EFFECT OF A HYDROGEN ENVIRONMENT ON THE CREEP
PROPERTIES OF POLYCRYSTALLINE VANADIUM METAL

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Effect of a hydrogen environment on the creep
properties of polycrystalline vanadium metal

by

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I. INTRODUCTION

The problems relating to acceptable first wall materials for the Controlled Thermonuclear Reactor (CTR) have been outlined by Scott (1). One of the potential problems cited was the possibility of an effect of a hydrogen environment on the creep resistance of refractory metals.

In an effort to evaluate this possibility Mather (2) designed and built a vacuum furnace especially for creep tests of refractory metals. Two test runs each were conducted on molybdenum, niobium, and vanadium. The test environments were dynamic very high vacuum at 1173°K and one atmosphere hydrogen gas at 1173°K. Comparison of data for the two test runs revealed an apparent increase in the creep rate of vanadium at 12.3 MPa shear stress tested in hydrogen. No effect of hydrogen on the creep rate was observed for molybdenum at 34.5 MPa shear stress or for niobium at 18.5 MPa shear stress.

Because vanadium displayed the most dramatic creep rate change when it was exposed to hydrogen, it was selected as the material around which future research would center.

A. Review of Proposed Creep Mechanisms Applicable to Pure Polycrystalline Vanadium

1. Basic creep characteristics

When metals creep at high temperatures, the type of curve shown in Fig. 1 is observed. It can usually be broken

Fig. 1. Standard creep curve

down into three regions of interest:

- 1) primary region
- 2) secondary or steady-state region
- 3) tertiary region

The primary region of the creep curve can be considered as a nonsteady-state or transient regime. During this stage of creep, the material is work-hardened. The probable cause of the decrease in strain rate with time is the generation and interaction of dislocations. One can envision a dislocation source producing glissile dislocations which move freely until some hindrance to their motion is encountered. Common obstacles might include a dislocation lock or a subgrain boundary. A dislocation immobilized by obstacles exerts a backstress on trailing dislocations. The net result is work-hardening and a decrease in the strain rate as is observed.

The secondary region of the creep curve is a steady-state regime. Here a recovery mechanism operates in opposition to the strain-hardening mechanism and a dynamic steady-state is achieved. Arguments concerning the choice of the correct recovery mechanism seem to highlight the current research efforts in creep (see section A. 3.).

The tertiary region of the creep curve also represents a nonsteady-state process. In this stage of creep, cracks are nucleated and grow until rupture occurs.

More complete reviews of phenomenological creep can be

found in texts on mechanical metallurgy (3,4).

2. Recovery in creep processes

In order to attain some direction in the study of recovery in creep processes, a list of possible recovery mechanisms should be considered before actual creep theories are discussed:

- 1) Self-diffusion (vacancy mechanism)
- 2) Vacancy diffusion
- 3) Dislocation climb (nonconservative motion involving vacancy diffusion)
- 4) Grain boundary sliding
- 5) Formation of subgrains and their interaction with mobile dislocations
- 6) Cross-slip

Since some creep processes listed above are dependent upon one another, it becomes obvious why simple explanations of creep processes are not available. A number of theories have been proposed; these correlate with some observed phenomena only under certain conditions.

3. Creep theories

Three distinct creep regions have been described (see section A. 1.). Since each creep region is characterized by unique creep processes, separate creep theories must be derived for idealized primary, secondary, and tertiary creep. The complex nature of primary and tertiary creep processes has prevented a simple analytical description. Only steady-

state creep theories are numerous due to the relative ease of analyzing a steady-state process.

a. Steady-state creep Herring (5) developed a creep mechanism which was directed toward applications where the creeping material was subject to very high temperature ($T > 0.8 T_{mp}$) and very low stress ($\tau \lesssim 10^8$ dyne/cm²).

Earlier, Nabarro (6) had shown that any crystal can change its shape by self-diffusion in such a way as to yield to an applied stress. Herring realized that if self-diffusion could change the shape, then the macroscopic behavior of the polycrystalline solid would resemble a viscous fluid. Herring went on to postulate the existence of material and vacancy fluxes due to the applied stress.

The resulting Nabarro-Herring equation of steady-state creep (Eq. 1) reflects the diffusion dependence of the creep process.

$$\dot{\epsilon} = \left(\frac{\alpha D}{L^2} \right) (\sigma \Omega / kT) \quad (1)$$

α = geometry factor (= 5 for uniaxial stress)

D = self-diffusion coefficient

L = grain diameter

σ = uniaxial stress

k = Boltzmann's constant

T = absolute temperature

Ω = atomic volume ($= Cb^3$, where $C = 0.7$, b = interatomic distance)

Stevens (7) later showed that if diffusion creep occurred in a polycrystalline material then grain-boundary sliding must also occur if material continuity is to be preserved.

Gibbs (8) has reviewed evidence which suggests that grain-boundary sliding is always easier than grain deformation in the high-temperature creep of polycrystalline aggregates. The result parallels the result stated by Stevens. Again, it is pointed out that compatibility conditions require grain-boundary sliding to be accompanied by other grain deformation processes in the absence of large scale boundary migration. Moreover, grain deformation processes generally determine the rate laws for creep. Vacancy diffusion and dislocation motion are the primary factors involved in grain deformation.

