MICROSTRUCTURAL EVOLUTION IN A FERRITIC-MARTENSITIC STAINLESS STEEL AND ITS

RELATION TO HIGH-TEMPERATURE DEFORMATION AND RUPTURE MODELS*

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Abstract

The ferritic-martensitic stainless steel HT-9 exhibits an anomalously high creep strength in comparison to its high-temperature flow strength from tensile tests performed at moderate rates. A constitutive relation describing its high-temperature tensile behavior over a wide range of conditions has been developed. When applied to creep conditions the model predicts deformation rates orders of magnitude higher than observed. To account for the observed creep strength, a fine distribution of precipitates is postulated to evolve over time during creep. The precipitate density is calculated at each temperature and stress to give the observed creep rate. The apparent precipitation kinetics thereby extracted from this analysis is used in a model for the rupture-time kinetics that compares favorably with observation. Properly austenitized and tempered material was aged over times comparable to creep conditions, and in a way consistent with the precipitation kinetics from the model. Microstructural observations support the postulates and results of the model system.

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Constitutive models for plastic deformation are often based on well-established phenomenology. The better models mathematically reflect the influence of microstructural evolution on mechanical behavior, and also display important aspects of the physics of plastic flow. When needed to describe the material's response to complex thermal-mechanical loading scenarios, it is best when the constitutive model is kept sufficiently simple to allow easy insertion into the necessarily complicated computer codes designed to follow loading history and geometry. It is better that the model describes the intrinsic mechanical behavior of the material itself and not include geometric aspects. In this way, one avoids counting geometric aspects twice or incorrectly. In this paper, we develop a general model for the deformation behavior of the stainless steel HT-9, applicable over the wide range of conditions of interest to the advanced reactor development community. We use a rather traditional framework in this model, but the nature of the alloy and its mechanical behavior necessitates giving attention to specific microstructural features and their effect on properties. This is a fortuitous occurrence, because it allows us to obtain a better understanding of the behavior of this material, and provides us with insight into other aspects of its mechanical behavior such as its rupture life.

Good strength, ample corrosion resistance, and excellent resistance to swelling in the fast neutron environment has made HT-9 the chief candidate alloy for use as fuel cladding in the current U.S. fast reactor designs. Service in the reactor core will expose the cladding to high temperatures and a wide range of loading conditions including hypothesized long and short term thermal transients. The expectancy of long time service and the relative inaccessibility of the actual components requires a good understanding of the mechanical behavior of this material over a wide range of rate and temperature including, but not restricted to, the creep regime. This understanding must be sufficient to provide a predictive capability of such quantities as the rupture life. One issue of interest is the microstructural stability of this alloy during its service life and the consequent changes in mechanical properties with changes in microstructure. The nominal composition of HT-9 is shown in Table I. In its properly

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>W</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.4</td>
<td>0.55</td>
<td>11.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

heat-treated condition, it is a martensitic-ferritic stainless steel. This class of alloys has exhibited secondary carbide precipitation over time during heating [1] and exposure to radiation [2]. In this paper, we reveal indirect evidence of this precipitation both as reflected in the observed flow behavior of HT-9 and from its role as a possible cause of the somewhat anomalous stress-rupture behavior in this alloy. We also present our own direct observations of this precipitation phenomenon, made possible as a result of guidance provided by the indirect evidence. Finally, we examine the effect that this precipitate distribution, as it evolves, has on mechanical properties obtained over the range of time, rate, and temperature of interest, and the ramifications of its existence on the prediction of rupture life.
Deformation Behavior

For the applications of interest, it is necessary that the model cover mechanical behavior of HT-9 over the range from high temperature creep to room temperature tensile deformation, and of course follow a natural transition between these two modes. The model will be developed around and fit to constant-stress creep [3] and constant-rate tensile [4] data. As we have stated, it will be based upon well-established formalisms for describing deformation-rate phenomena and strain-hardening behavior. For example, we assume that creep flow in HT-9 can be described by a Dorn-type [5] power-law form:

\[
i_p = i_o \left(\frac{E}{\sigma_s}\right)^n \left(\frac{\sigma}{E}\right)^n \exp\left(-\frac{Q_c}{kT}\right).
\] (1)

