Long-Time Creep Behavior of the Niobium Alloy C-103

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Summary

The creep behavior of the niobium alloy C-103 (Nb-10Hf-1Ti-0.7Zr) has been studied as a function of stress, temperature, and grain size for test times to 19 000 hr. Over the temperature range 827° to 1204° C and the stress range 6.89 to 138 MPa, only tertiary (accelerating) creep was observed. The creep strain can be related to time by an exponential relation recently developed by the authors:

\[ \varepsilon = \varepsilon_0 + K(e^{st} - 1) \]

where \( \varepsilon_0 \) is the initial creep strain, \( K \) is the tertiary creep strain parameter, and \( s \) is the tertiary creep rate parameter. The initial tertiary creep rate \( K_s \) (the zero-time intercept of the differential of the strain-time relation) can be related to stress, temperature, and grain size by a modified power-law relation:

\[ K_s = A(\sigma/E)^a(1 + f/d^2)e^{-Q/RRT} \]

where \( A \) is the proportionality constant, \( \sigma \) is stress, \( E \) is Young’s modulus, \( f \) is the grain-size factor, \( d \) is grain size, \( Q \) is the activation energy, \( R \) is the gas constant, and \( T \) is temperature. The observed stress exponent 2.87 is similar to the three-power law generally observed for secondary (linear) creep of Class I solid solutions. The apparent activation energy 374 kJ/g mol is close to that observed for self-diffusion of pure niobium. The initial tertiary creep rate was slightly faster for fine-grained than for coarse-grained material. The strain parameter \( K \) can be expressed as a combination of power functions of stress and grain size and an exponential function of temperature. Strain-time curves generated by using calculated values for \( K \) and \( s \) showed reasonable agreement with observed curves to strains of at least 4 percent. The time to 1 percent strain was related to stress, temperature, and grain size in a similar manner as the initial tertiary creep rate.

Introduction

Expressions relating creep strain to time during tertiary creep have been proposed for several alloys, for example, Nimonic 80 (ref. 1), iron (ref. 2), alpha-brass (ref. 3), and stainless steel (ref. 4). Although these expressions appear capable of mathematically describing tertiary creep curves, they all require as input the time to initiation of tertiary creep. This requirement limits the usefulness of these expressions in predicting tertiary creep curves as functions of the usual inputs of stress, temperature, and grain size.

Power terms of time have also been used to represent creep curves containing segments of tertiary (accelerating) creep (ref. 1). For refractory alloys we previously proposed relations of one or more power terms of the total creep time to represent tertiary creep in tantalum and niobium alloys, such as \((A t)^{3/2}\) (refs. 5 and 6) and \((A t)^{3/2} + (B t)^{5/2}\) (ref. 7). This type of relation does not require knowledge of the time to the initiation of tertiary creep, but the requirement for multiple power terms to model extensive portions of tertiary creep makes this approach cumbersome.

More recently we proposed an exponential term for tertiary creep that overcomes at least some of the objections to previous approaches. This tertiary creep term is similar to the Garofalo exponential term proposed for primary creep (ref. 8) and can be combined with that primary creep term to express curves exhibiting both primary and tertiary creep:

\[ \varepsilon = \varepsilon_0 + \varepsilon_p(1 - e^{-rt}) + K(e^{st} - 1) \]  

(1)

This relation is capable of describing well the creep curves for the tantalum alloy Astar 811C to creep strains of 3 percent (ref. 9).

The usefulness of the new exponential tertiary creep term in describing the creep behavior of the niobium alloy C-103 is examined in this paper. The original purpose for conducting this creep study was to provide design data to facilitate use of C-103 in the heat exchanger and related components of a small, 2-kW, electric, isotope-fueled Brayton cycle space power system (ref. 10). An analysis of the time to 1 percent strain for C-103 alloy is included, since it was the design criterion for this system.

The nonlinear regression programs used in this study were designed by Steven M. Sidik and Raymond W. Palmer of the Lewis Research Center.