Barrett and Nix (9) have presented a model for steady-state creep based on the motion of jogged screw dislocations. They assume that the chemical force on jogs in screw dislocations is balanced by the force on the dislocations due to the applied stress. Their steady-state model yields Eq. 2.

$$\dot{\epsilon} = 2\pi\rho_s D\alpha\left(\frac{b}{a_0}\right)^3 \sinh\left(\frac{\sigma b^2 \lambda}{2kT}\right) \quad (2)$$

ρ_s = mobile screw dislocation density

D = self-diffusion coefficient

α = number of atoms per unit cell

b = Burgers vector

a_0 = lattice parameter

λ = average spacing of jogs

Weertman (10) has developed several empirical models to characterize steady-state creep through dislocation climb:

$$\dot{\epsilon} = \text{constant } (\sigma^\alpha/kT) \exp(pQ/kT) \quad (3)$$

$\alpha \sim 3$ to 4

Q = activation energy of self-diffusion

σ = stress

other variables as before.

This equation assumes that the rate-controlling process is the diffusion of vacancies between dislocations which are vacancy sources and those which are vacancy sinks.

Another model suggested by Weertman (11) is:

$$\dot{\epsilon} = A\sigma^3 \sinh\left(\frac{B\sigma^{1.5}}{kT}\right) \exp(-Q/kT) \quad (4)$$

A and B = constants

other variables as before.

Equation 4 assumes a dislocation climb creep model which does not require the production of immobile dislocations.

All the above steady-state creep equations contain exponential reciprocal temperature factors modulated by other "less powerful" factors which are functions of stress and temperature. This type of relation suggests that the steady-state creep rate may be diffusion controlled since the self-diffusion coefficient of vanadium also displays an exponential reciprocal temperature dependence (12).

The above generalization is pointed out specifically for vanadium by Wheeler, Gilbert, Yaggee, and Duran (13). They state that correlations between results of diffusion and creep experiments have convincingly demonstrated that creep in vanadium occurs by diffusional processes over a temperature range including temperatures near the melting point down to temperatures as low as $0.3 T_{mp}$.

Sherby (14) has outlined some basic material parameters which should indicate a material's ability to promote high-temperature steady-state creep resistance:

- 1) Crystal structure (close packed)
- 2) High melting temperature
- 3) High elastic modulus
- 4) High valence state
- 5) Fine stable grain size

From the material parameters of Sherby it is obvious that vanadium should display above average high-temperature creep resistance. Vanadium has a high melting point, high valence state, and high elastic modulus. Detrimental factors for the vanadium used in this investigation include B.C.C. crystal structure and large grain size.

Some controversy does exist concerning the effect of grain size on high-temperature steady-state creep. Begley, et al. (15) claim that fine grain size generally provides superior creep resistance although there seem to be exceptions at very high temperatures. Extensive work by Klopp, et al.

(16) on tungsten indicates that the grain size dependence of creep in the pure metals is relatively small.

Grain size could be controlled by annealing (17). The recrystallized grain size should be decreased by additional cold-working prior to the heat-treatment. Further investigation is needed to define the relationships between annealing temperature, percent cold-work, annealing time, and recrystallized grain size for electrolytically refined vanadium.

Any creep model which might be used to characterize the results of this investigation must be valid under the conditions of moderately high temperature ($T \sim 0.5 T_{mp}$), low applied stress ($\tau \sim 10^8$ dyne/cm²), and variable material composition (due to the solution of hydrogen, oxygen, and nitrogen in the vanadium). Each model presented thus far would have to be modified in some way to account for the above factors.

b. Transient creep Since transient creep is a non-steady-state process, it is difficult to describe and understand quantitatively. Mukherjee, Bird, and Dorn (18) claim that no satisfactory theoretical model exists for primary (transient) creep where the structure continually changes with time. Only a few attempts have been made to outline the basic pattern which future research concerning transient creep will follow.

An early attempt to describe transient creep was made by Dorn (19):

$$\epsilon - \epsilon_0 = f\{t \exp(-Q_c/RT)\} \quad \text{for } \sigma = \text{constant} \quad (5)$$

where ϵ_0 = initial strain

ϵ = sum of the initial strain ϵ_0 upon stressing at $t=0$ and the creep strain up to time t .

Q_c = apparent activation energy for creep (insensitive to stress, strain, grain size, and temperature)

Rohlin (20) has proposed an extension of Weertman's dislocation climb model for secondary creep to include primary creep. A number of simplifying assumptions are made:

- 1) The number of sources is constant and all sources start to operate simultaneously, causing the dislocation density to increase during the primary stage up to the constant value characteristic of secondary creep.
- 2) The dislocation velocity is arbitrarily assumed to be proportional to C_i/x^{m-1} , with x being the distance from the source. The constants C_i are obtained from Eshelby et al.'s (21) model for a static pile-up, and the exponent m by assuming an Andrade primary creep law ($\epsilon \propto t^{1/3}$).
- 3) At time $t_1 = 0$ the first dislocation leaves the source, at some time t_2 the second one starts, at the time t_3 the third one, and so on. A dislocation leaves the source when its predecessor has reached the point x_1 .
- 4) All the dislocations reach their static equilibrium positions simultaneously at time t . In order for $\dot{\epsilon}$ to decrease it becomes necessary (since the dislocation density is increasing) that the dislocations are strongly retarded so that the area overswept per second decreases.

The strain versus time relationships calculated by the above method (via a numerical integration procedure) resemble a classic creep curve. However, many unrealistic assumptions have gone into this theory, which make its value questionable.

Stang, et al. (22) have stated that no relationships can be established concerning the amount of transient creep elongation a material will undergo during a creep test. These investigators claim that transient creep elongations are strongly dependent on the substructure of the material prior to testing. Because no good way exists to control substructure accurately, wide variation in transient creep elongations is expected.

B. Purpose of the Present Investigation

The purpose of the present investigation was to characterize the creep behavior of pure polycrystalline vanadium tested in a dynamic vacuum environment and to define any variation from its vacuum creep behavior brought about by exposure to hydrogen during creep.

