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Long-Time Creep Behavior of Nb-1Zr Alloy Containing Carbon

R.H. Titran
National Aeronautics and Space Administration
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Work performed for
U.S. DEPARTMENT OF ENERGY
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SUMMARY

A preliminary study was conducted to determine the feasibility of using a carbon-modified (0.06 wt %) Nb-1Zr alloy to meet the elevated temperature requirements of advanced space power systems. A Nb-1Zr-0.06C alloy was creep tested at 1350 and 1400 K (approximately 1/2 melting point) and the data compared to similar results from tests of a Nb-1Zr alloy. The Nb-Zr-C alloy in the annealed condition (1 hr at 1755 K plus 2 hr at 1475 K) was more than five times stronger than the annealed (1 hr at 1475 K) Nb-1Zr alloy. Aging the Nb-Zr-C alloy for 1000 hr at 1350 or 1400 K drastically reduced the high stress creep strength. However, even in the weakened, aged condition, the strength of the Nb-Zr-C alloy was more than four times that of the Nb-1Zr.

INTRODUCTION

Space power systems necessary to furnish electrical power for advanced communication satellites, or manned space craft or stations will be required to produce electrical power levels ranging from several hundred kilowatts to many megawatts. These high power requirements will exceed the capability of photovoltaics or batteries. The dynamic power-conversion systems such as the Stirling, Brayton or Rankine cycles afford a promising growth potential for the higher power level systems.

Advanced materials for these dynamic conversion systems play a major role in meeting the stringent size and performance requirements of future space power systems. The conversion systems which have requirements of extended lives in the 7 to 10 year realm and operating temperatures in excess of 1350 K dictate the use of refractory metals (ref. 1) for the construction of the heat source and ancillary power-conversion components. Nb-1Zr has historically (refs. 2 and 3) been suggested as suitable for low power level designs of space nuclear power systems, primarily for its resistance to liquid alkali metal corrosion, and for its elevated temperature (1100 K) creep strength. However, at temperatures above 1350 K, the suitability of Nb-1Zr as a creep-resistant space power system component material becomes questionable, especially in view of an expected 7 to 10 yr service life.

In order to increase the high-temperature strength and creep resistance of these components, a preliminary study was conducted at the NASA Lewis Research Center (ref. 4) to determine the feasibility of using the Pratt and Whitney Aircraft Corporation carbon-containing niobium alloy, PWC-11 (ref. 5). The PWC-11 alloy, with a nominal composition of Nb-1Zr-0.1C, was developed during the mid 1960's (ref. 6). Through experimentation with the carbon level and various thermomechanical processing treatments, it was shown (ref. 7) that the short-term tensile creep strength was 3 to 4 times that of the base Nb-1Zr alloy. However, because the PWC-11 alloy's high-temperature creep strength has been attributed to the presence of very fine precipitates of $(Nb,Zr)_2C$ and (Nb,Zr)C ranging in size from ten to hundreds of nanometers (ref. 6), the long-term effectiveness of these carbides is suspect. Tensile tests performed at 1335 K on PWC-11 specimens after aging for 1000 to 3000 hr at 1335 K showed a 50 percent drop in yield strength with a 50 percent increase in elongation (ref. 6), classical indications of an overaged material. The purpose of this study was: (1) to determine the 1000 to 6000 hr creep strength of an annealed Nb-Zr-C alloy between 1350 and 1400 K; (2) to determine if the Nb-Zr-C alloy would maintain its creep strength superiority over Nb-1Zr when tested at very low stress levels; and (3) to assess the effect of isothermal aging on the creep strength and microstructure. It was intended that the 1000 hr thermal aging would simulate a portion of a possible stress-free condition during initial operation of a space power system.

MATERIAL

The Nb-Zr-C alloy (table I) was received from the Oak Ridge National Laboratory in the form of as-rolled, 1 mm thick tensile creep test specimens machined as shown in figure 1. Unfortunately, a detailed processing history of this particular lot of specimens was not available. This material was part of an early attempt at a manufacturing scale-up from laboratory development, and derived from a single arc-melt followed by a single primary breakdown extrusion at about 1350 K. The subsequent processing of this "scale-up" material into sheet is believed to have yielded a material which does not reflect proper conditioning of the Nb-Zr-C alloy. Thus, the creep properties reported in this study are presumably less than optimum.

