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Effect of Oxygen on Creep-Rupture of Niobium

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The creep-rupture properties of electron-beam-melted niobium with additions of oxygen up to 0.35 weight-percent were determined at 1900°F (1038°C), 2300°F (1260°C), and 2600°F (1427°C) at vacuums of 1×10^{-5} torr or better. Rupture life generally increased and minimum creep rate decreased as the level of oxygen was raised. There was no deleterious effect on ductility even with the high oxygen additions. Increases in hardness as a function of cold work and oxygen content were obtained. Activation energies for high-temperature creep were determined which showed good agreement with the reported experimental activation energies for self-diffusion.

At 1900°F, but not at 2300° and 2600°F, an anomalous behavior occurred which was manifested by a rapid acceleration followed by a deceleration in the flow process. The irregularity, which is represented as a step in the creep curve, occurs only under certain combinations of temperature, stress, and oxygen content. It appears to be related to substructure formation, and not to recrystallization or grain growth.

INTRODUCTION

In recognition of the susceptibility of niobium at elevated temperature to contamination by oxygen in most environments, including inert gases and practical vacuums, considerable attention has been given to the influence of this interstitial on mechanical properties. Much of the work has been directed toward the study of strain-aging phenomena and low-temperature properties.

Several investigators (1-3) have shown that the addition of oxygen to niobium in amounts up to approximately 0.4 percent raises yield and tensile strengths at room temperature. In addition, it has been demonstrated by others (4-6) that the strengthening effect extends to 1292°F (700°C). This temperature was observed to be the maximum for oxygen strengthening by Sheely (6) who found no apparent difference between tensile properties of materials containing 0.02 and 0.12 percent oxygen in the range 1292° to 2192°F (700° to 1200°C). Conflicting data by McCoy (7) which show oxygen improves strength properties at 1800° and 1950°F (982° and 1010°C) introduce uncertainty as to the effect of this interstitial element at the higher temperature range. A peak in strength which occurs in the region of 660° to 930°F (350° to 500°C) has been generally attributed to strain aging.

Although studies have been made on tensile properties, examination of the influence of oxygen

on creep properties has been neglected. On the basis of the above tensile data, the effect of the interstitial on creep is often assumed to be small at the higher temperatures. On the other hand, effects of section size and environment on creep strength are frequently attributed to contamination by atmospheric gases, particularly oxygen. Although indications have been obtained (7) that air contamination improves creep-rupture strength at 1800°F (982°C), no systematic study had been made of the influence of interstitial gases on creep properties. Also, knowledge of these effects at higher temperatures is lacking.

It was the purpose of this investigation to determine the effect of oxygen on the creep-rupture properties of niobium in the range 1900° to 2600°F (1038° to 1427°C). Materials with controlled additions of oxygen (up to 0.35 weight-percent) in solid solution were examined. In addition, a part of the study was devoted to exploration of an anomaly in the creep behavior, observed as a step in the creep curve. The discontinuity consists of a rapid acceleration followed by a deceleration in the creep process.

EXPERIMENTAL PROCEDURE

Material Preparation

Three electron-beam melted ingots, heats CF, CH, and CJ, whose compositions are given in Table 1 were used in the study. The heats contained no more than 30 ppm each of oxygen,

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TABLE 1
Impurity Contents of Niobium

Element	Impurity Content (wt-%)		
	Heat CF	Heat CH	Heat CJ
O	0.0030	0.0025	0.0028
N	0.0004	0.0011	0.0015
H	0.0001	0.00008	0.0003
C	0.003	0.002	0.0019
Ta	0.13	0.053	0.015
W	0.01	0.04	< 0.015
Mo	0.004	0.003	< 0.005
Zr	< 0.02	—	< 0.002
Ti	< 0.005	—	< 0.002
Fe	< 0.005	0.001	< 0.002
Cu	0.02	< 0.001	—
Al	0.01	< 0.001	—
Cr	0.003	—	—
Mn	< 0.002	< 0.001	—
Ni	< 0.002	< 0.001	—
Si	< 0.01	< 0.001	—
V	< 0.002	0.02	—
Mg, Sn, Co, Pb	each < 0.002	—	—

nitrogen, and carbon. The ingots, of 1-1/2-in. (38-mm) diameter, were cold swaged to 3/8-in. (9.5-mm) diameter. One of the heats, CF, which was examined in detail, attained a hardness of only 92 VHN, from an initial value of 56 VHN (10-kg load), after a reduction of 94 percent, as shown in a comparison with previously reported data (8-10) in Fig. 1.

The swaged material was machined into threaded-end creep-rupture specimens of 0.250-in. (6.35-mm) diameter and 1.0-in. (25.4-mm) gage length. As-machined specimens then were vacuum annealed prior to the introduction of oxygen. Heats CF and CJ, earmarked for testing at 1900°F (1038°C), were annealed at 2300°F (1260°C) for 10 hours, while heat CH to be tested mainly at 2300° and 2600°F (1260° and 1427°C) was annealed at 2800°F (1538°C) for 1 hour. The average grain diameters of heats CF and

CJ were 0.13 and 0.35 mm respectively, while that of heat CH was 0.45 mm.

Oxygen was added to and then uniformly distributed in the niobium in two stages. First, the niobium was exposed to either a helium-oxygen mixture or oxygen at a low pressure in a retort at intermediate temperatures to form a tightly adhering surface oxide. In the second stage, the surface oxygen was uniformly dispersed throughout the matrix by homogenization annealing at higher temperatures but still about 150°F (83°C) below the initial annealing temperature. Unoxidized niobium, which was to be used for comparison purposes, also was given the same annealing treatment. After these treatments, there was no significant increase in the content of gas or change in grain size. Oxygen additions were held within the solubility range of the lowest test temperature. Specimens containing oxygen at approximate levels of 0.02, 0.08, 0.10, 0.18, and 0.35 weight-percent were prepared. These were used for the tests, along with specimens of the base material, containing 0.003 weight-percent oxygen.

As a means of checking the condition of test specimens at various stages, control rods of 1/4-in. (6.35-mm) diameter were processed along with the creep-rupture specimens. Uniformity in hardness obtained on cross sections of the control rods after homogenization indicated that the oxygen was equally distributed throughout the material. The oxygen raised the hardness of the niobium from 60 to 325 VHN, which is in general agreement with the data of other investigators (11, 12), Fig. 2. No significant difference in hardness was observed between materials annealed at the two different temperatures.