II. SAMPLE PREPARATION

The vanadium used in this investigation was originally prepared by fused salt electrolysis (23). Chemical analysis of the metal appears in Table 1. Oxygen, nitrogen, and hydrogen concentrations were determined by the vacuum fusion method, the metallic impurities were determined by spectrographic analysis, and the carbon concentration was determined by combustion analysis.

Table 1. Chemical analysis of vanadium

Element	Content, ppm	Element	Content, ppm
Cr	200	Ti	<50
Cu	200	O	115
Fe	<100	H	3
Ni	<50	N	8
Si	<50	C	10

The vanadium was cold-swaged from the ingot form to finished wire according to the swage/anneal sequence described by Sherman (24) and shown in Table 2.

In an attempt to reduce the amount of primary creep elongation sustained by the samples, the amount of pre-anneal strain administered to the sample wires in the tensile test machine was two percent uniaxial elongation. Following the above mechanical treatment, the sample wires were chemically cleaned according to the following sequence:

- 1) Wash in trichloroethane and rinse in acetone.

- 2) Etch in a 50/50 by volume $\text{HNO}_3/\text{H}_2\text{O}$ solution at room temperature.
- 3) Etch was followed by a water rinse, acetone rinse, and dry.

Table 2. Swage/anneal sequence

Operation	Starting diameter	Final diameter	% Area reduction	Comment
Anneal	0.250	0.250	----	1000°C for 4 hours
Swage	0.250	0.230	15.4	@ 10 ⁻⁶ Torr for all anneals
	0.230	0.187	33.9	
	0.187	0.150	35.7	
	0.150	0.125	30.6	
	0.125	0.100	36.0	
Anneal	-----	-----	----	1000°C for 4 hours
Swage	0.100	0.078	39.2	
	0.078	0.063	34.8	
	0.063	0.051	34.5	
	0.051	0.040	38.5	
	0.040	0.031	39.9	
Anneal	-----	-----	----	1000°C for 4 hours

Each sample wire was formed into a helical shape on a specially made sample mandrel. This mandrel features a 16 pitch thread with a root diameter of 0.220 inches. It was designed to accept 0.031 inch wire for forming. The surface of the mandrel was covered with Teflon tape to protect the sample wires from abrasion during the winding procedure. The winding of the sample onto the mandrel was carried out by placing the mandrel in a lathe and then turning the lathe chuck by hand as the sample wire was fed onto the mandrel.

An in-situ anneal (1 hour @ 1060°C and $<10^{-6}$ Torr) was executed prior to several early test runs. However, because wide variation in the primary creep rate was observed, the in-situ anneal was abandoned. In an attempt to stabilize the primary creep elongation, a final anneal (4.5 hours @ 1060°C and $<10^{-6}$ Torr) was carried out prior to loading the samples into the test rig. Details concerning the different heat treatments are shown in Table 3.

Table 3. Sample wire heat treatments^a

Creep test number		Temperature of final anneal (°C)	Time of final anneal (hours)
I	In-situ anneal	1060	1.0
II		1060	1.0
III		1060	1.0
IV		1060	1.0
V		1060	1.0
VI		1060	1.0
VII	External anneal	1060	4.5
VIII		1000	14.5
IX		1060	4.5
X		1060	4.5
XI		1060	4.5
XII		1060	4.5
XIII		1060	4.5
XIV		1060	4.5

^aAll at $<10^{-6}$ Torr.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

A. Creep Rig Revisions

Several alterations were made on the creep rig and associated equipment originally constructed by Mather (2) before the tests of this investigation began:

- Square-threaded mating mandrel and sample holders were designed and fabricated so that sample loading was simplified.
- The loading weights were combined with small molybdenum rings in order that the total loading mass could be changed quickly and easily.
- In order to reduce outside vibration excitation of the test chamber, a DC power supply was procured to replace the previously used AC unit.
- The basic design of the creep rig was changed to allow the introduction of several additional ports. Also, the ion pump placement was changed to allow permanent mounting on vibration-free floor pilings.
- A Schulz-Phelps type gage was installed. This gage has high vacuum integrity and it will measure system pressure in the range 10^{-1} to 10^{-6} Torr.
- An automatic pressure controller unit was installed. This unit is a proportional set-point type controller which is designed to control a dynamic system pressure over a wide range.

- A 0.750-inch mini valve was installed as an up-to-air valve.
- A gold-seal valve was added in order to allow isolation of the test chamber from the roughing line.

B. Hydrogen Admission System

After the alterations were completed on the main creep rig, a new hydrogen admission system was designed and implemented as part of the creep rig. The basic functioning of this hydrogen admission system is identical to the system used by Mather (2). The major improvement in the new hydrogen admission system lies with the automatic pressure controller servo valve. Fig. 2 outlines the basic details of the system.

C. Experimental Procedure

Three sample wires were loaded into the test rig at the beginning of each run. The samples remained unloaded during the system bakeout period. At the start of a creep test the samples were raised into the test position by moving the sample holder fixture vertically. Once the samples were under load, the test began. During the test, elongation of the sample wires was measured by an optical cathetometer. The raw sample wire elongation data was processed into creep rates and strain versus time data using the computer programs developed by Mather (2).

Fig. 2. Schematic drawing of the hydrogen admission system

IV. RESULTS

A. Very High Vacuum Creep Tests

Creep tests A, B, I, and II were run to determine creep properties of pure polycrystalline vanadium in very high vacuum (VHV) @ 900°C. Calculated creep rates can be interpreted as an approximate steady-state creep rate. No guarantee can be made that true steady-state creep was actually achieved.