The Nb-1Zr alloy (table I), also procured from the ORNL in sheet form, had been processed by the industry's normal and acceptable practices. Thus, it is believed that the test results for Nb-1Zr will be typical of the properties which can be obtained from this alloy.

EXPERIMENTAL PROCEDURE

The tensile creep specimens were machined with the longitudinal axis parallel to the rolling direction. Prior to creep testing, all of the specimens were degreased, rinsed successively in distilled water and alcohol, wrapped in cleaned tantalum foil, and then annealed in titanium sublimation-pumped systems at a pressure below 5×10^{-5} Pa as follows:

Nb-1Zr alloy: 5 specimens for 1 hr at 1475 K. In addition 1 specimen for 1 hr at 1755 K and 1 specimen for 1 hr at 1755 K plus 2 hr at 1475 K.

Nb-Zr-C (PWC-11): 11 specimens for 1 hr at 1755 K plus 2 hr at 1475 K. In addition, two of this latter group of annealed specimens were subsequently aged in vacuum for 1000 hr at 1350 K and another two samples were vacuum exposed for 1000 hr at 1400 K.

The 1000 hr aging heat treatment of the Nb-Zr-C alloy prior to creep testing was chosen to answer several questions and concerns: (1) does thermal aging have the same detrimental effect on creep strength as was previously reported for tensile yield strength (ref. 5), and (2) would the Nb-Zr-C alloy lose its creep strength with time due to aging, thus becoming weaker than Nb-1Zr.

Creep testing was conducted in internally loaded constant-load, high-vacuum (bakeable titanium sublimation-pumped) chamber (ref. 8), equipped with tantalum split-sleeve resistance heaters. The pressure was generally in the 10^{-5} Pa range at the start of the test and decreased to about 5×10^{-6} Pa after several hundred hours of testing. Creep testing was conducted at 1350 and 1400 K with stresses ranging from 45 to 5 MPa, and strains were measured by frequent optical readings of fiducial marks in the reduced gauge section. Although tests were generally terminated after 1 percent strain, a few tests were continued to strains as high as 3 percent.

RESULTS AND DISCUSSION

Figure 2 shows the microstructure of the as-rolled condition (a) and of the annealed condition (b) for the Nb-Zr-C alloy. The annealed material had a mixture of elongated and equiaxed grains with an average grain size of approximately 25 μm measured by the circle-intercept method, with an aspect ratio of approximately 5:1. Numerous shapes and sizes of particles were apparent in the microstructure. The morphology ranged from massive 5 μm particles decorating grain boundaries to submicron needle-like particles which appeared to be oriented on slip planes. The majority of particles were believed to be primary carbides which were formed during the initial solidification and were neither broken up nor dissolved during the sheet rolling processes. Figure 3 shows the microstructure of the 1475 K, 1 hr annealed Nb-1Zr which resulted in a small grained microstructure (average grain diameter of approx 20 μm) and a fine dispersion of ZrO_2 particles.

All creep curves generated for the two Nb-base alloys during this study are presented in figures 4 to 7. Comparison of the data for Nb-Zr-C in figures 4 and 5 indicate that aging prior to creep testing considerably weakens this material. Contrast of the behavior for Nb-1Zr (figs. 6 and 7) and Nb-Zr-C (figs. 4 and 5) for identical conditions shows that the carbon addition strengthens the alloy considerably. These trends are reinforced by the time-to-1-percent-strain creep data in tables II and III, clearly showing that Nb-Zr-C is superior to Nb-1Zr.

Although neither alloy is considered to be in its optimum creep-resistant condition (the Nb-1Zr was annealed 1 hr at 1475 K with a relatively small average grain size of 20 μm, and the Nb-Zr-C had a grain size of about 25 μm with large particles present, possibly primary carbides from the melt), it is believed that the creep strength ranking would not change in samples processed at the optimum conditions. For example, the Nb-1Zr annealed for 1 hr at 1755 K (approx grain size of 45 μm), tested at 1350 K and 40 MPa, reached 1 percent strain in 105 hr while the Nb-Zr-C in the annealed condition required 3450 hr to achieve 1 percent strain. Even though doubling the grain size of Nb-1Zr reduced the creep rate at 1 percent strain (Table III) by almost a factor of 3, the carbon addition to the Nb-1Zr composition resulted in reducing its creep rate by over two orders of magnitude.