Symbols

- \( A \): proportionality constant, various dimensions
- \( a \): stress exponent, dimensionless
**Experimental Procedure**

The niobium C-103 alloy was commercially procured as 0.076-cm-thick sheet. The principal constituents of the alloy were determined to be:

- Hafnium, wt% ........................................... 9.75
- Titanium, wt% ........................................... 1.11
- Zirconium, wt% ........................................... 0.45
- Tantalum, wt% ........................................... 0.31
- Tungsten, wt% ........................................... 0.25
- Oxygen, wt ppm ........................................... 214
- Nitrogen, wt ppm ........................................... 0.62
- Carbon, wt ppm ........................................... 0.37
- Hydrogen, wt ppm ........................................... 0.8
- Niobium ........................................... Balance

Creep specimens having a 0.635-cm-wide by 2.54-cm-long gage section were machined from the 0.076-cm-thick sheet. These specimens were degreased, rinsed in distilled water and alcohol, wrapped in tantalum foil, and annealed in a vacuum of \(10^{-16}\) Pa at 1204° to 1760° C for 1 to 5 hr before creep testing. Average grain diameters (measured by the intercept method) ranged from 15 μm after annealing for 1 hr at 1204° C to 83 μm after annealing for 1 hr at 1760° C. Weight changes associated with annealing generally amounted to only a few milligrams, equivalent to changes in interstitial content of a few tens of ppm.

Constant-load creep tests were conducted in the internally loaded, high-vacuum creep units described in reference 11. A tantalum split-sleeve resistance heater was used for heating the specimens. The pressure was generally about \(10^{-10}\) Pa at the start of a creep test and decreased into the \(10^{-12}\)-Pa range after several hundred hours. Strains were measured by frequent optical readings of fiducial marks in the reduced gage section during creep. Strains on loading were of the order of 0.05 percent and are not included in the creep strain data.

Test temperatures ranged from 827° to 1204° C, and stresses from 6.89 to 138 MPa. Tests were generally terminated after 1 percent strain, although a few were continued to strains as high as 4 percent.

Grain sizes measured after creep are included in table 1; these values are essentially the same as those measured on annealed and uncrept specimens, an indication that the grain sizes were stable under the creep conditions studied.

**Results and Discussion**

**Shapes of Creep Curves**

Typical long-time creep curves for C-103 are shown in figures 1 and 2. These curves consist entirely of tertiary (accelerating) creep, with no apparent period of primary (decelerating) or secondary (linear) creep. All strain-time data were computer fitted by using nonlinear regression techniques based on the exponential relation recently developed by the authors to described tertiary creep in the tantalum alloy Astar 811C (ref. 9):

\[ \epsilon = \epsilon_0 + K(\epsilon^{n_f} - 1) \]  

The good fits of the data to this relation seen in figures 1 and 2 are representative of those obtained in the 35 tests included in this analysis. Table 1 presents the creep curve parameters derived from regression fitting of the individual curves and other pertinent creep data from this study.

Differentiating equation (2) gives the creep rate as a function of time:
\[ \dot{\epsilon} = K_s e^{nt} \]  \hspace{1cm} (3)

This relation predicts a linear increase in log creep rate with time. In contrast, the Garofalo primary creep term (ref. 8) predicts a linear decrease in log creep rate with time. Creep rates determined by linear regression over sequential segments of several creep tests are seen in figure 3 to be fairly well related to time by equation (3). The initial tertiary creep rate, which is equal to \( K_s \), is the creep rate at zero time (intercept of the rate-time curve with the ordinate in fig. 3). Equation (3) appears valid to at least a threefold range in creep rates.

Relation of Tertiary Creep Rate to Stress, Temperature, and Grain Size

In determining the effects of stress, temperature, and grain size on tertiary creep, the initial tertiary creep rate \( K_s \) was used rather than the rate parameter \( s \). Stresses were compensated for modulus by dividing the applied stress by the modulus for unalloyed niobium at the creep temperature (ref. 11), since dynamic moduli data for C-103 are not available. It is expected that the moduli for C-103 are close to those for unalloyed niobium.

