INVESTIGATION OF THE EFFECT OF A LOW-OXYGEN LITHIUM ENVIRONMENT ON THE CREEP OF THE V-4Cr-4Ti ALLOY–M. L. Grossbeck (Oak Ridge National Laboratory), R. J. Kurtz (Pacific Northwest National Laboratory), L. T. Gibson, and M. J. Gardner (Oak Ridge National Laboratory)

Objective

This investigation is being conducted to evaluate thermal creep behavior in the Fusion Energy Sciences Program reference vanadium alloy, V-4Cr-4Ti, under conditions where the oxygen concentration is not increased during the life of the test. This will allow thermal creep to be separated from irradiation and helium effects in DHCE (Dynamic Helium Charging Experiments) and will aid in interpretation of the vacuum thermal creep experiments now being performed.

Summary

In order to evaluate the effect of decreasing oxygen concentration on creep behavior in vanadium alloys, high temperature pressurized tube specimens of V-4Cr-4Ti were exposed to molten Li and the deformation in the tubes monitored periodically by laser profilometry. It was determined that at 665°C deformations were below 0.05% for all stresses in the range of 59-117 MPa effective stress at 1105 hours and below 6% at 765°C at 1927 hours. However, deformations over 20% were reached at 800°C at times as short as 100 hours for a stress level of 100 MPa and 30% at 457 hours at a stress level of 91 MPa. At all temperatures, it is evident that creep rates are higher in the Li environment where oxygen levels decreased compared to a vacuum environment where the oxygen levels increased.

Experimental Procedures

Specimen geometry and other experimental parameters were chosen to match those of the vacuum environment creep experiment conducted at PNNL [1]. Pressurized tubes were chosen as the specimens for both experiments 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 [2,3]. End caps of the same alloy were electron-beam welded in place, after which the tubes received an anneal at 1000°C/1h. The tubes initially had a grain size of 10 µm, but following the heat treatment the grain size was expected 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 TZM alloy with components of Mo and Nb-1Zr in order to contain the high-temperature liquid Li. The retort, has a 25.4 mm diameter Mo tube with caps and flanges of Mo welded in place. The mating flange on top uses a knife edge seal of the ConFlat[1] design with a mating flange of Nb-1Zr for ease of welding a 4 mm Nb-1Zr tube leading to a pressure transducer used to monitor pressure, an indicator of tube rupture. A gasket of Nb-1Zr was used for the flange seal. The retort serves an additional purpose as a prototype containment for a similar proposed 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. At first, 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 performed by placing a shielded thermocouple directly into the molten Li through a hole in the cap for a short-term test. For the last two intervals, a thermocouple well was incorporated into

[1]Registered trademark of Varian Inc.

the retort cap so that a shielded thermocouple could be placed in the well in contact with the liquid lithium at the level of the specimens.

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 120-300 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 [4]. 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.

Results and Discussion

Pressurized tubes have now been exposed to a vacuum environment and to a lithium environment for a sufficiently long period to make a comparison between high and low levels of oxygen. Results from the Li environment tests are available at a temperature of 665°C for 242 and 1105 hours, at 765°C for 200, 1064, and 1927 hours, and at 800°C for 561 and 1353 hours. Vacuum environment results are available at 700°C for nearly 10,000 hours and at 800°C for over 6000 hours [1]. Results from uniaxial tests made at Argonne National Laboratory on the same alloy and heat are also used for comparison where available at similar test parameters [5]. Results of the Li environment tests appear in Table 1.

Table 1 Creep data in terms of effective stress and strain

Specimen	Eff. Stress, MPa	Effective Strain, %			
665°C		**242 Hrs**	**1105 Hrs**		
V12	59	.023	.034		
V2	75	.025	.031		
V11	75	.0074	.0022		
V9	83	.027	.040		
V6	100	.022	leaked		
V1	117	-.010	.0044		
V13	133	.014	leaked		
765°C		200 Hrs	**1064 Hrs**	**1927 Hrs**	
V5	25	-.0037	-.017	-.016	
V8	42	.017	.016	.078	
V3	59	.027	.039	.38	
V10	59	.0007	-.016	.36	
V7	75	.033	.13	2.5	
V4	84	.031	.30	5.9	
800°C		**100 Hrs**	**457 Hrs**	**561 Hrs**	**1353 Hrs**
V5	30			-0.0037	0.022
V8	52			0.95	3.3
V3	69			5.6	20.7
V10	69			leaked	
V7	91		30.5*		
V4	100	20.3*			