Thermal aging for 1000 hr at 1350 or 1400 K prior to creep testing reduced the creep strength of the NB-Zr-C alloy, similar to the effect of thermal aging on the tensile yield strength of PWC-11 (ref. 6). For comparison to creep tests of unaged (annealed) specimens at 1350 and 1400 K, samples aged at 1400 K were creep tested at 1350 and 1400 K and samples aged at 1350 K were tested at 1350 K. The 1000 hr aging heat treatments prior to testing resulted in a ~90 percent reduction in the time to achieve 1 percent strain at 1350 K and 40 MPa (3500 hr versus 310 hr). Aging at 1400 K compared to aging at 1350 K resulted in about a 40 percent reduction in the time to achieve 1 percent creep strain under 1350 K and 40 MPa test conditions (170 hr for 1400 K aged versus 310 hr for 1350 K aged. This effect is small, however, compared to the effect of any prolonged aging, per se, on creep strength.

The high temperature creep strength of the Nb-1Zr-0.01C alloy (PWC-11) has been attributed to the presence of very fine precipitates of $(Nb,Zr)_2C$ and/or (Nb,Zr)C ranging in size from tens to hundreds of nanometers in diameter (ref. 7). However, initial metallographic examination (optical and SEM) of the aged and creep tested specimens could not explain the differences in creep strength on the basis of carbide morphology. The microstructure of the aged then tested specimens is characterized by extensive fine matrix precipitation (fig. 8) and is similar to the structure prior to testing. This annealed and tested microstructure is quite different from that of the annealed condition (fig. 2(b)) where:

(1) The large integrangular precipitates found in the annealed material are no longer evident after creep testing, and

(2) Considerably more matrix precipitation is evident in the creep tested 1000 hr aged alloys than in the annealed condition.

Since the Nb-Zr-C material is stronger in the annealed condition, it appears that the presence of large intergranular precipitates may act by pinning the elongated grains to prevent grain boundary sliding. It is also probable that the large primary carbides undergo dissolution and reprecipitation as a coherent phase. This is supported by previous work (ref. 10) on a tantalum alloy, where the carbide phase transformed in the presence of a stress. In the T-222 alloy (Ta-9.6W-2.4Hf-0.01C), the HCP phase $(Ta,Hf)_2C$ was found both in as-cast material and after stress-free aging; however, after aging in the presence of a stress, only the FCC phase (Ta,Hf)C was found. It is possible that a similar process occurs in the Nb-Zr-C system, but optical metallography and SEM are insufficient to identify the changes in the carbide microstructure which affect the creep strength; hence additional work is being undertaken (ref. 9).

To aid in assessing the potential of the Nb-Zr-C as a material for long term applications in space power systems, pseudo strain rates, defined as the inverse of time in hours for 1 percent creep strain, were calculated and compared to similar data from creep tests on Nb-1Zr (ref. 11) and PWC-11 (ref. 12) in lithium. Utilizing the Orr-Sherby-Dorn (refs. 13 and 14) relationship to compensate the pseudo strain rate for stress and temperature, figures 9 and 10 show the compensated pseudo strain rate values of base-line Nb-1Zr and PWC-11, respectively, tested in Li as a function of stress. The lithium data is used as a comparison base because it presently best represents the actual operational environment these materials will be exposed to in a space power system.

As shown in figures 9 and 10, the stresses estimated to yield 1 percent creep in 7 yr at 1350 K are about 4 MPa for Nb-1Zr annealed 1 hr at 1475 K prior to testing, about 20 MPa for the annealed Nb-Zr-C, and about 15 MPa for the 1000 hr-aged Nb-Zr-C. This latter material is believed to represent the worst microstructural condition for this composition. Nevertheless, in this weakened aged condition, the Nb-Zr-C material is almost four times stronger than the Nb-1Zr material that was tested.