The samples in creep test A (see Fig. 3) elongated to the sample holder platform (see Fig. 4) before a steady creep rate was achieved. The small amount of shear strain observed resulted from incorrect positioning of the sample holder fixture in the test rig (see Fig. 4). This problem was corrected in all later runs. No creep rates were calculated for this test.

Creep test B (see Fig. 5) yielded one calculated creep rate. This test was conducted under conditions identical to creep test A. However, the samples used in this test contained varying amounts of pre-anneal strain. The pre-anneal strain was changed in order to control primary creep elongation. The sample numbers in this test indicate the amount of pre-anneal strain they received. Since sample 2 displayed a steady creep rate with a minimum of primary creep elongation, it was decided that all samples used in later tests would receive two percent pre-anneal strain. The calculated creep

Fig. 3. Strain versus time for vanadium metal @ 900°C in dynamic vacuum of 4×10^{-8} Torr with $\tau = 11.7$ MPa

Fig. 4. Schematic drawing of the creep rig testing stage

Fig. 5. Shear strain versus time for vanadium metal @ 900°C in dynamic vacuum of 4×10^{-8} Torr with $\tau = 11.7$ MPa to determine the effect of prestrain on the test samples

rate for sample 2 is shown in Table 4.

All samples in creep test I (see Fig. 6) displayed steady creep rates. The calculated creep rates are shown in Table 4.

Creep test II (see Fig. 7) resulted in some unusual creep curve results. It appears that two separate creep rate regions were observed. Since thunderstorm power interruptions occurred during this test, there is a high probability that some thermal excursion may have taken place. This would explain the inflections observed in the data. To best interpret the data, two creep rates (regions A and B as shown in Fig. 8) in addition to the overall creep rate were calculated as shown in Table 4.

B. Hydrogen Creep Tests

All creep tests after test II were run to determine the creep properties of pure polycrystalline vanadium in hydrogen at temperatures ranging from 735°C to 900°C as shown in Table 4.

Creep test III (see Fig. 9) yielded one data set for sample 16. The hydrogen gas was admitted to the test rig prior to the application of the load. Upon application of the load, all three samples remained stationary for the first 25 hours of the test. Samples 17 and 18 then elongated to the sample holder platform during primary creep and failed to achieve a steady creep rate. Sample 16 did reach a steady

Table 4. Summary of results and testing parameters

CREEP TEST NUMBER	SAMPLE NUMBER	INTERSTITIAL IMPURITIES (PPM)			CALCULATED CREEP RATES (SEC ⁻¹) · 10 ⁴				SEE FIG. NO.	TEMP. (°C)	ENVIRONMENT	LOADING
		OXYGEN	HYDROGEN	NITROGEN	OVERALL	A	B	C				
A	V-1	—	—	—					3	900	VHV	$\tau_0 [1.1 \cdot 10^8 \frac{\text{dyn}}{\text{cm}^2}]$
	V-3	—	—	—								
	V-5	—	—	—								
B	V-2	—	—	—	0.4897				5	900	VHV	τ_0
	V-4	—	—	—								
	V-8	99	2	4								
I	V-10	99	2	6	0.5837				6	900	VHV	τ_0
	V-11	—	—	—	0.5984							
	V-12	—	—	—	0.6190							
II	V-13	—	—	—	0.7525	0.4782	0.6199		7,8	900	VHV	τ_0
	V-14	110	2	8	0.7335							
	V-15	—	—	—	0.6157	0.4450	0.5132					
III	V-16	270	160	720	0.5407				9	900	Hydrogen P=1 torr	τ_0
	V-17	400	180	1400								
	V-18	350	180	1500								
IV	V-20	110	3	13						900	Hydrogen P=3·10 ⁻⁴ torr FAST CREEP	τ_0
	V-21	120	3	15								
	V-22	110	2	12								
V	V-23	98	2	5						900	VHV FAST CREEP	τ_0
	V-24	94	2	4								
	V-25	120	2	5								
VI	V-26	190	66	20						900	Hydrogen P=2·10 ⁻¹ torr	τ_0
	V-27	—	—	—								
	V-28	200	63	15								
VII	V-30	320	540	130		0.1286			10, 11	850	VHV & Hydrogen P=0.3 torr	τ_0
	V-31	510	470	570		0.4587	0.1749	0.0711				
	V-32	450	490	410		0.9381	0.3678					
VIII	V-34	120	2	7						850	VHV FAST CREEP	τ_0
	V-35	120	1	7								
	V-36	120	2	3								
IX	V-37	240	<1	82					12	800	VHV & Hydrogen P=0.4 torr	τ_0
	V-38	390	2	340								
	V-39	270	3	120								
X	V-40	270	9	110					13	800	VHV & Hydrogen P=0.6 torr	1.1 τ_0
	V-41	320	5	160								
	V-42	300	3	100								
XI	V-43	310	2	520					14	735	VHV & Hydrogen P=0.4 torr	τ_0
	V-44	350	<1	520								
XII	V-45	440	5	380					15	900	VHV & Hydrogen P=0.5 torr	0.5 τ_0
	V-46	500	5	520								
XIII	V-47								16	750	VHV & Hydrogen P=0.5 torr	τ_0
	V-48											
XIV	V-49								17	900	VHV & Hydrogen P=0.5 torr	0.5 τ_0
	V-50

Fig. 6. Shear strain versus time for vanadium metal @ 900°C in dynamic vacuum of 4×10^{-8} Torr with $\tau = 11.7$ MPa

Fig. 7. Shear strain versus time for vanadium metal @ 900°C in dynamic vacuum of 4×10^{-8} Torr with $\tau = 11.7$ MPa

Fig. 8. A schematic drawing of Fig. 6 showing the regions of the calculated creep rates A and B

Fig. 9. Shear strain versus time for vanadium metal @ 900°C in contaminated hydrogen with $\tau = 11.7$ MPa

creep rate after approximately 250 hours of testing. The calculated creep rate is shown in Table 4.