*Indicates tube failure by creep

Stresses are reported in terms of an effective uniaxial stress and strains are reported as an effective mid-wall uniaxial strain [6]. In cases where negative values of strain appear, the strains were below the limit of experimental error. Such tubes have either failed or have not had sufficient time to creep to a value for which reliable measurements can be obtained. In cases where the tubes leaked due to early weld or defect failures, leakage is indicated in the table. In cases where the tubes failed by creep, an asterisk appears.

Curves of strain as a function of stress for the Li-environment tests are shown in Fig. 1 for 800°C. Results of vacuum-environment tests on similar tubes and of uniaxial specimens are shown for comparison. Expressing strain rate as a power law function of stress,

$$\dot{\varepsilon} = A\sigma^{n} \qquad (1)$$

where $\dot{\varepsilon}$ is the strain rate, σ is the stress, and A and n are constants, a stress exponent in the range of 3-7 is obtained for both the Li and vacuum tests, indicative of diffusion controlled dislocation climb creep. It is clear that the low-oxygen Li-environment test has a higher creep rate than the corresponding vacuum tests and the uniaxial test, although only one datum point is available for the latter. For the case of the Li-environment, creep rate may be expressed as:

$$\dot{\varepsilon} = 0.56 \times \sigma^{6.34} \exp(-3.2\mathrm{eV}/kT) \qquad (2)$$

where k is Boltzmann's constant and T is the absolute temperature, for the range of parameters investigated. At low stresses and higher temperatures, the stress dependence becomes linear as diffusional atomic migration creep mechanisms become dominant. This was shown at low stresses in the case of vacuum-environment tests [7]. Difficulty was experienced in expressing all of the data in the present study in the form of equations (1) and (2) because the material was constantly changing in strength properties as oxygen was removed. For this reason and the onset of diffusional creep mechanisms, it is recommended to use the graphical expressions to predict behavior within the range investigated.

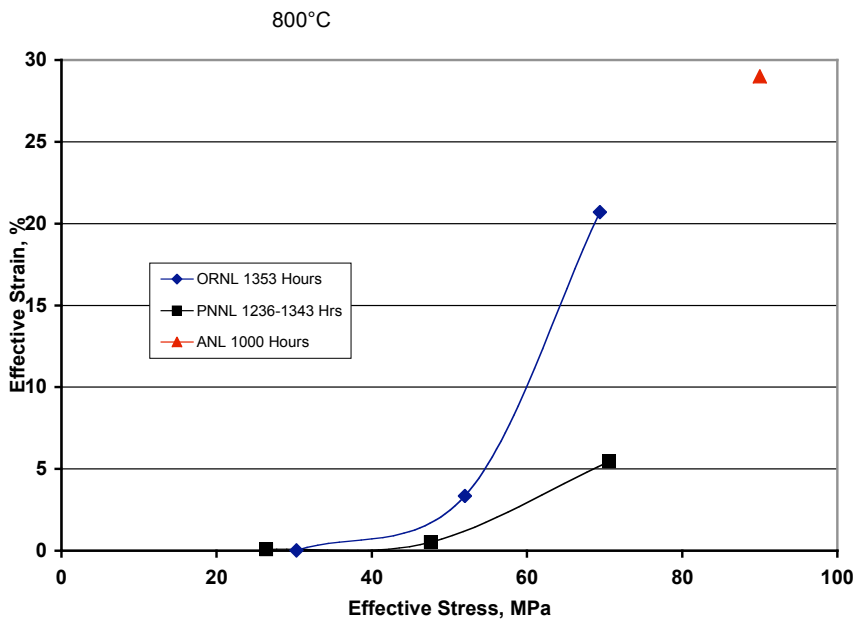

Figure 1 – Effective strain as a function of effective stress for Li-exposed specimens, ORNL. Vacuum-exposed specimens, PNNL and uniaxial specimens, ANL are shown for comparison

Creep response as a function of time is shown in Fig. 2 where curves are again shown for 800°C for stress levels of approximately 50 MPa. The early positive curvature demonstrates a very short period of steady state creep and early onset of tertiary creep. As is characteristic of pressurized tubes, there is little or no observable primary creep in the vacuum test results. For the Li tests, it is not possible to

observe primary creep due to the large deformation exhibited by the first measurement. It is again evident that the Li-environment tests demonstrate a higher creep rate than the higher-oxygen vacuum tests.