SUMMARY OF RESULTS

Based on a preliminary study of Nb-1Zr and Nb-Zr-C materials, the following observations could be drawn:

1. The Nb-Zr-C material in the annealed state (1 hr at 1755 K plus 2 hr at 1475 K) was the most creep resistant condition tested, and it is significantly stronger than Nb-1Zr.

2. Aging Nb-Zr-C for 1000 hr at either 1350 or 1400 K greatly reduces the creep strength of the annealed Nb-Zr-C. However, it is still more creep-resistant than Nb-1Zr.

3. Any possible means to avoid stress-free thermal aging of Nb-Zr-C prior to use would be highly desirable in potential service conditions.

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TABLE I. - CHEMICAL ANALYSES OF Nb-1Zr AND THE Nb-Zr-C ALLOY

	Nb-Zr-C	Nb-1Zr
Zirconium	0.90 wt %	1.1 wt %
Carbon	630 ppm wt	16 ppm wt
Oxygen	80 ppm wt	170 ppm wt
Nitrogen	53 ppm wt	41 ppm wt
Hydrogen	11 ppm wt	0.4 ppm wt
Niobium	Balance	Balance

TABLE II. - ONE PERCENT CREEP STRAIN DATA FOR ANNEALED AND AGED Nb-1Zr-0.06C

Specimen number	Heat treated condition	Test temperature, K	Test stress MPa,	Time to 1 percent strain, hr	Strain rate to 1 percent in./in./hr
10	1 hr-1755 K + 2 hr-1475 K annealed	1350	34.5	3200	3.13×10^{-6}
11	↓	1350	40.0	3450	2.90×10^{-6}
12	↓	1400	40.0	355	2.82×10^{-5}
16	↓	1400	35.0	900	1.11×10^{-5}
17	↓	1350	45.0	980	1.02×10^{-5}
18	↓	1400	27.6	2760	3.62×10^{-6}
13	Annealed + 1000 hr-1400 K	1400	35.0	150	6.67×10^{-5}
14	Annealed + 1000 hr-1400 K	1350	40.0	168	5.95×10^{-5}
15	Annealed + 1000 hr-1350K	1350	40.0	314	3.19×10^{-5}
28	1 hr-1755 K + 2 hr-1475 K	1350	10.0	(a)	---------
34	Annealed + 1000 hr-1350 K	1350	10.0	(b)	---------

[a]Test in progress; 9300 hr with 0.03 percent strain.
[b]Test in progress; 7100 hr with 0.04 percent strain.

TABLE III. - ONE PERCENT CREEP STRAIN DATA FOR ANNEALED Nb-1Zr

Specimen number	Heat treated condition	Test temperature, K	Test stress MPa,	Time to 1 percent strain, hr	Strain rate to 1 percent in./in./hr
36	1 hr-1475 K	1350	34.5	75	1.33×10^{-4}
37	↓	1350	27.6	160	6.25×10^{-5}
31	↓	1400	10.0	870	1.15×10^{-5}
30	↓	1350	10.0	3500	2.86×10^{-6}
32	↓	1400	5.0	(a)	---------
40	1 hr-1755 K	1350	40.0	105	9.52×10^{-5}
41	1 hr-1755 K + 2 hr-1475 K	1350	10.0	(b)	---------

[a]Test in progress; 5000 hr with 0.85 percent strain.
[b]Test in progress; 6000 hr with 0.40 percent strain.