Test Procedure

Creep-rupture tests were conducted in the range 1870° to 2600°F (1021° to 1427°C) in constant-load machines at vacuums of 1×10^{-5} torr or better for durations up to 600 hours. In most tests in the region of 1900°F (1038°C), the specimen was enclosed in an Inconel tube and heated externally by a resistance wound furnace. Tests at 2300° and 2600°F (1260° and 1427°C) were conducted in a cold-wall vacuum furnace equipped with a tantalum-tube heating element. Specimens were protected from desorbed gases in both vacuum chambers by enclosing them in a sheath

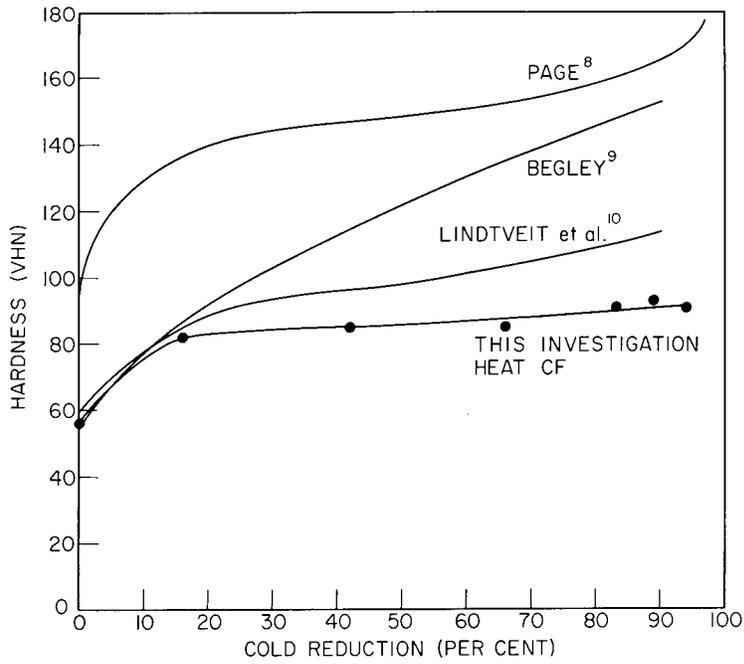


Fig. 1 - Effect of cold work on the hardness of niobium

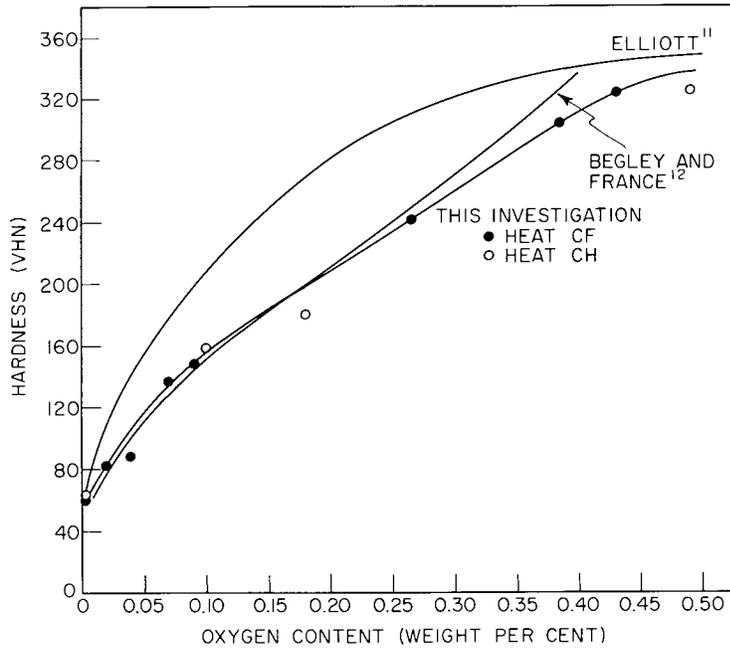


Fig. 2 - Effect of oxygen on the hardness of niobium

of niobium foil. No significant pickup of gases occurred during creep as revealed by weight gain measurement and vacuum fusion analysis. Strain measurements were made by means of both a dial gage attached to the pull rod and an autographic recorder attached to the lever arm. In addition, for the two higher temperatures, strains were measured by means of an extensometer connected to the specimen. In order to permit a detailed study of the creep behavior, some tests were interrupted at various stages.

Activation energies for creep were determined over temperature increments of 40°F (22°C) in three stages between 2280° and 2400°F (1249° and 1316°C) at a stress level of 1000 psi. In order to isolate the effect of temperature and maintain a constant structure during the determination, the technique (13) employed was to measure on a single specimen the steady-state creep rate at one temperature, lower the temperature rapidly and, after stabilization, measure the creep rate again. Calculations were made using the rate equation $R \ln(\dot{\epsilon}_1/\dot{\epsilon}_2) = \Delta H[(1/T_2) - (1/T_1)]$, where $\dot{\epsilon}$ is the creep rate, ΔH is the activation energy, T is the absolute temperature, and R is the gas constant.

RESULTS

Rupture Life

A marked improvement in the rupture life of niobium was evident at 1900°, 2300°, and 2600°F (1038°, 1260°, and 1427°C) for all levels of oxygen additions except 0.02 percent (Table 2). The strength of the material containing 0.02 percent oxygen, which was evaluated only at 1900°F (1038°C), was not significantly different from that of the base material (0.003 percent oxygen), as shown in Fig. 3. In tests at this temperature, the addition of 0.08 percent oxygen substantially increased rupture life, but higher amounts produced very little additional strengthening. In fact, the material of 0.35 percent oxygen usually had a shorter life than those of the intermediate oxygen levels. The closed symbols in Fig. 3 indicate irregular creep behavior. It is not certain whether the irregularity shortened or prolonged rupture life from that predicted by extrapolation of the normal data, but the change, if any, was small.

In contrast to the inconsistent trend of the oxygen effect at 1900°F (1038°C), the rupture life at 2300° and 2600°F (1260° and 1427°C) steadily increased with increase in oxygen content,

as shown in Fig. 4. This trend was characteristic for all stress levels. The rise in rupture life due to oxygen was generally slightly greater up to 0.1 percent than it was beyond that point.

