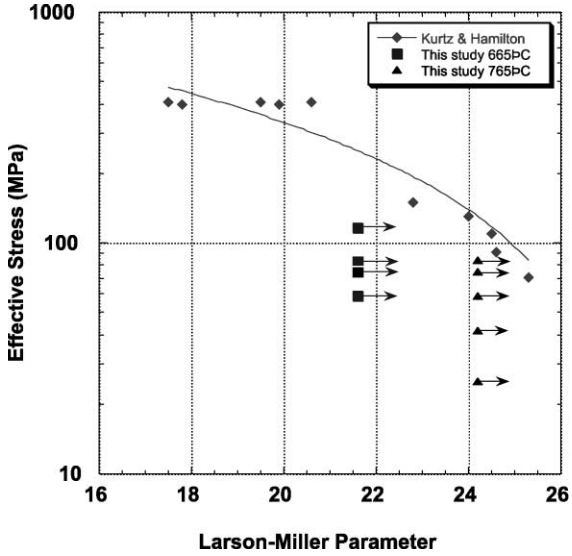

Fig. 4. Pseudo-Larson-Miller parameter plot showing that the Li-exposed samples are not expected to fail.

Table 2
Activation energy for creep and self-diffusion

Stress state	Laboratory	Activation energy (eV)
Biaxial	Present study	2. 8
Biaxial	PNNL	3.1
Uniaxial	ANL	5.7
Uniaxial	Bohm and Schirra	2.3
Self-diffusion [18]		3.2

The range of the stress exponent of 1–5 is expected to be narrowed as more data are obtained, but values greater than one are indicative of diffusion-controlled dislocation climb creep. For solid-solution alloys, a value of 3 is often observed [15].

The activation energy is compared with other studies in Table 2. The observed value of 2.8 eV is in close agreement with the value measured in the vacuum experiment of 3.1 eV. It is also close to the value of 2.3 eV observed by Bohm and Schirra in a V–5%Ti alloy [17].

5. Conclusions

1. An experimental apparatus has been developed for handling liquid lithium for creep testing of pressurized tubes. All metals in contact with Li are refractory metal, including gaskets. It was concluded that a thermocouple well protruding into the liquid lithium is necessary and will be incorporated. Operating experience was also obtained for using a retort with a tritium barrier in anticipation of the next series of experiments.
2. The creep rates observed are consistent with those obtained from specimens in a vacuum environment, with the exception of 665 °C where creep rates are higher for the lithium environment. Longer exposures will have to be achieved before confidence can be gained in this observation.
3. At 765 °C, no creep failures were observed after an exposure of 1927 h at effective stress levels up to 87 MPa.
4. Tertiary creep initiates early, with a short region of steady-state creep.
5. The observed activation energy of 2.8 eV is consistent with other measurements and with the activation energy for self-diffusion within experimental error.

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