The initial tertiary creep rate \( K_s \) was found to vary as a power function of the stress modulus ratio, as shown in figures 4 and 5. The exponent \( n \) was determined to be 2.87 and did not vary significantly with stress, temperature, or grain size. The proximity of the stress exponent to 3 suggests that C-103 behaves like a Class I solid solution (ref. 12). The rate-controlling reaction for secondary (linear) creep for this type of alloy is considered to be solute viscous drag on gliding dislocations and is termed microcreep. Although C-103, under the conditions of this study, showed only accelerating creep, a similar type of reaction may be rate controlling.

The initial tertiary creep rate was also found to vary exponentially with inverse temperature, as shown in figure 6. The apparent activation energy was determined from the slope of figure 6 to be 374 kJ/g mol and did not vary with stress, temperature, or grain size. This activation energy is close to the 402 kJ/g mol determined for self-diffusion in niobium (ref. 13) and is consistent with solute-drag-controlled creep.

The effects of grain size were evaluated at 982°C and 48.3 MPa. The variation of the initial tertiary creep rate \( K_s \) with grain size under these conditions is shown in figure 7. The finest-grained material, with an average grain diameter of 15 \( \mu \)m, had a significantly higher creep rate than materials with grain sizes from 27 to 83 \( \mu \)m. Based on previous observations of the variation of creep rate with grain size for niobium and tantalum alloys (refs. 5, 6, and 9), it was assumed that the creep rate tended toward a \( 1/d^2 \) variation with grain size at small grain sizes but became constant at large grain sizes.
Based on these observations of C-103 and prior observations of other refractory alloys (refs. 5, 6, and 9), the relations for initial tertiary creep rate as a function of stress, temperature, and grain size is expressed as

\[ K_s = A \left( \frac{\sigma}{E} \right)^n (1 + f/d^2) e^{Q/RT} \]  

(4)

Values for the constants in equation (4) are given in table II. The plot of temperature- and grain-size-compensated initial tertiary creep rate as a function of stress-modulus ratio in figure 8 shows a reasonable fit to equation (4).

The strain parameter \( K \) was also studied and was determined to vary as a power function of stress and grain size and an exponential function of inverse...
with the proportionality constant $A$ determined by regression fitting to be $17.9 \text{ cm}^{-b}$; the exponents $a$ and $b$ to be $-0.23$ and $0.717$, respectively; and $c$ to be $-7960 \text{ K}^{-1}$. Figure 9 compares calculated and observed values of $K$.

The variation of $K$ with stress and temperature for C-103 is different from that observed previously for Astar 811C (ref. 9), although for both materials $K$ increased with increasing grain size.

Comparison of Calculated and Experimental Creep Curves

It is of interest to compare calculated creep curves with experimental data. The strain parameter $K$ can be calculated from equation (5); the rate parameter $s$ can be obtained by dividing $Ks$ from equation (4) by $K$. The creep curve can then be generated by inserting these calculated parameters into equation (2) and

$$K = A(\sigma/E)^a b^e c^/T$$

(5)
TABLE II. - CREEP CONSTANTS FOR C-103

<table>
<thead>
<tr>
<th>Constant</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proportionality constant, ( A ), sec(^{-1} )</td>
<td>( 1.31 \times 10^{16} )</td>
</tr>
<tr>
<td>Stress exponents:</td>
<td></td>
</tr>
<tr>
<td>( n ) (grain-size independent)</td>
<td>2.87</td>
</tr>
<tr>
<td>( n_1 ) (grain-size dependent)</td>
<td></td>
</tr>
<tr>
<td>Grain-size factor, ( f ), cm(^2)</td>
<td>( 1.2 \times 10^{-6} )</td>
</tr>
<tr>
<td>Activation energy, ( Q ), kJ/g mol</td>
<td>374</td>
</tr>
<tr>
<td>Correlation coefficient, ( R^2 )</td>
<td>0.962</td>
</tr>
</tbody>
</table>

assuming \( \epsilon_0 \) to be zero. Figure 10 and 11 compare calculated curves with experimental data points. The agreement is reasonable, especially considering the probable error in calculation of the strain parameter \( K \) as indicated by the scatter in figure 9.