Of the three heats of niobium used in the study, heat CJ, which had the lowest impurity content, also possessed the lowest strength. A comparison of the data for the 0.08-percent oxygen materials at 1900°F (1038°C), in Table 2, shows that for heat CJ a stress of 4500 psi produces rupture in about the same time (approximately 185 hours) as a stress of 6000 psi does for heat CF. Similarly, heat CJ, on the basis of the 0.18-percent-oxygen material at 1900°F (1038°C), also appears weaker than heat CH, exhibiting a 225-hour rupture strength of approximately 4500 psi compared to 5000 psi for the more impure heat. Differences in tantalum contents, the major impurity (Table 1), were most likely responsible for the differences in strengths between the heats. The amounts of the tantalum increased in the same order as the indicated relative strengths: 0.015 percent in heat CJ, 0.053 percent in heat CH, and 0.13 percent in heat CF.

At all test temperatures, regardless of oxygen content, the niobium displayed high elongation and high reduction of area. Elongation-at-fracture values, listed in Table 2, were over 32 percent under all test conditions. The ductility values at 1900°F (1038°C) in most cases were lower than those at the higher temperatures. No effect of oxygen was observed on the ductility except at the two highest temperatures, where the material with 0.35 percent oxygen showed lower elongation at fracture than did those with less oxygen.

Minimum Creep Rates

The addition of oxygen to niobium generally reduced minimum creep rates, consistent with its effect on rupture life. This trend was indicated at 1900°F (1038°C), Fig. 5, despite the presence of considerable scatter in data for the two lots containing the lowest oxygen. No minimum creep rate values were plotted in Fig. 5 for the irregular creep curves. This excluded a curve for 0.08 percent oxygen, since most of the creep curves for this level were irregular. Minimum creep rates at 2300° and 2600°F (1260° and 1427°C) clearly decreased with increasing oxygen additions, as shown in Fig. 6.

TABLE 2
Creep Rupture Data

Temp.		Stress (psi)	Oxygen Content (wt-%)	Rupture Life (hr)	Minimum Creep Rate (%/hr)	Elong. (%)
(°F)	(°C)					
Heat CF						
1870	1021	4500	0.003	> 185.5	*	—
1900	1038	7000	0.003	8.9	0.047	37
			0.02	2.4	0.14	54
			0.08	23.7	0.025	52
			0.18	65.6	*	36
			0.35	40.9	*	41
			6500	0.003	11.5	0.054
		0.003	14.0	0.029	54	
		0.02	14.9	0.048	62	
		0.02	12.7	0.080	40	
		0.08	151.7	*	44	
		0.18	148.9	*	42	
		0.35	68.5	0.041	50	
		6000	0.003	16.9	0.033	40
		0.02	11.4	0.039	38	
		0.02	11.8	0.040	49	
		0.08	177.0	*	46	
		0.18	276.8	0.020	44	
		0.35	90.6	0.027	44	
		5500	0.003	20.4	0.033	36
		0.02	19.7	0.014	41	
0.02	25.1	0.020	56			
0.08	475.5	*	53			
0.18	363.3	0.013	43			
0.35	292.6	0.013	48			
5000	0.003	66.6	0.0073	54		
0.02	101.7	*	47			
4500	0.003	146.7	*	45		
0.003	497.5	*	47			
1930	1054	4500	0.003	146.4	*	56
Heat CH						
1900	1038	5000	0.18	233.3	*	59
		4800	0.27	323.1	*	40
2300	1260	2230	0.003	2.0	23.	84
			0.18	6.3	3.8	60
		2000	0.003	13.6	2.1	86

TABLE 2 (Continued)
Creep Rupture Data

Temp.		Stress (psi)	Oxygen Content (wt-%)	Rupture Life (hr)	Minimum Creep Rate (%/hr)	Elong. (%)		
(°F)	(°C)							
Heat CF (Continued)								
2600	1427	1500	0.10	21.3	1.5	73		
			0.18	55.2	0.42	79		
			0.35	153.6	0.11	51		
		1800	0.003	92.2	0.35	87		
			0.10	329	0.065	62		
			0.18	467.6	0.044	73		
			0.35	632.6	0.031	54		
		1800	0.003	0.7	46.	82†		
			0.18	3.5	7.7	70†		
		2600	1427	1500	0.003	2.5	13.5	78†
					0.003	3.5	8.3	—
					0.10	12.6	2.3	75†
0.18	11.				2.8	73†		
0.35	36.				0.58	60†		
Heat CJ								
1900	1038	6500	0.08	<0.1	—	68		
			0.08	0.4	—	60		
		5000	0.08	2.4	0.17	64		
			0.08	4.6	1.0	46		
			0.003	108.3	0.0029	—		
		4500	0.08	189.6	*	39		
			0.18	218.2‡	0.029	33		
			0.08	187.2	*	40		
		4200	0.08	262.3§	*	51		

*Irregular creep curve.

†Rupture prevented by test machine.

‡Annealed 2800°F (1538°C), 1 hr.

§Prestrained a small amount at room temperature.

Creep Curves

In contrast to the normal creep behavior of the materials at 2300° and 2600°F (1260° and 1427°C) as illustrated in Fig. 7, the creep curves in the region of 1900°F (1038°C) in a number of instances showed a pronounced irregularity in

the form of a step. As shown in Fig. 8, the irregularity which has been observed to occur usually in the steady-state stage of creep consists of a rapid acceleration followed by a deceleration in the flow process. It may also take place shortly after application of the load as well as relatively late in the test. The phenomenon has been found

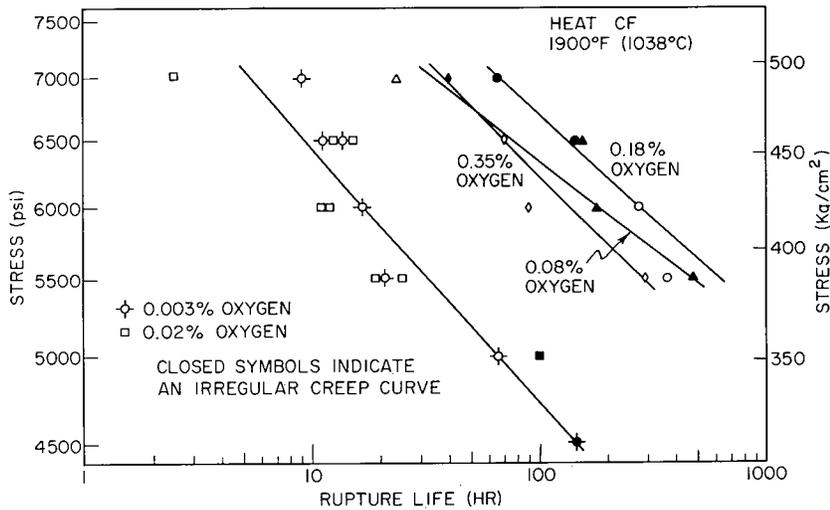


Fig. 3 - Influence of oxygen on the rupture life of niobium at 1900°F (1038°C)

in niobium of all oxygen levels and in all three heats tested, demonstrating its generality even though it does not occur under all test conditions, as indicated in Tables 2 and 3.