After creep test III was completed, it was discovered from vacuum fusion analysis of the samples that contamination was occurring during hydrogen gas admission. The contamination seemed to be associated with residual air in the hydrogen admission system since both oxygen and nitrogen impurities were found in excessive amounts in the test specimens. These interstitial gas impurities probably adsorbed on the hydrogen admission system walls.

To eliminate this source of impurities, the entire hydrogen admission system was baked out at 270°C for several days. Vacuum fusion analysis carried out on samples from hydrogen creep tests following a hydrogen admission system bakeout showed reduced contamination.

Creep tests IV, V, and VI supplied no additional data. All samples in the above tests displayed "fast creep." Fast creep is defined as full sample elongation in a short period of time during the primary stage of creep.

Creep test VII (see Figs. 10 and 11) displayed three separate creep regions (A, B, and C) separated by areas of zero creep rate. The admission of hydrogen gas temporarily stopped creep in all samples. Fifty to 100 hours after the hydrogen gas was admitted, the samples began to creep again. The creep rates established after hydrogen gas admission (region B) were less than the initial creep rates established

Fig. 10. Shear strain versus time for vanadium metal @ 850°C. The test was VHV until hydrogen was admitted as shown with $\tau = 11.7$ MPa

Fig. 11. A schematic drawing of Fig. 9 showing the regions of the calculated creep rates A, B, and C

in VHV (region A). Hydrogen was again admitted to the test chamber at 490 hours. Again, the creep rate became zero. After approximately 50 hours had elapsed, the sample established a finite creep rate (region C) which was less than the creep rates established earlier (regions A and B). Table 4 contains numerical creep rates for the samples in regions A, B, and C.

Creep test VIII supplied no data. All samples displayed fast creep.

Since some minor contamination of the samples had occurred in creep tests III, VI, and VII (see Table 4), it was decided to expose a set of samples to VHV, hydrogen gas, and VHV in sequence. Because oxygen and nitrogen dissolved in vanadium are very stable at 735 to 900°C, these gases cannot be degassed from vanadium in a reasonable amount of time in VHV. However, hydrogen gas, which is only slightly attracted by vanadium chemically (thermodynamically at 735 to 900°C) and diffuses rapidly, can be degassed from vanadium in a short time (estimated to be less than 15 seconds) in VHV.

The testing procedure for creep test IX (see Fig. 12) follows:

- 1) VHV test until a steady creep rate is established.
- 2) Admit hydrogen gas (and contaminates).
- 3) Remove hydrogen gas (but not oxygen and nitrogen contaminates) by pumping the system to VHV.

Fig. 12. Shear strain versus time for vanadium metal @ 800°C. The test was conducted in three parts: VHV, hydrogen environment (hydrogen admitted twice), and VHV with $\tau = 11.7$ MPa

After 300 hours of testing was completed, the creep rig was evacuated. The creep rate of the samples increased immediately upon hydrogen evacuation.

Creep test X (see Fig. 13) displayed a dramatic decrease in creep rate following the admission of hydrogen. Only minor creep rate recovery was observed during the 150 hours following hydrogen admission. Upon evacuation of the hydrogen from the creep rig, all samples displayed an increase in creep rate.

Creep test XI (see Fig. 14) displayed little change in creep rate when hydrogen was admitted and evacuated. This test was started at 900°C. Because fast creep was observed upon loading, the temperature was lowered to 735°C. The creep test was then carried out at 735°C. The results of this test indicate that the hydrogen effect is less pronounced at lower temperatures ($T < 0.5T_{mp}$) and high interstitial impurities levels.

Creep test XII (see Fig. 15) displayed little change in creep rate when hydrogen was admitted and evacuated. This creep test was carried out at 900°C and $\tau = 0.5 \tau_0$ ($\tau_0 = 11.7$ MPa). The results of this test indicate that the hydrogen effect is less pronounced at lower stress levels.

Creep test XIII (see Fig. 16) displayed little strain during the first 100 hours of testing due to the low testing temperature of 750°C. Gas was admitted and evacuated in an unsuccessful attempt to initiate an increased creep rate in

Fig. 13. Shear strain versus time for vanadium metal @ 800 C. The test was conducted in three parts: VHV, hydrogen environment, and VHV with $\tau = 11.7$ MPa

Fig. 14. Shear strain versus time for vanadium metal @ 735°C with $\tau = 11.7$ MPa. The test was conducted in three parts: VHV, hydrogen environment, and VHV

Fig. 15. Shear strain versus time for vanadium metal @ 900°C with $\tau = 5.85$ MPa. The test was conducted in three parts: VHV, hydrogen environment, and VHV

Fig. 16. Shear strain versus time for vanadium metal with $\tau = 11.7$ MPa. Testing temperature was varied from 750°C to 825°C

the samples. After 100 hours of testing, the test temperature was slowly increased in fifteen degree increments to 825°C where an increased creep rate was observed (at approximately 210 hours). The rest of the test was carried out at 825°C. Upon gas admission at 250 hours, creep was dramatically reduced for approximately 25 hours. Recovery of the creep rate was then observed, and it was followed by an additional transient increase in the creep rate upon evacuation.

Creep test XIV (see Fig. 17) displayed results very similar to the results of creep test XII. Both tests were carried out at $T = 900^{\circ}\text{C}$ and $\tau = 0.5 \tau_0$.