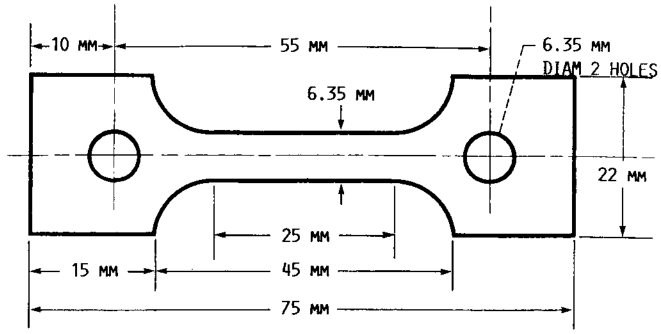

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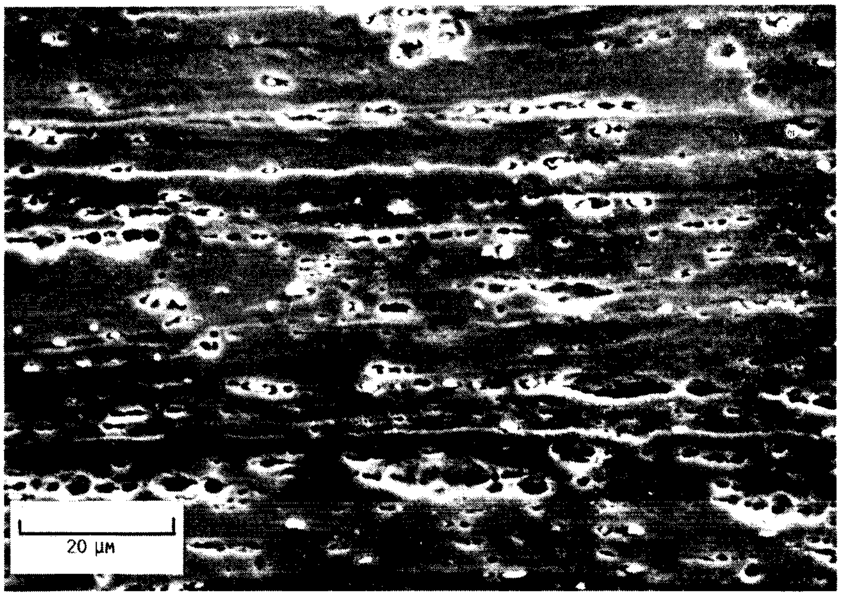
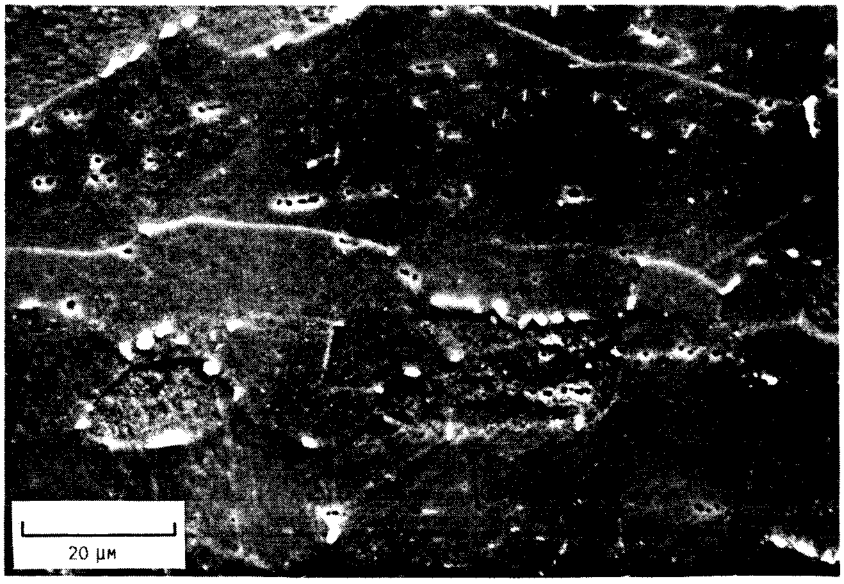
FIGURE 1. - TENSILE CREEP SPECIMEN.



ROLLING DIRECTION

(A) PRIOR TO ANNEALING, SHOWING LARGE PARTICLES ALIGNED PARALLEL TO THE ROLLING DIRECTION.



(B) THE RESULTANT ELONGATED GRAIN STRUCTURE AND PARTICLE DISTRIBUTION FOLLOWING THE 1 HR AT 1755 K PLUS 2 HR AT 1475 K ANNEAL.

FIGURE 2. - MICROSTRUCTURE OF THE Nb-1Zr-0.06C ALLOY.