Perhaps some uncertainty remains in the interpretation of Fig 2 because the low-oxygen tests were for samples at a slightly higher stress level. In Fig. 3 results are shown for 800°C at an approximate stress level of 70 MPa where the vacuum environment tests are now at the same or slightly higher stress level. However, a higher creep rate is again demonstrated by the Li-environment tests. The very high temperature sensitivity is also shown in Fig. 3 where results from vacuum tests conducted at 700°C and Li-environment tests conducted at 765°C appear.

The observation of higher creep rates for low-oxygen, Li-environment specimens is also true at the lower temperature of 665-700°C. As seen in Fig. 4, the results from Li-environment tests exhibit higher creep deformations despite the lower temperature. In addition, small primary creep is observed for the case of the Li-environment tests.

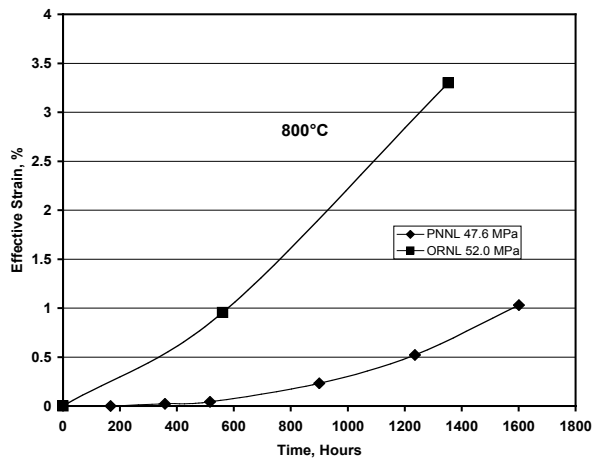

Figure 2 – Creep strain in V-4Cr-4Ti as a function of time showing enhanced creep in a lithium environment, ORNL compared to creep in a vacuum, PNNL.

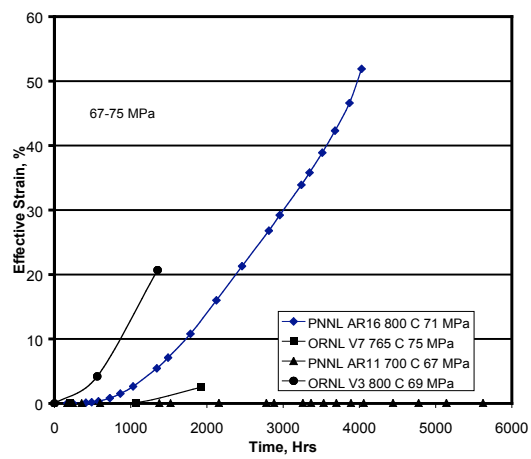

Figure 3 –Creep strain in V-4Cr-4Ti as a function of time comparine a Li-environment, ORNL, with a vacuum environment, PNNL.

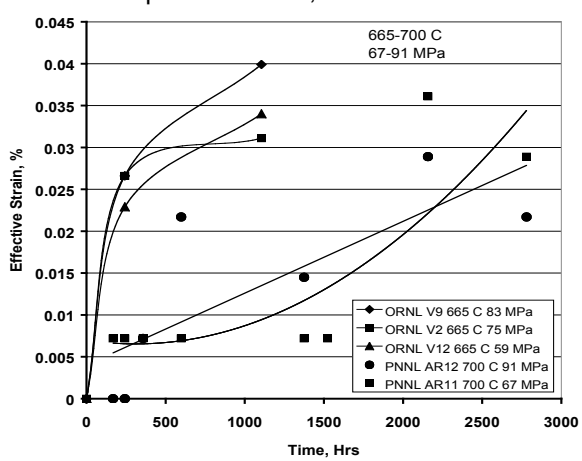

Figure 4 – Creep strain as a function of time for V-4Cr-4Ti at 665-700°C. Curves designated ORNL are for a Li environment, and curves designated PNNL are for a vacuum environment.