C. Hydrogen Environment Effect

The main concern of this investigation was to determine whether or not hydrogen gas would cause a change to occur in the creep rate of pure polycrystalline vanadium metal. The experimental work done in this investigation indicates that a definite effect does exist. The basic characteristics of the hydrogen environment effect follow:

- 1) Vanadium stops creeping immediately when hydrogen gas is admitted to the test chamber, at least under certain conditions.
- 2) After 50 to 150 hours have elapsed, vanadium assumes a creep rate which is somewhat less than the original VHV creep rate observed before the hydrogen was admitted.
- 3) If the hydrogen gas is removed, a creep rate approximately equal to the VHV creep rate will be observed after steady creep is reestablished.

Fig. 17. Shear strain versus time for vanadium metal @ 900°C with $\tau=5.85$ MPa. The test was conducted in three parts: VHV, hydrogen environment, and VHV

V. DISCUSSION

A. Comparison of Results with other Creep Investigations

1. Mather's results

Mather (2) completed two creep tests involving polycrystalline vanadium creep samples. The tests were conducted at 900°C in VHV and in hydrogen (see Fig. 18). The data indicated that the steady creep rate of the sample tested in hydrogen was greater than the steady creep rate of the sample tested in VHV.

The difference in steady creep rates observed by Mather must be viewed with caution. This result is based on only one data set for each environment. To better understand the steady creep rates of samples exposed to the two environments, additional tests would have to be carried out duplicating exactly Mather's test conditions.

Close examination of the data for the hydrogen run indicates the existence of a 20 hour delay in the onset of creep. This delay is not present in the data of the VHV test. Data collected in this investigation indicates that some period of delay in the onset of creep can be expected in creep tests carried out at temperatures greater than 735°C when hydrogen was present prior to application of load to the sample.

2. Stoop's results

Stoop and Shahinian (25) conducted a number of creep rupture tests involving niobium at elevated temperatures ($T >$

Fig. 18. Shear strain versus time for vanadium metal at 900°C with $\tau = 12.3$ MPa and in dynamic vacuum as reported by Mather (2)

0.5 T_{mp}). Stress was held constant at 44.8 MPa. Nitrogen concentration in the samples was varied. The results of testing showed that strengthening of niobium by nitrogen in solid solution occurred below 0.5 T_{mp} but not above. The author claims that the above situation is caused by a change in the mechanism controlling creep. In bcc metal the most likely rate-controlling mechanism at intermediate temperatures ($T < 0.5 T_{mp}$) is the interaction of dislocations and interstitials, while at high temperatures ($T > 0.5 T_{mp}$) it is dislocation climb.

At temperatures above 0.5 T_{mp} , oxygen in solution strengthens niobium while nitrogen does not. Stoop claims that oxygen may form some type of complex cluster with substitutional impurities in niobium and thus strengthen the material at high temperatures.

Several samples included in Stoop's data show anomalously high creep rates. Similar "fast creep" was observed in the present investigation. Fast creep may be related to dynamic recrystallization. Dynamic recrystallization implies recrystallization initiated by the combined effects of shear strain and temperature. Since there is no way to examine the microstructure of a test sample during a creep run, no direct evidence concerning dynamic recrystallization can be presented. Recrystallization experiments carried out during this investigation showed that no static recrystallization occurred in

test samples below 950°C.

3. Wheeler's results

Wheeler et al. (13) conducted extensive creep investigations of polycrystalline vanadium. The samples were loaded in uniaxial tension from 477 to 1600°C in VHV. Although none of their tests matched the conditions used in the present study, several of them were close enough to provide pertinent results. The minimum-creep-rates observed in the current tests were approximately one thousand times faster than Wheeler et al. reported. The differences in minimum-creep-rates might have been caused by the following factors:

- 1) Inability to correctly compare tensile and shear stress loading effects on creep rates.
- 2) Different levels of dissolved interstitial and substitutional impurities.
- 3) Different sample geometries.

Only VHV tests were conducted by Wheeler et al.

The minimum-creep-rate for a number of stresses and temperatures was plotted versus reciprocal temperature during the above study. The slopes of these curves are the creep activation energies at a particular stress. These activation energies were compared with diffusivities over the temperature range of the study. A distinct similarity between the temperature dependence of the diffusivity and creep behavior in vanadium was observed. Both creep and diffusivity showed non-linearity on the Arrhenius-type plot and therefore provided

evidence that creep in vanadium is diffusion controlled. Peart and Askill (26) have attributed the non-linear Arrhenius-type plot in vanadium to the change from divacancy diffusion at high temperatures to mono-vacancy diffusion at intermediate temperatures.

From this comparison of creep and diffusivity Wheeler et al. (13) concluded that the mechanisms of creep in vanadium in order of decreasing temperature are: dislocation climb by divacancy diffusion, dislocation climb by mono-vacancy diffusion, and short-circuited diffusion (this last mechanism is not discussed above because it operates at low temperature). Since the present investigation was carried out at an intermediate temperature ($T \approx 0.5 T_{mp}$), dislocation climb by single vacancy diffusion is the most probable creep mechanism.

B. Possible Explanation of the Hydrogen Environment Effect

Temporary cessation of creep concomitant with the introduction of gaseous hydrogen to the evacuated test chamber was unanticipated at the outset of this investigation. In the following paragraphs an attempt is made to isolate those factors, inherent to the test procedures, which might explain this unique phenomenon.

Wheeler et al. (13), as described above, have concluded from their systematic investigation that the creep rate of vanadium in VHV is controlled by mono-vacancy diffusion over the range of temperatures and stresses employed in the present

investigation. Consequently, the hydrogen gas induced creep cessation phenomenon must be explained in the context of that mechanism. Furthermore, the influence of test temperature and adventitious impurities (oxygen and nitrogen) on the hydrogen induced creep cessation behavior must be accounted for in the explanation.