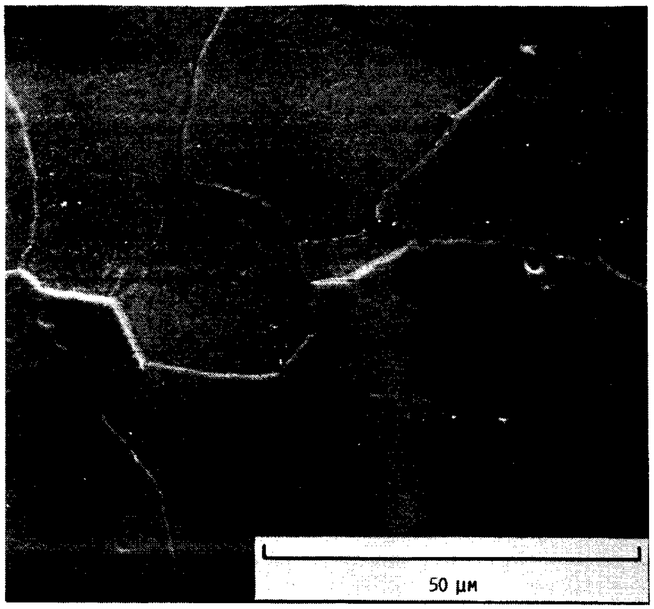


FIGURE 3. - RESULTANT EQUIAXED GRAINED MICROSTRUCTURE OF THE Nb-1Zr ALLOY ANNEALED FOR 1 HR AT 1475 K PRIOR TO VACUUM CREEP TESTING.

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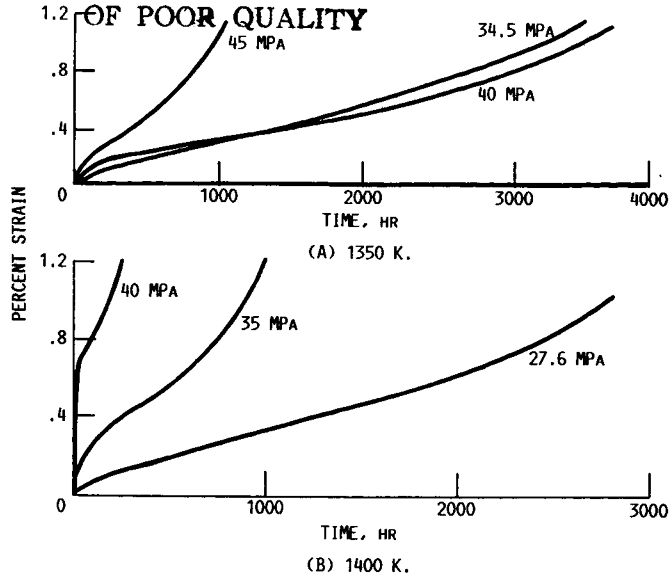

FIGURE 4. - VACUUM CREEP CURVES FOR 1 HR AT 1755 K PLUS 2 HR AT 1475 K ANNEALED Nb-1Zr-0.06C ALLOY AT INDICATED STRESS LEVELS.

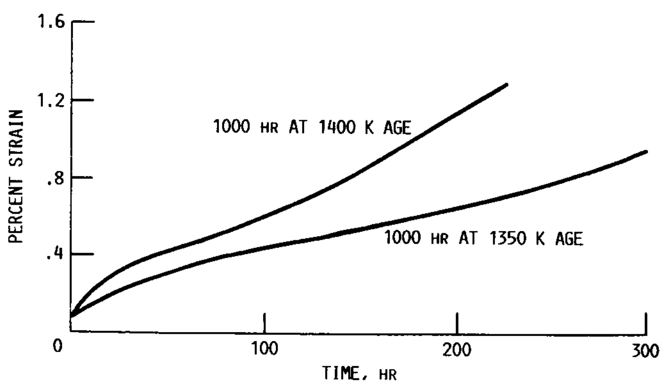

FIGURE 5. - 1350 K AT 40 MPa VACUUM CREEP CURVES FOR ANNEALED AND AGED Nb-1Zr-0.06C ALLOY.