Relation of Time to 1 Percent Strain to Stress, Temperature, and Grain Size

The time-to-1-percent-strain data were analyzed in a manner similar to that used for analyzing the initial tertiary creep rate \( K_s \). The time to 1 percent strain varied as a power function of the applied stress; however, unlike for \( K_s \), the stress exponent \( n \) for the time to 1 percent strain decreased from 2.97 to 2.75 as the grain diameter decreased from 75 to 27 \( \mu m \). A decrease in \( n \) with decreasing grain size had been observed previously for Ta-10W (ref. 5), tantalum T-222 (ref. 6), and stainless steel (ref. 14). Matlock...
and Nix (ref. 15) also have suggested that the $n$ for grain-boundary sliding, which predominates at small grain sizes, is about 1 less than the $n$ for intragranular creep.

The apparent activation energy for time to 1 percent strain was determined to be 336 kJ/g mol, less than the 402 kJ/g mol for self-diffusion of niobium (ref. 13). The apparent activation energy did not vary significantly with stress, temperature, or grain size.

The time to 1 percent strain varied with grain size in a similar manner as observed for $K_s$. The inverse time (proportional to a linear creep rate to 1 percent strain) increased with decreasing grain size. The data were analyzed as done previously for $K_s$ by assuming that the inverse time to 1 percent strain was proportional to $1/d^2$ at fine grain sizes but invariant at large grain sizes. The variation of inverse time to 1 percent strain with grain size is shown in figure 12.

A relation expressing time to 1 percent strain as a function of stress, temperature, and grain size was developed as

$$1/t_{1\text{pc}} = A[(\sigma/E)^{n_1} + f/d^2(\sigma/E)^{n_2}]e^{-Q/RT} (6)$$

Values for the constants in equation (6) are given in table 11. Here, two stress exponents are required since the stress dependency varies with grain size. Figure 13 shows the good correlation between temperature-compensated inverse time to 1 percent strain and stress for C-103 with average grain diameters of 27 and 75 μm.

The calculated stress for 1 percent creep strain in 10 000 hr for C-103 is shown in figure 14. This stress ranges from about 50 MPa at 900°C to about 6 MPa at 1100°C and is about 15 percent greater for coarse-grained than for fine-grained material. C-103 is about one-fourth as strong as the commonly used niobium alloy FS-85 (ref. 16).
Conclusion

From a study of the creep behavior of C-103 as a function of stress, temperature, and grain size the following conclusions were drawn:

1. The exponential relation for tertiary creep strain as a function of time can well describe creep curves for C-103, which shows only tertiary creep at 827° to 1204° C at stresses of 6.89 to 138 MPa. This relation is

\[ \epsilon = \epsilon_0 + Ke^{st} - 1 \]

where \( \epsilon \) is creep strain, \( \epsilon_0 \) is initial creep strain, \( K \) is the tertiary creep strain parameter, \( s \) is the tertiary creep rate parameter, and \( t \) is time.

2. The initial tertiary creep rate \( Ks \) can be related to stress through the well-known power law. The rate \( Ks \) can be expressed by a single activation energy (over the range of this study) that is slightly less than the self-diffusion activation energy for niobium. Fine-grained C-103 creeps slightly faster than does coarse-grained C-103.

3. The strain parameter \( K \) can be expressed as a function of grain size, stress, and temperature.

4. Strain-time curves calculated from predicted values of \( K \) and \( s \) agree fairly well with observed strain-time curves.
References


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Creep; Refractory metals; Niobium (columbium); C-103; Primary creep rate; Secondary creep rate; Tertiary creep rate; Grain size; Stress dependency; Activation energy

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