In Eq. (1), \(i\) is the steady state equivalent creep rate, \(\sigma\) is the equivalent applied stress, \(E\) is the temperature dependent dynamic Young's Modulus, \(Q_c\) is the creep activation energy, \(T\) is the absolute temperature, \(k\) is Boltzmann's constant, and \(\sigma_o\) and \(i_o\) are constants. We further assume that the strain hardening behavior can be characterized by an equation of the Voce [6] type:

\[
\frac{\sigma}{E} = \sigma_s - \left((\sigma_s - \sigma_1) / E\right) \exp\left(-\frac{\epsilon_p}{\epsilon_c}\right)
\] (2)

where \(\sigma\) is the flow stress at some level of plastic strain, \(\epsilon\) is measured from the as-heat-treated material reference state (\(\epsilon = 0\)), \(\sigma_1\) is the yield stress of the material in the reference state, \(\sigma_s\) is the saturation or steady-state flow stress (approached at large plastic strain), and \(\epsilon\) is a temperature dependent parameter related to \(\sigma_s\), \(\sigma_1\) and the initial strain-hardening rate. The quantities \(\sigma_s\) and \(\sigma_1\) are temperature and rate dependent, and, as implied by the use of the same symbol in Equations (1) and (2), \(\sigma_s\) can be calculated from Eq. (1) at the temperature and strain-rate of the tensile test of interest. It is therefore an inherent assumption that high-temperature tensile-test results and creep-test results should be compatible via the saturation stress. This assumption is supported by our experience at modeling another material over wide ranges of rate and temperature [7].

We will examine creep and tensile data on the alloy HT-9 in terms of the framework established by Eqs. (1) and (2). Published creep data [3] from two different heats, but given the same heat-treatment, are analyzed first. Before testing, the material was austenitized at 1038° C for five minutes, air cooled, then tempered at 760° C for 30 minutes, and again air cooled. These creep results are analyzed first, because tensile data on material from one of these heats and given the same heat-treatment is available for comparison. Other creep data on differently fabricated material given a slightly different heat-treatment will be examined later within the context of the developed model.

In analyzing creep data, we note that the greater part of the temperature dependence comes from an Arrhenius factor (Eq. (1)) with some contribution from \(E(T)\). To find \(Q_c\), one must make Arrhenius plots at constant values of \(\sigma/E\). We examine creep data in this way over various temperature ranges.
From the slopes of the Arrhenius plots, we obtain a value of 
\[ Q_c = 73 \text{ kcal/mole} \] for the creep activation energy, which is in agreement with the self-diffusion activation energy in \( \alpha \)-iron [9]. As noted, an additional temperature dependence comes from that of the modulus:

\[ E = 2.12 \times 10^{11} (1.144 - 4.856 \times 10^{-4} T) \text{ Pa} \] (3)

Figure 1 shows a plot of the creep data where the rate is normalized by the Zener-Hollomon parameter \( \dot{\epsilon} \exp(Q_c/kT) \), and the stress is normalized by the temperature-dependent modulus. The slope of this plot gives the stress exponent in Eq.(1) as \( n = 2.3 \). It can be seen that creep data taken over a wide range of temperature (0.46 T_m to 0.59 T_m) and stress are coordinated by Eq.(1).

![Figure 1 - Creep data [3] plotted in accordance with the Dorn Equation. The slope of the solid line is \( n = 2.3 \), and the activation energy is \( Q_c/k = 36,739 \text{ K} \).](image)

To study the efficacy of Eq.(2) for describing tensile data, an expression for \( \sigma_1/E \) and \( \epsilon_c \) as functions of temperature and strain-rate is needed, presuming that \( \sigma_c/E \), the saturation stress in a tensile test is the same as the creep stress in Eq.(1). Unfortunately, the tensile data [4] used in this analysis (and the only data available for HT-9 under these conditions) is not reported as stress-strain curves or tabulated data. Instead, the engineering ultimate strength (UTS), uniform elongation (\( e_u \)), and the yield stress (0.2% offset) are reported for the temperatures: 25, 232, 400, 450, 500, 550, 600 and 650°C. To analyze this data, all obtained at a strain rate of \( 4 \times 10^{-4} \text{ s}^{-1} \), we have assumed the measured yield stress to be equal to \( \sigma_1/E \) in Eq. (2), calculated the true stress at ultimate to be given by \( \sigma_u = UTS (1 + e_u) \), and determined the true strain at the ultimate from the
expression $\epsilon = \log(1 + e)$. It is noted that the true stress at ultimate is given by (from Eq. (2)):

$$\sigma_u/E = \sigma_s/E - [(\sigma_s - \sigma_1)/E] \exp(-\epsilon_p/\epsilon_c)$$

(4)

Also, since it occurs at maximum load,

$$\sigma_u/E = [(\sigma_s - \sigma_1)/E] \exp(-\epsilon_p/\epsilon_c)$$

(5)

Equations (4) and (5) can be solved simultaneously for $\sigma$ and $\epsilon_c$ at the temperatures of the tests. It is convenient to express the temperature dependence of $\epsilon_c$ algebraically as:

$$\epsilon_c(T) = 0.127 - 3.50 \times 10^{-4} T + 2.99 \times 10^{-7} T^2$$

(6)

Figure 2 shows values of $\sigma_u/E$ calculated from the data [4] and Eqs (4) and (5) in conjunction with the creep data. From the low temperature asymptote of the tensile results we calculate a constant value of the parameter $\sigma_u/E = 3.96 \times 10^3$. From this, and the value of the ordinate of the creep data plotted in Fig. 1, we find $\epsilon_c = 5.2 \times 10^{-5} s^{-1}$.