In order to isolate the primary factors which caused creep cessation the various potential factors are considered in the following order: a) The effect of adsorbed or dissolved oxygen and nitrogen per se; b) The effect of hydrogen per se; c) Alterations in the effect of hydrogen at different test temperatures; d) Alterations in the effect of hydrogen by the presence of oxygen and nitrogen contamination.

Before a hydrogen effect on the creep rate of vanadium can be discussed, the effects of the interstitial impurities oxygen and nitrogen on the creep rate of vanadium must be considered. Dissolved oxygen and nitrogen in vanadium would probably increase creep resistance via a solution strengthening process. Because the motion of dislocations would be impeded by the interstitial impurities, the creep rate would be expected to decrease. Dilute solutions of oxygen and nitrogen might also effect the creep recovery mechanism operating due to interaction between solutes and climbing dislocations.

The nature of oxygen and nitrogen in solution in vanadium

is not well understood. There is evidence that oxygen atoms in niobium appear in pairs and triplets, the degree of association increasing with concentration (25). Similar constellations of interstitials may be expected to exist in vanadium. These constellations would also cause solution strengthening, and therefore a decreased creep rate.

As the amounts of oxygen and nitrogen in the vanadium increase, the probability of oxide and nitride precipitation becomes greater. Since vanadium oxides and nitrides are brittle and hard, the presence of these phases in the vanadium would probably increase creep resistance by blocking the motion of dislocations.

Adsorbed oxygen and nitrogen might also impart a strengthened surface layer which would reduce the creep rate.

The effect of hydrogen per se on the creep rate of vanadium is based on the creep mechanism proposed by Wheeler et al. (13) for $T \approx 0.5 T_{mp}$. Recall that the creep mechanism operating in vanadium at this temperature is dislocation climb by mono-vacancy diffusion. If vacancies in vanadium were attracted to interstitial hydrogen more strongly than to a climbing dislocation, the dislocation-vacancy interaction would be reduced and the mobility of the vacancy-hydrogen bound pair would be lessened. Both effects would reduce a vacancy diffusion controlled creep rate. The decrease of creep rate would depend on the strength of the vacancy-hydro-

gen interaction, and the concentration of hydrogen and vacancies.

Another observation associated with hydrogen creep tests has been the exponential decrease of hydrogen pressure (it is assumed that the hydrogen pressure is equal to the total pressure) following hydrogen admission to the creep rig. Permeability calculations concerning the migration of hydrogen through the stainless steel walls of the creep rig indicated that small amounts of hydrogen probably leave the rig where temperatures approach 300°C. Actual hydrogen loss from the test rig is difficult to predict because the test rig displays complex geometry and thermal gradients.

The eventual return of a measurable creep rate to the samples following hydrogen admission seems to be associated with the hydrogen pressure drop. Therefore, it is probable that the degassing of hydrogen from the samples frees vacancies to take part in dislocation climb. This increase in the number of free vacancies would lead to the observed creep rate recovery.

Alterations in the effect of hydrogen at different test temperatures should be expected since the creep mechanism (dislocation climb by vacancy diffusion) is diffusion controlled. If the temperature is changed with hydrogen present, several different processes might take place. Considering the increased temperature situation, increased thermal energy

of the metal lattice enhances the probability that mono-vacancy-hydrogen pairs would dissociate. Also, as the temperature is increased, additional free vacancies would be generated as demanded by thermodynamic equilibrium. Since a fixed amount of hydrogen exists in the vanadium to interact with the mono-vacancies, a modest temperature increase would guarantee an excess of free vacancies in addition to the mono-vacancy-hydrogen constellations. Furthermore, an increased temperature would decrease the equilibrium concentration of hydrogen. All these factors indicate that increases in temperature will minimize the hydrogen effect and increase the net creep rate.

The effect of temperature (contaminates and loading combinations are shown in Table 4) on the hydrogen effect is illustrated when creep tests IX and X (see Figs. 12 and 13) are compared with creep tests XII and XIV (see Figs. 15 and 17). Both creep tests IX and X were carried out at 800°C, and creep tests XII and XIV were carried out at 900°C. The hydrogen effect is dramatically present in IX and X, while XII and XIV shows almost no change upon hydrogen admission and evacuation. Since load and contamination were variable in samples of these runs, no absolute conclusions may be reached concerning the effect of temperature on the hydrogen effect.

In all the hydrogen creep tests of this investigation the effect of hydrogen was altered by the presence of oxygen and

nitrogen contamination. Closer scrutiny of the data indicated that increased levels of oxygen and nitrogen tended to minimize the hydrogen effect. The results of creep tests IX and X (see Figs. 12 and 13) showed dramatic change in creep rate due to hydrogen admission and evacuation. The samples of these tests were only slightly contaminated with oxygen and nitrogen (see Table 4). Conversely, the results of creep test XI (see Fig. 14) showed little change in the creep rate due to hydrogen admission and evacuation. Analysis of the samples from creep test XI revealed that they were more contaminated than the samples of creep tests IX and X (see Table 4). Again, further creep testing with absolute control of load, contamination, and temperature combinations would have to be completed before any conclusions could be drawn concerning the effect of the above parameters on the hydrogen effect.

From these results and observations it would appear that hydrogen has a higher affinity for oxygen and nitrogen than for vacancies in the vanadium. If this is true, the admitted hydrogen will interact with the oxygen and the nitrogen and leave the vacancies free to interact with dislocations.