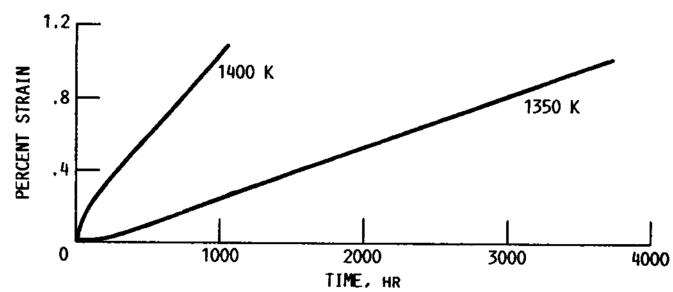

FIGURE 6. - CREEP CURVES FOR 1 HR AT 1475 K ANNEALED Nb-1Zr TESTED IN VACUUM AT A STRESS LEVEL OF 10 MPa AT 1350 K AND 1400 K.

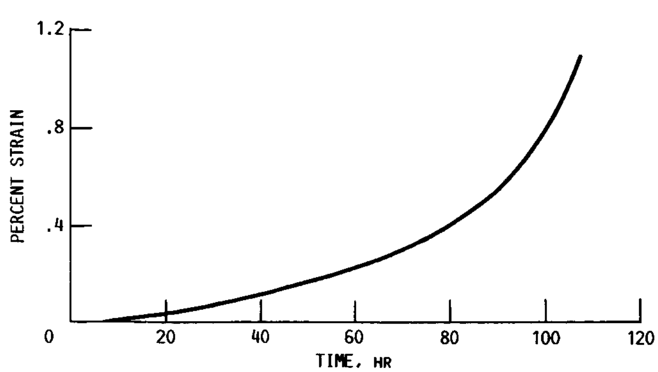

FIGURE 7. - 1350 K AT 40 MPa CREEP CURVE FOR Nb-1Zr ANNEALED FOR 1 HR AT 1755 K PRIOR TO TESTING IN VACUUM.

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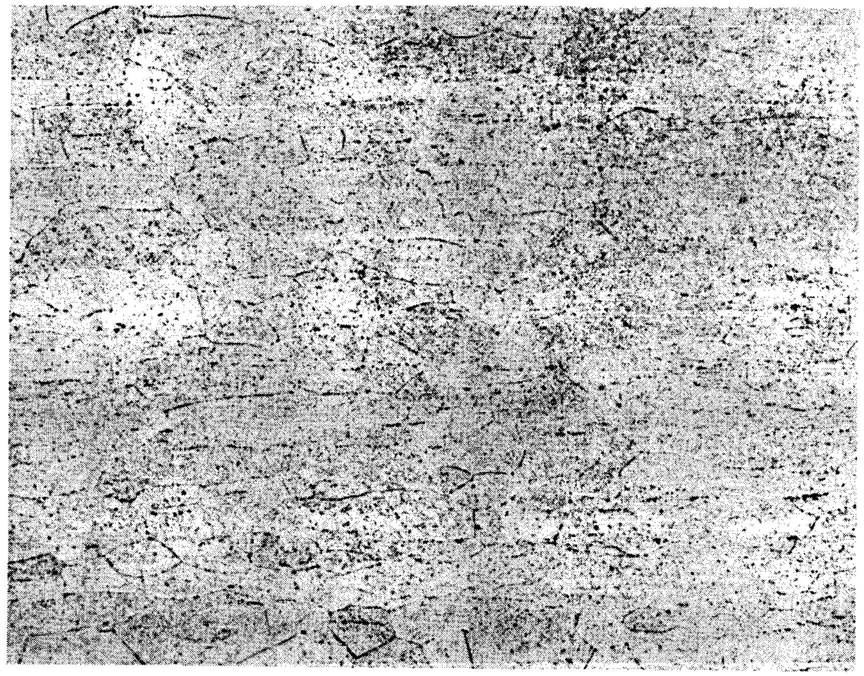

FIGURE 8. - MICROSTRUCTURE OF Nb-1Zr-0.06C SPECIMEN 15, ANNEALED PLUS 1000 HR AGED AT 1350 K, FOLLOWING CREEP TESTING FOR 531 HR (1.75% STRAIN).