Certain characteristics of the irregularity appear to be related to test temperature, initial stress level (or a related parameter), and oxygen content of the material (Table 3). By lowering the temperature, the initiation of the step is delayed and the duration generally is increased. For example, the time in test before appearance of the step was increased from 35.7 to 81.5 hours by a reduction in temperature from 1930° to 1870°F (1054° to 1021° C). The dependence on stress of the development of the step is shown in Fig. 9. An increase in the initial stress level reduces the initiation time, generally shortens the duration of the step, and increases the magnitude of the strain involved (Fig. 10). With increase in oxygen content, the phenomenon is delayed to a later period in creep and the magnitude of the strain is reduced (Fig. 8). Also, with higher oxygen, the stress range in which the step appears shifts to a higher level. Another factor which was found to affect initiation time was pre-strain. A small prestrain of a test specimen in tension at room temperature, imparted unintentionally, delayed the beginning of the step to 37 hours whereas without the prestrain the time would have been approximately 1 hour. It is noteworthy that the total strain of the irregularity may be as high as 10 percent.

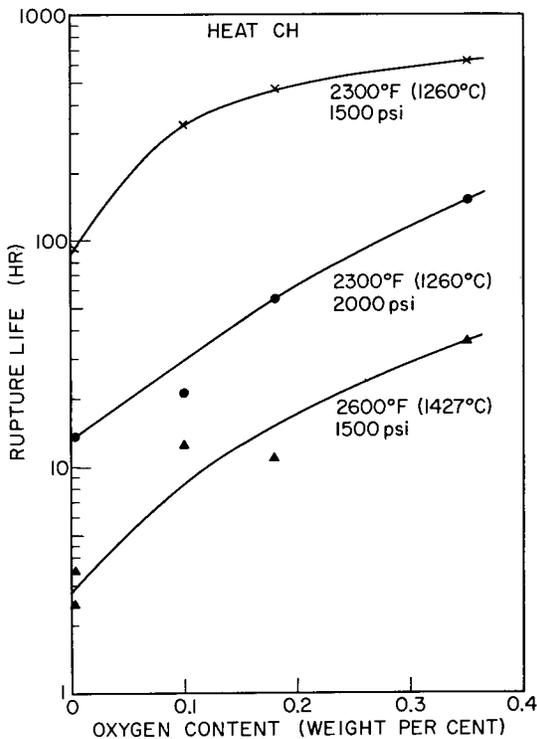


Fig. 4 - Influence of oxygen on the rupture life of niobium at 2300° and 2600°F (1260° and 1427°C)

An interesting characteristic of the irregularity is that the creep rate was greater before acceleration than after completion of the step (except in several instances when the step occurred shortly

TABLE 3
Characteristics of Creep Irregularity

Temp. (°F)	Temp. (°C)	Stress (psi)	Oxygen Content (wt-%)	Rupture Life (hr)	Initiation of Step (hr)	Total Strain During Step	Duration of Step (hr)	Creep Rate (%/hr)		
								Lowest Before Step	Lowest After Step	Maximum of Step
Heat CF										
1870	1021	4500	0.003	> 185.5	81.5	0.047	20.7	0.0052	0.0055	0.45
1900	1038	7000	0.18	65.6	0.05	0.057	0.8	2.51	0.017	14.57
			0.35	40.9	26.9	0.022	0.8	0.069	0.084	3.67
		6500	0.08	151.7	5.9	0.11	2.2	0.068	0.016	6.33
			0.18	148.9	41.7	0.049	3.5	0.017	0.010	1.70
		6000	0.08	177.0	8.1	0.040	8.8	0.034	0.016	1.51
		5500	0.08	475.5	16.0	0.010	2.4	0.023	0.017	0.71
		5000	0.02	101.7	21.3	0.081	16.5	0.011	0.013	0.74
		4500	0.003	146.7	55.4	0.066	16.0	0.010	0.0070	0.72
			0.003	497.5*	1st 108.0	0.088	80.0	0.0046	0.0027	0.15
					2nd 332.0	0.078	48.0	0.0027	0.062	0.24
1930	1054	4500	0.003	146.4	1st 35.7	0.037	13.9	0.014	0.0085	0.53
					2nd 70.4	0.086	33.0	0.0085	0.078	0.43
Heat CJ										
1900	1038	4500	0.08	†	0.6	—	—	0.43	—	—
			0.08	‡	0.3	0.070	2.3	0.52	—	7.12
			0.08	189.6	1.3	0.054	3.1	0.15	0.0028	3.44
		4200	0.08	‡	0.95	0.079	3.0	0.34	0.022	4.41
			0.08	187.2	1.9	0.048	3.6	0.15	0.0037	1.80
			0.08	262.3‡	37.0	0.057	3.6	0.018	0.0028	2.31
Heat CH										
1900	1038	5000	0.18	233.3	119.3	0.029	4.5	0.0060	0.0057	1.16
		4800	0.27	323.1	237.7	0.018	2.4	0.0034	0.017	0.84

*Annealed at 2300°F (1260°C) for 10 hours.

†Test interrupted at the beginning of the step.

‡Test interrupted immediately after the completion of the step.

§Prestrained a small amount at room temperature.