Oxygen has also been shown to extend creep rupture life in vanadium alloys [8-10]. In the present study, only two specimens have failed through creep rupture as shown in Table 1. A useful way to display creep rupture is through the Larson-Miller parameter:

$$P = T(\log t_r + 20)/1000 \qquad (3)$$

where T is the absolute temperature and t_r is the rupture time in hours [11]. Effective stress is plotted as a function of the Larson-Miller parameter in Fig. 5 for the two ruptured specimens from the Li-environment study as well as for the ruptured specimens from the vacuum tests. The two Li-environment samples failed prematurely compared with the vacuum-environment samples, as predicted from the previous study [8].

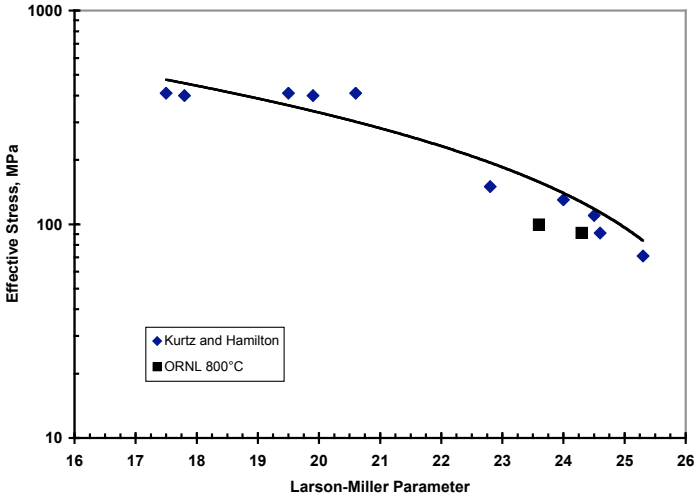

Figure 5 - Plot of effective applied stress as a function of Larson-Miller parameter showing reduced life for V-4Cr-4Ti in a Li environment, ORNL, at 800°C compared to that for a vacuum environment, Kurtz and Hamilton.

The total strain at failure is more difficult to understand. In the vacuum-environment tests at 800°C, a low-stress, long term specimen failed with a strain greater than 50%; shorter term specimens failed with lower strains, but no clear trend was observed. The 20-30% strains observed in the Li-environment tests were within the extremes of the vacuum tests. The absence of a clear trend in strain to failure could be the result of the prevalence of initial defects in portions of the tubing used for the study. Nondestructive tests were used to examine the tubing prior to making specimens, but clearly some defects were missed, and this could introduce some scatter in the results and influence the measured strain to failure.

For vanadium, it can be calculated that Li_2O has a lower free energy than the oxides of vanadium [12]. It then follows that oxygen will partition preferentially in lithium at equilibrium. The distribution coefficients for the lithium-vanadium system have been calculated by Smith and Natesan [12]. For the case of oxygen, the concentration ratio $C_V/C_{Li}=3.8\times10^{-7}$, and for the case of nitrogen, $C_V/C_{Li}=186$ for 800°C at equilibrium. Thus, vanadium will be depleted of oxygen to very low levels but will be enriched in nitrogen. These trends are observed in Fig. 6 where it can be seen that the oxygen concentration increases during the vacuum tests but decreases during exposure to lithium. Nitrogen concentrations in vanadium increase slowly for both vacuum and lithium tests as predicted. The rates of change are determined by

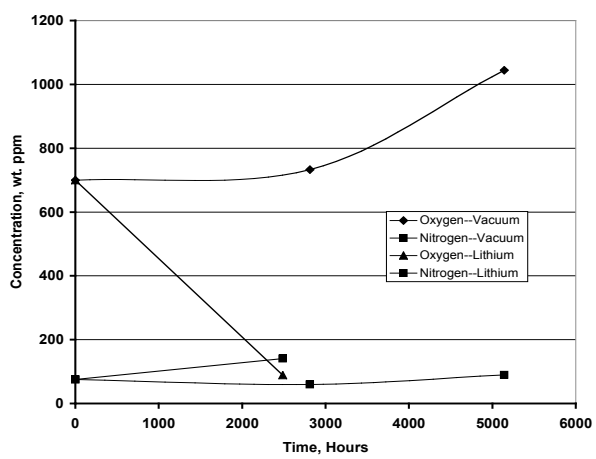

Figure 6 – Measured values of impurity concentration for V-4Cr-4Ti tubing as a function of exposure time.

the diffusivities of the species involved and the rate of impingement of the gases on the samples as well as surface effects and trapping.