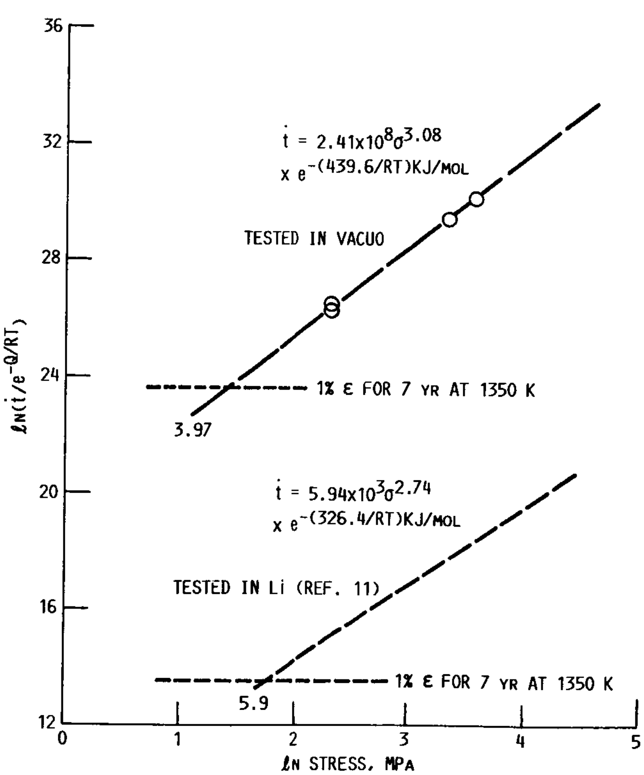

FIGURE 9. - TEMPERATURE COMPENSATED PSEUDO STRAIN RATE AS A FUNCTION OF APPLIED CREEP STRESS FOR ANNEALED Nb-1Zr.

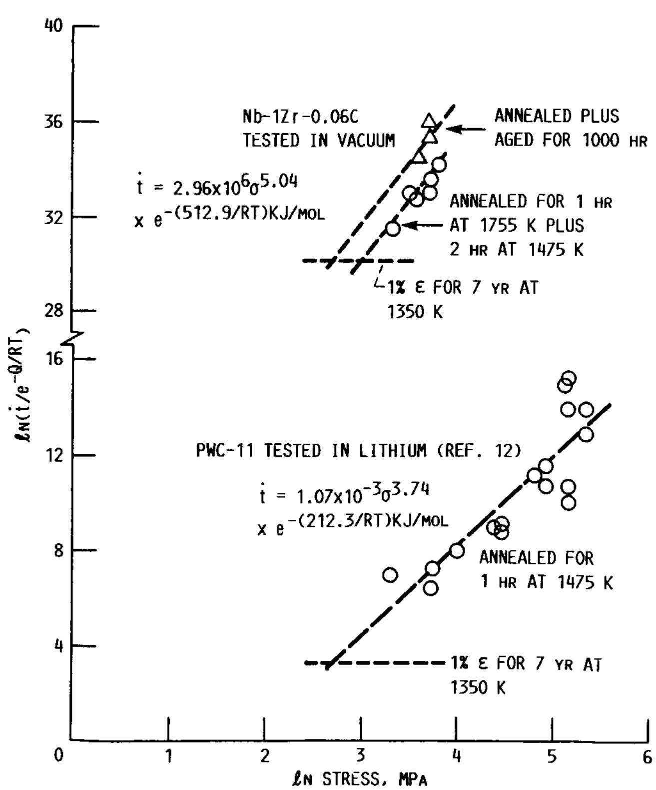

FIGURE 10. - TEMPERATURE COMPENSATED PSUEDO STRAIN RATE AS A FUNCTION OF APPLIED STRESS.

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16. Abstract

Creep tests were conducted on the Nb-1Zr base alloy with and without carbon. Testing was performed at 10^{-6} MPa in the 1350 to 1400 K range. Creep times, to 1 percent strain, ranged from 60 to 6000 hr. All 1 percent creep data were filled by linear regression to a temperature compensating rate equation. The Nb-1Zr-0.06C alloy, tested in a weakened aged condition, appears to be four times as strong as the Nb-1Zr alloy.

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