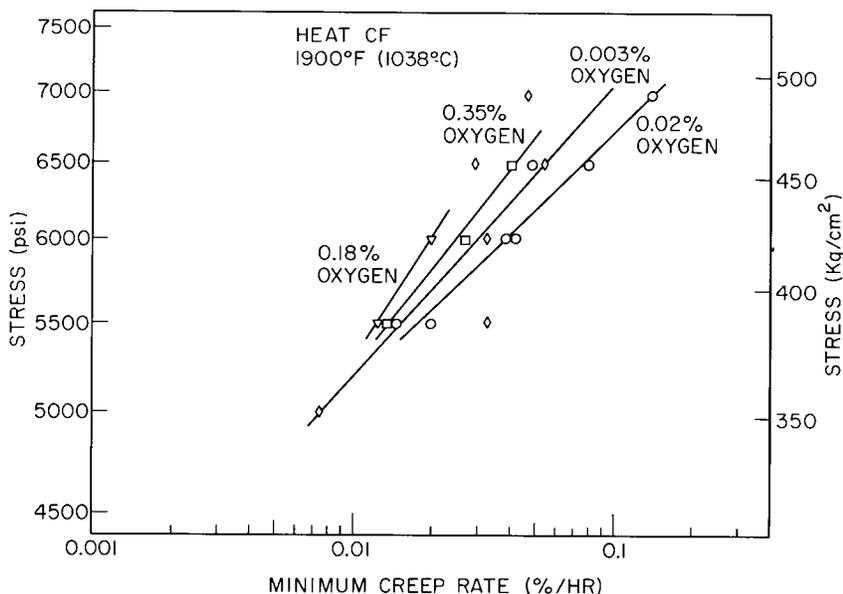


Fig. 5 - Influence of oxygen on the minimum creep rate of niobium at 1900°F (1038°C)

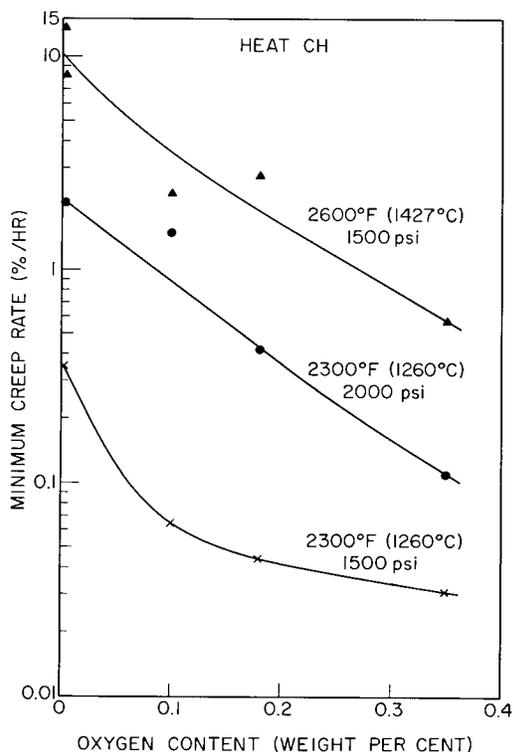


Fig. 6 - Influence of oxygen on the minimum creep rate of niobium at 2300° and 2600°F (1260° and 1427°C)

before the final stage of creep leading to rupture). In view of the higher stress the reduced area must support after the step as a result of the straining, the lower creep rate indicates strengthening has taken place.

It is evident that certain combinations of conditions (temperature, stress, oxygen content) must exist for the irregularity to appear, and these are confined to a relatively limited range. Yet the discontinuity is remarkably reproducible as demonstrated by the data for heat CJ containing 0.08 percent oxygen (Table 3), which for several tests consistently show the step shortly after loading in what were expected to be relatively long-time tests. It should be further noted that heat CF with the same amount of oxygen (0.08 percent) also exhibits a step relatively early in the test. In all of the tests the discontinuity was observed only once except in two tests for heat CF where double steps occurred. Only the first step was considered in the correlations.

The irregularity appears in a temperature range in the neighborhood of half the melting point. At each test temperature it is limited to a stress range which is raised by increases in oxygen content.

In an experiment to determine if the decelerating creep in the irregularity is due to strain

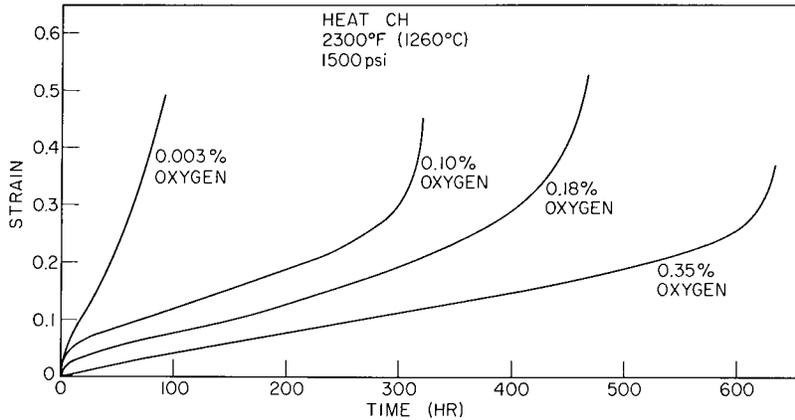


Fig. 7 — Creep curves of niobium containing various amounts of oxygen at 2300°F (1260°C) and 1500 psi

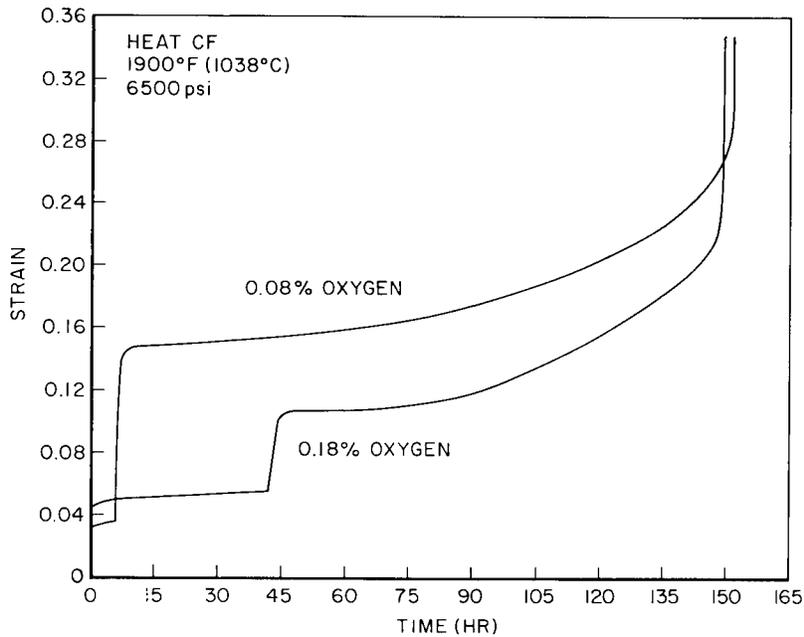


Fig. 8 — Anomalous creep behavior of niobium at 1900°F (1038°C) for two levels of oxygen

hardening, a specimen of heat CJ, in test at 1900°F (1038°C) and 4200 psi, was unloaded after completion of the step, held at temperature for 16 hours, and then reloaded. Although the original step had begun to form in 1 hour, a discontinuity did not reappear even in 4 hours after the recovery anneal. Instead, the material continued to creep at a very low rate along the line it would be expected to follow had no interruption occurred. It was apparent that the anneal did not affect the creep behavior, indicating that strain

hardening did not play a significant part in the decelerating creep phase of the step.