This study is part of a larger effort to evaluate the mechanical behavior of vanadium alloys over a wide range of strain rates. Higher strain rates have been explored to study the plastic flow regime [13]. The present study explores the dislocation climb creep regime and the entry into the diffusional creep regime.

FUTURE DIRECTIONS

The higher creep rates and shorter rupture times in a lithium environment have been demonstrated for temperatures of 700 and 800°C. It remains to determine creep behavior in a Li-environment for lower temperatures, especially in light of the rather high creep rates at 800°C. The experiment was performed on the highest quality tubing of V-4Cr-4Ti available; however defects resulting from a heterogeneous microstructure clouded the results, making this a worst case study. Research should continue using tubing that is in preparation using careful control of the microstructure during processing. Testing should also be extended to lower temperatures.

CONCLUSIONS

1. Creep rates in a lithium environment are higher than those experienced in a vacuum environment at 700 and 800°C. This results from the hardening effect of oxygen in solution in the vanadium alloy.

2. Creep failures were observed in a Li-environment at 800°C after 100 hours at 100 MPa and after 457 hours at 91 MPa. These lifetimes are slightly below those expected from the vacuum environment tests.

3. Tertiary creep initiates early, with a short region of steady-state creep.

4. Oxygen concentration increases during exposure to an ultra-high vacuum but decreases in a Li-environment as predicted by thermodynamics. Nitrogen increases in both cases but at a slower rate.

REFERENCES

[1] R.J. Kurtz and M.L. Hamilton, J. Nucl. Mater. 283-287 (2000) 628.
[2] D.L. Smith, H.M. Chung, B.A. Loomis, H.-C. Tsai, J. Nucl. Mater. 233-237 (1996) 356.
[3] M.L. Grossbeck, R.L. Klueh, E.T. Cheng, J.R. Peterson, M.R. Woolery, E.E. Bloom, J. Nucl. Mater. 258-263 (1998) 1778.
[4] D.L. Crandall, D.J. Marts, T.R. Reed, G.R. Smolik, *Space Nuclear Poweer Systems 1987*, Ed. M.S. El-Genk, M.D. Hoover, Orbit Book, Malabar, FL (1988) 457.
[5] K. Natesan, W.K. Soppet, and D.L. Rink, "Uniaxial Creep Behavior of V-4Cr-4Ti Alloy," *Fusion Reactor Materials Semiannual Progress Report for Period Ending June 30, 2000*, DOE/ER/0313/28 (2000) p. 39.
[6] E.R. Gilbert and L.D. Blackburn, Trans ASME, J. Eng. Mater Tech. 99 Series H, No. 2 (1977) 168.
[7] R.J. Kurtz, A.M. Ermi, and H. Matsui, "An Update on Biaxial Thermal Creep of Vanadium Alloys," *Fusion Materials Semiannual Progress Report for Period Ending December 31, 2001*, DOE/ER/)313/31 (2002) p. 7.
[8] M. Schirra, KfK 2440, 2nd ed, Kernforchungszentrum Karlsruhe (1989).
[9] R.E. Gold, D.L. Harrod, R.L. Ammon, R.W. Buckman,Jr., R.C. Svedberg,COO-4540-1, Vol. 2, Westinghouse Electric Corp. (1978).
[10] M. Schirra, in: Kernforchungzentrum Karlsruhe, 2nd Edn., KfK 2440, 1989.
[11] F.R. Larson and J. Miller, Trans. ASME 74 (1952) 765.
[12] D.L. Smith and K. Natesan, Nucl. Tech. 22 (1974) 392.
[13] A.F. Rowcliffe, S.J. Zinkle, and D.T. Hoelzer, J. Nucl. Mater. 283-287 (2000) 508.