Because the chemical combination of oxygen and hydrogen is favored by a lowering of the free energy at test temperatures, one can envision greater energetic stability in oxygen-hydrogen constellations and vacancies versus unreacted oxygen, vacancies, and hydrogen; or unreacted oxygen and vacancy-

hydrogen pairs. The oxygen-hydrogen combinations would be preferred over the vacancy-hydrogen pairs only if the free energy of combination of the first is lower than the free energy of combination of the second. Since the free energy of formation of vacancy-hydrogen pairs has not been measured, no final conclusions can be reached concerning the associations of oxygen, hydrogen, and vacancies. Also, since the contaminate gases enter the test rig with the hydrogen, a surface layer barrier to hydrogen on the samples consisting of oxygen and nitrogen might explain the observed minimization of the hydrogen effect.

The possible existence of pressurized gas bubbles in the vanadium would probably cause a change to occur in the creep rate. If the bubbles nucleated along grain boundaries in the vanadium, an increased creep rate might result due to grain boundary sliding. Conversely, if small voids nucleated in the bulk material during creep, a decreased creep rate would be expected due to dislocation pinning by the voids. Thermodynamic calculations indicate very low steam ($P_{H_2O} < 10^{-27}$ Torr) and very low ammonia ($P_{NH_3} < 10^{-4}$ Torr) pressures will be evolved in the vanadium due to chemical combination of oxygen, nitrogen, and hydrogen. Microscopic examination (150X) of several samples did not reveal any bubbles. Since the expected gas pressures are extremely low, it can be assumed that gas bubbles have no influence on the creep rate of

vanadium.

In conclusion, all the creep interaction modes discussed in previous paragraphs fail to explain the cessation of creep in vanadium with the exception of the hydrogen-vacancy interaction mechanism. The actual details of the possible hydrogen-vacancy interaction mechanism proposed here are not understood. Only further study of this proposed mechanism will lead to its acceptance or rejection as an explanation of the observed cessation of creep in vanadium when exposed to hydrogen.

VI. RECOMMENDATIONS

During this investigation, several ways to improve the experimental apparatus and materials have been proposed.

A. Uniform Samples

The vanadium wire used in this investigation was fabricated especially for this experiment (see section II). Because significant variation in hand-swaged wire does exist, an attempt to obtain commercial vanadium wire should be made. Machine-made wire would help eliminate material variation due to fabrication.

B. Sublimator Addition

Mather (2) suggested that a titanium sublimator be added to the system to increase pumping capacity at high vacuum. A new ion pump-sublimator system has been proposed in the group's budget for next year. Economic conditions will decide the future of the sublimator addition.

VII. LITERATURE CITED

1. Scott, T. E., USERDA Report W-7405-eng-82, Ames Laboratory, Ames, Iowa, June 1975.
2. Mather, J. C., Effect of Hydrogen on the Creep Properties of Vanadium, Niobium, and Molybdenum, M.S. Thesis, Iowa State University, 1975.
3. Dieter, G. E., "Mechanical Metallurgy," McGraw-Hill Book Company, New York, N.Y., 1961, pp 335-367.
4. Kennedy, A. J., "Processes of Creep and Fatigue in Metals," John Wiley and Sons, Inc., New York, N.Y., 1963, pp 147-280.
5. Herring, C., J. Appl. Phys., 21, 437 (1950).
6. Nabarro, F. R. N., "Report of a Conference on the Strength of Solids," (Physical Society, London, 1948), p 75.
7. Stevens, R. N., Phil. Mag., 23, 265 (1971).
8. Gibbs, G. B., Mat. Sci. and Engr., 2, 269 (Jan. 1968).
9. Barrett, C. R., and Nix, W. D., Acta Met., 13, 1247 (1965).
10. Weertman, J., J. Appl. Phys., 26, 1213 (1955).
11. Weertman, J., J. Appl. Phys., 28, 362 (1957).
12. Weertman, J., Trans. ASM, 61, 681 (1968).
13. Wheeler, K. R., Gilbert, E. R., Yaggee, F. L., and Duran, S. A., Acta Met., 19, 21 (1971).
14. Sherby, O. D., Acta Met., 10, 135 (1962).
15. Begley, R. T., Harrod, D. L., and Gold, R. E., "High Temperature Creep and Fracture Behavior of the Refractory Metals," IMD-NASA Symposium on Metallurgy and Technology of Refractory Metal Alloys, Washington, D.C., April 25-26, 1968.
16. Klopp, W. D., Witzki, W. R., and Raffo, P. L., "Effects of Grain Size on Tensile and Creep Properties of Arc-Melted and Electron-Beam-Melted Tungsten at 2250 to 4140°F," Trans. AIME, 233, 1860-1866 (Oct. 1965).

17. Loria, E. A., Ludemann, W. D., and Rowe, E. A., "Recrystallization of Vanadium," Bureau of Mines Report of Investigations 6547, U.S. Department of the Interior, Washington, D.C., 1964.
18. Mukherjee, A. K., Bird, J. E., and Dorn, J. E., Trans. ASM, 62, 155 (1969).
19. Dorn, J. E., J. Mech. Phys. Solids, 3, 85 (1954).
20. Rohlin, L., Scripta Met., 3, 353 (1969).
21. Eshelby, J. D., Frank, F. C., and Nabarro, F. R. N., Phil. Mag., 42, 351 (1951).
22. Stang, R. G., Nix, W. D., and Barrett, C. R., Trans. Met. Soc. AIME, 6A, 2065 (Nov. 1975).
23. Sullivan, R. A., J. Metals, 17, 45-48 (1965).
24. Sherman, D. H., An Investigation of the Characteristics of Hydrogen Charged Vanadium Metal, M.S. Thesis, Iowa State University, 1967.
25. Stoop, J., and Shaninian, P., Trans. ASM, 59, 411 (1966).
26. Peart, R. F. and Askill, J., Phys. Status Solidi 23, 263 (1967).

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