For those specimens of heat CF which displayed normal three-stage creep behavior at 1900°F (1038°C), oxygen produced an effect which altered the shape of the curve. The creep curves of the 0.003-percent and 0.02-percent oxygen materials, although of the conventional type, were unusual for a ductile material in that the initial and tertiary stages were of very short duration, while the steady-state stage comprised generally

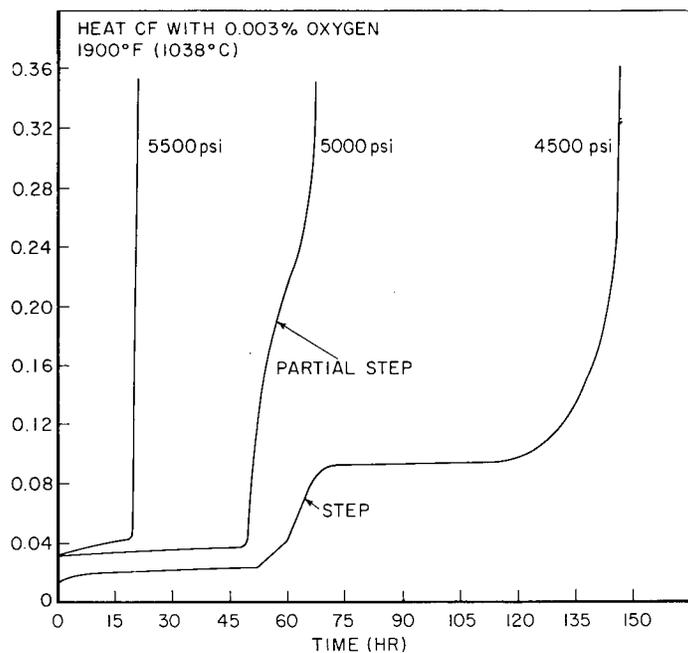


Fig. 9 - Dependence on stress of the development of the step in creep curves for niobium at 1900°F (1038°C)

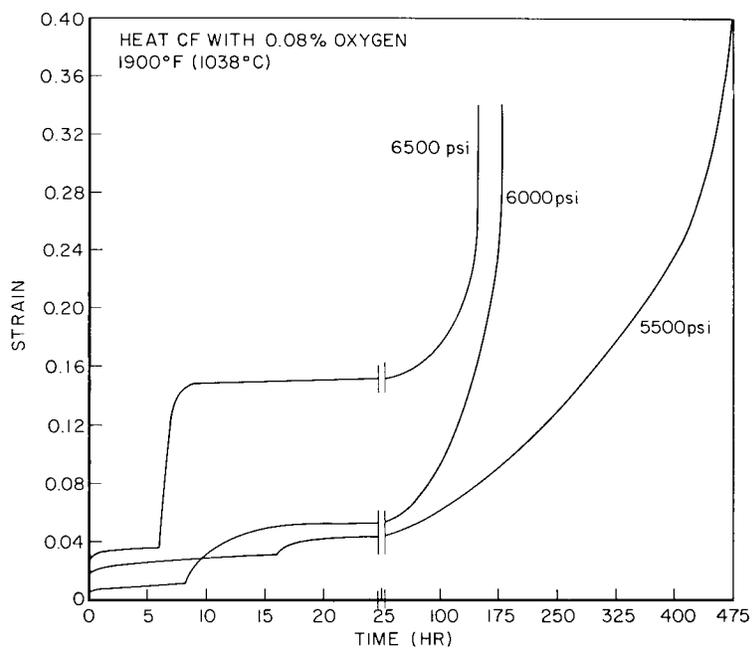


Fig. 10 - Effect of stress on the initiation time, duration, and magnitude of the step in creep curves for niobium at 1900°F (1038°C)

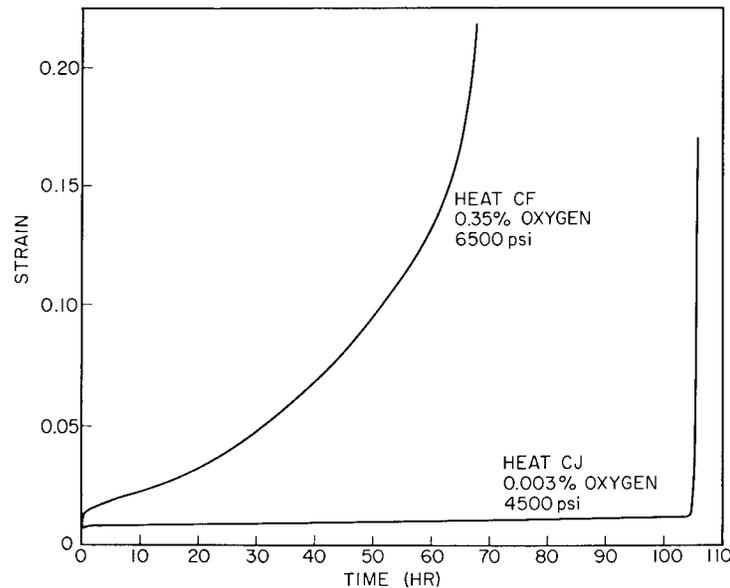


Fig. 11 — Typical creep curves showing the influence of oxygen on the shape of the curves at 1900°F (1038°C)

over 90 percent of the test. A typical curve (that of heat CJ) is shown in Fig. 11. During the second stage, creep strain was unusually low, reaching a maximum of about 1 percent. With increase in oxygen content of the material, the shape of the creep curve changed to include substantially larger portions of accelerating creep at the sacrifice of the second stage, as illustrated by the curve for Heat CF in Fig. 11. On the basis of limited evidence, heat CH displayed the same behavior as heat CF, but heat CJ was different in that even the high oxygen material underwent a comparatively long period of steady-state creep.

Activation Energy Determinations

The average value of the activation energy for high-temperature creep of the base niobium (0.003 percent oxygen) computed using the drop in temperature method in the range 2280° to 2400°F (1249° to 1316°C) was 95,000 cal/mole (Table 4). For comparison, activation energies for creep were determined using the minimum creep rate values obtained at 2300° and 2600°F (1260° and 1427°C) and were found to be in reasonably good agreement with the aforementioned value, averaging 106,000 cal/mole. An effect of oxygen on the creep activation energies of the niobium was not discernible.

An attempt made to determine the activation energy for creep at 1900°F (1038°C) employing the drop in temperature technique was unsuccessful. The steady-state creep rates, attainable for reasonable durations, were of such low magnitude that no accurate measurements could be made. An increase in the initial stress made in order to raise creep rates produced rapid extension and early rupture.

Inasmuch as the time interval before the appearance of the step phenomenon displayed a certain regularity with respect to temperature, it was considered of interest to determine an activation energy for its formation. In order for the activation energy value to have significance, the assumption is made that a single process is effective in causing the discontinuity and that it operates without interference while the specimen is under load. In any event the value shows the temperature dependence of the step formation. The activation energy for the beginning of the step, determined for heat CF in the range 1870° to 1930°F (1021° to 1054°C), Table 3, was 86,000 cal/mole. This value was determined from the slope of an Arrhenius plot of the logarithm of the reciprocal of the time for beginning of the step against the reciprocal of the test temperature (Fig. 12).

TABLE 4
Activation Energies for High-Temperature Creep of Niobium

Oxygen Content (wt-%)	Stress (psi)	Temp. ₁ (°K)	Temp. ₂ (°K)	Creep Rate ₁ (%/hr)	Creep Rate ₂ (%/hr)	Activation Energy (cal/mole)
Determined by Drop in Temperature Method at 1000 psi						
0.003	—	1589	1563	0.80	0.51	100,000
0.003	—	1563	1544	0.66	0.42	96,000
0.003	—	1544	1522	0.48	0.31	89,000
Determined from Minimum Creep Rates						
0.003	1500	1533	1700	0.35	13.5	113,000
0.003	1500	1533	1700	0.35	8.3	98,000
0.10	1500	1533	1700	0.065	2.3	111,000
0.35	1500	1533	1700	0.031	0.58	91,000

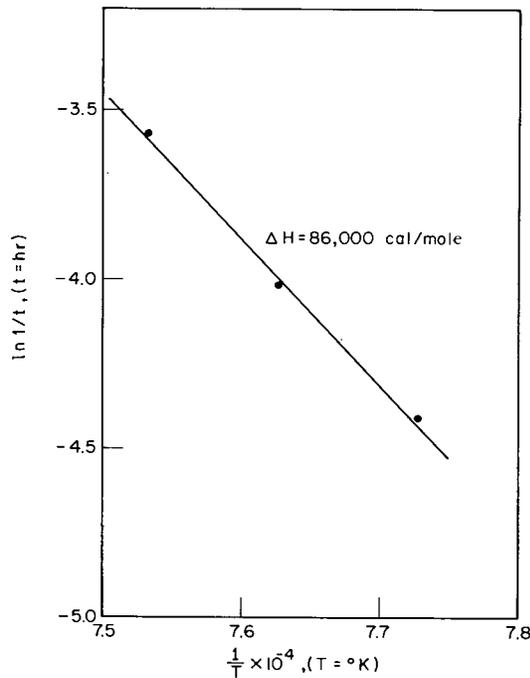


Fig. 12 - Arrhenius plot of the initiation time for the irregular creep behavior of niobium in the region of 1900°F (1038°C)

Structural Examination

Metallographic examination of ruptured specimens showed a single phase structure and dis-

closed no voids or cracks, regardless of oxygen content. The presence of substructure, shown in Fig. 13, was revealed in materials tested at all the temperatures. For the higher test temperatures, the subgrain size was noticeably larger. In addition, prominent subgrain formation in many cases was accompanied by serrations in the grain boundaries. No effect of oxygen on the formation or size of the substructure was noted.

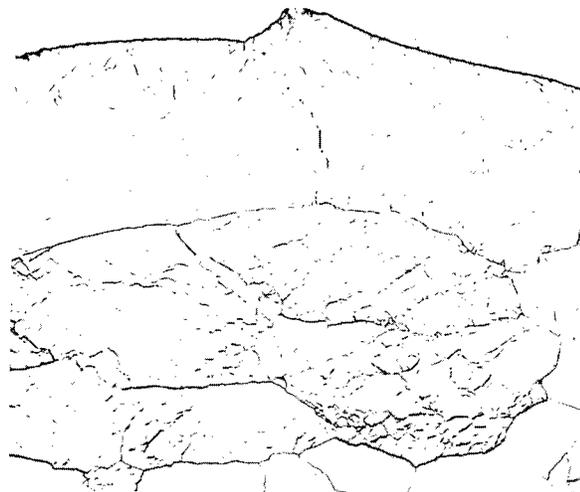


Fig. 13 - Typical substructure in niobium (0.08 percent oxygen) tested at 1900°F (1038°C) and 5500 psi. Etched in HF, HNO₃, and lactic acid (1:1:9). 200X. (Reduction in printing approximately 30%.)

Evidence of recrystallization was not observed in the test materials except in the neighborhood of the rupture surfaces of a few specimens. In these, recrystallization occurred at about the time of rupture and is not considered of significance. Grain size measurements of the heat CJ material which was tested at 1900°F (1038°C) and interrupted after completion of the step disclosed that the creep irregularity was not associated with recrystallization or grain growth. However, substructure was revealed (Fig. 14) which was not observed immediately prior to the step. Also, after completion of the step there was no evidence of localized necking in the specimen which had been strained 7 percent; the extension had taken place uniformly over the entire gage section.

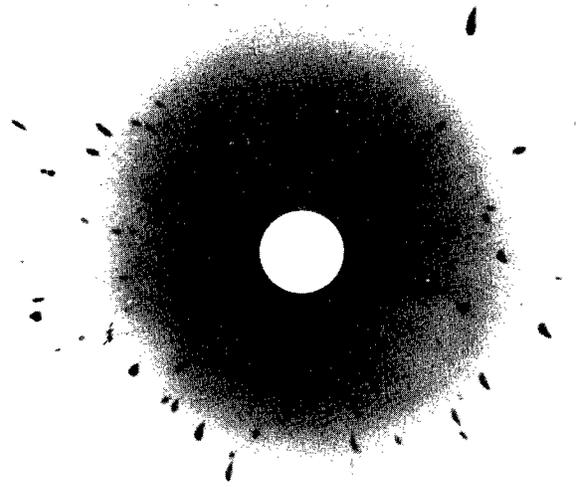
Laue back-reflection patterns made of interrupted test specimens showed evidence of subgrain formation, a breakup of spots, upon completion of the step but not immediately before (Fig. 15). The breakup of the spots was accompanied by faint asterism, indicating possibly strain hardening.

DISCUSSION

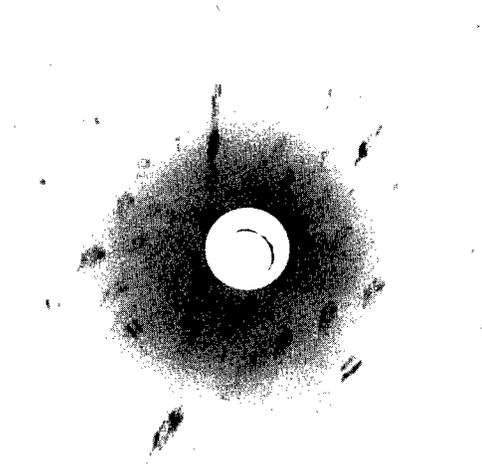
Although irregularities in creep curves reported in the literature have been attributed to strain aging or recrystallization in test, the creep anomaly observed in this study, represented as a step in



Fig. 14 — Substructure in niobium tested at 1900°F (1038°C) and interrupted after completion of the step. Etched in HF, HNO₃, and lactic acid (1:1:9). ~500X. (Reduction in printing approximately 30%.)



(a) Test interrupted before step formation



(b) Test interrupted after step formation

Fig. 15 — Laue back-reflection pattern of niobium (heat CJ) of test interrupted (a) before step formation and (b) after step formation

the creep curve, did not appear to be caused by either of these processes. Strain aging, on the basis of theoretical consideration of the diffusivity of the interstitials (14, 15) should produce the greatest strengthening for oxygen and nitrogen at about 572° and 1112°F (300° and 600°C) respectively and be relatively ineffective at 1900°F (1038°C). A shift of the strain aging reaction to higher temperatures by the addition of substitutional solutes, as reported by Sheely (16), is

unlikely in the base niobium of this study because of the low concentration of substitutional as well as interstitial elements. In addition, the absence of evidence of recrystallization after occurrence of the step also eliminates this process as being responsible for the irregularity.

Any explanation of the phenomenon must account for the sudden acceleration in creep after a relatively steady period, and the subsequent rapid decline, during which time local necking of the specimen did not take place. The abrupt increase from a low to a high rate of creep suggests a change in the rate-controlling mechanism.

At the temperatures under consideration, creep in the early steady-state part of the test may be controlled by slip, or another nondiffusion-controlled process, while later, diffusion-controlled climb may supersede it. The climb process involves the diffusion of vacancies to or from the dislocations and therefore is governed by temperature and time. At the temperature at which the acceleration takes place, a certain interval of time is required for vacancies in sufficient number to arrive at dislocations to permit climb to become pronounced, and controlling. Climb allows dislocations to move out of their slip planes and facilitates the rearrangement of dislocations into subgrain boundaries. The operation of these mechanisms as described could produce an abrupt discontinuity, such as the observed step, in the creep curve.

In the initial part of the step, rapid dislocation climb produces an acceleration in creep, and leads to subgrain formation. The creation of a more stable substructure, accompanied possibly by a small amount of strain hardening, results in a deceleration of creep at the top of the step when a steady-state condition is reached. X-ray and metallographic evidence was obtained which showed subgrain formation during the period of the irregularity. Although there appeared to be faint asterism connected with spots in the Laue pattern, the role of strain hardening was indicated to be minor by the fact that a recovery anneal given the specimen at the completion of the step did not alter the course of subsequent creep.

On the basis of this explanation, many of the characteristics of the phenomenon can be understood. Other explanations, of course, may also appear suitable because of the lack of more definitive experiments.

Although activation energies for self-diffusion and high-temperature creep (> 0.5 m.p.) have been shown to be equal in a number of metals (13), no corroborative data were available for niobium. The activation energies for creep in the literature (17-19), determined in the range 0.42 to 0.54 of the melting temperature were inconsistent and generally lower than the reported values for self-diffusion of 105,000 cal/mole by Resnick and Castleman (20) and 95,000 cal/mole by Peart *et al.* (21). The activation energy for creep-rupture determined by Orr and Bainbridge (18), for example, was 75,000 cal/mole. Although the value was obtained for the range 0.42 to 0.46 of the melting temperature, it has been considered as the value for high-temperature creep (13).

Activation energies of 95,000 and 106,000 cal/mole obtained in this investigation (Table 4) in the range 0.56 to 0.62 of the melting temperature agree favorably with the values above for self-diffusion. Of the two values for high-temperature creep which were obtained by different methods, the lower one determined by the temperature-drop technique is considered more reliable.

SUMMARY

In this study the influence of oxygen additions (to 0.35 percent) on the creep-rupture behavior of electron-beam melted niobium was determined in the range 1900° to 2600°F (1038° to 1427°C). The following are considered to be the main findings of the investigation:

1. The addition of oxygen generally increased rupture life and reduced minimum creep rate in the temperature range under study. An exception was the material containing 0.02 percent oxygen, which had about the same strength as the base niobium (0.003 percent oxygen).
2. A proportionately larger improvement in creep-rupture strength was generally produced by an oxygen addition of 0.08 percent than by larger amounts, especially at 1900°F (1038°C).
3. Niobium of all oxygen levels possessed high elongation at fracture and high reduction of area under all test conditions. No cracks or voids were present in ruptured test specimens.
4. The creep behavior in a number of tests in the region of 1900°F (1038°C) was irregular in that a step was produced in the creep curve. The

phenomenon was characterized by a rapid acceleration followed by a retardation in the normal course of creep. It occurred in test under certain combinations of temperature, stress, and oxygen content which controlled its time of appearance, total strain involved, and other characteristics.

5. Structural examination disclosed that the creep irregularity was not associated with recrystallization or grain growth. The acceleration of creep in the initial phase of the irregularity was attributed to recovery by dislocation climb and the deceleration near the termination principally to the formation of a more stable substructure.

6. The activation energy for high-temperature creep of niobium, determined by the drop in temperature method (95,000 cal/mole), was observed to be in good agreement with that for self-diffusion.

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