We have observed that, within a 10% deviation, the measured yield stress $\sigma_1$ is equal to 0.8 $\sigma_s$ for the tested temperature range. Hence we assume that $\sigma_1$ has a temperature and rate dependence identical to that for 0.8 $\sigma_s$. Using this approximation, and Eqs. (2) and (6), we can construct tensile curves for the temperature range and strain-rate of the data [4]. These
are shown in Fig. 3 along with values of the true stress at ultimate both measured [4] and calculated using a fit [7] for the saturation stress. The measured and calculated values of the true stress at ultimate also agree within 10%.

![Figure 3 - Calculated stress-strain curves for the temperatures indicated. Also shown are the calculated (Eq.(2)) and measured values of the true stress at ultimate.](image)

One aspect of the tensile data to be noted (Fig. 2) is that at low temperatures, the saturation stress appears independent of \( \dot{\varepsilon} \exp(Q_s/kT) \), reflecting the rate insensitivity usually encountered in this regime. On the other hand, at high temperatures, the normalized-rate dependence of \( \sigma_s/E \) becomes very much like that of the creep data. This would seem to support the assumption, inherent in the use of the same stress parameter (\( \sigma_s \)) in both the creep and tensile flow equations (Eqs.(1) and (2)), that the creep and tensile data would make a smooth transition into each other. In fact, in our previous experience, modeling the behavior of the austenitic alloy Type 316 [7], we observed just such a smooth and direct transition from low-temperature rate-independent behavior to high-temperature rate-dependent behavior. In Fig. 2 we extrapolate the tensile data in the same manner. It can be seen that, while the rate-sensitive portion of the tensile results is compatible with the creep data (slope \( n = 2.3 \)), the normalized rate is orders of magnitude greater for a given value of \( \sigma_s/E \) for the tensile results than for the creep data. In this sense, the tensile tested material appears weaker than the creep tested material even though both had the same heat treatment. Of course, the tensile tests were performed on the time scale of minutes, while the creep experiments lasted for thousands of hours. This apparent discrepancy between the results of short and long time tests is not the only one of its kind for the alloy HT-9. A similar observation has been made in the case of rupture life measurements. It has been observed that the timing of rupture has a decidedly different temperature dependence for tests conducted over long times versus those performed over short times [10]. In a microstructurally stable material, one might expect high-stress creep test and high-temperature tensile test results to be
compatible, as we have observed in the past [7] for type 316. However, as we have suggested, HT-9 may not exhibit this kind of microstructural stability over long times at high temperature. In the next portion of this paper, we take the view that these apparent discrepancies in mechanical behavior are real effects attributable to changes in microstructure. We quantify this relationship, by presuming that the correlation between the model and shorter-time tensile data represents the intrinsic deformation behavior of the as-heat-treated material. We then calculate the nature and timing of the microstructural change that would produce the observed higher strength during long-time creep deformation. After this, we examine the ramifications of these calculations with regard to other mechanical property data, and use them as a guide to our own direct microstructural observations.

Microstructural Effects

We have just discussed an apparent discrepancy between the long-time and short-time measured strength of HT-9 when viewed within the context of our model. The extrapolation in Fig. 2 from the tensile results into the creep regime exhibits the correct stress dependence (n = 2.3) for compatibility with the creep data. However, the tensile-tested material appears much weaker than the creep-tested material, even though both had the same heat treatment. These results suggest that microstructural instability may be an issue of importance with regard to modeling this material's high-temperature mechanical behavior during long-time service. It has been reported [1] that, even after being subjected to prescribed stabilizing heat treatment, this class of alloys exhibits secondary carbide precipitation after exposure to high temperatures for long times. It is not unreasonable to suggest that the creeping material is actually stronger because of precipitation that occurred relatively early during these tests, which lasted thousands of hours. This could not have occurred during the much shorter duration (minutes) of the tensile tests even at high temperatures. In this section, we estimate the precipitate density that would be necessary to cause this apparent strengthening at each temperature for the actual creep data, using the simple Orowan formula. Noting that this precipitate structure evolves in some characteristic time at temperature for each test, we extract a kinetic law for this process. We use these results as a guide in determining an appropriate aging treatment that will produce secondary carbide precipitation in HT-9. We also use the precipitation kinetic law to analyze additional creep data [11] obtained at lower temperatures than those discussed above (Fig. (1)), and to help reconcile observed anomalies in measured rupture time parameters.

Precipitation Kinetics. When we extrapolate the high-temperature tensile flow correlation into the creep regime, we find that it predicts a higher creep rate at a given temperature and stress than is actually observed. We can account for this discrepancy by invoking the "effective stress" concept [12]. For each creep test data point in Fig. 2, corresponding to a particular applied stress and temperature, we can determine an effective stress that causes our extrapolated model to fit the data. This effective stress is defined as

\[ \sigma_e = \sigma_s - \sigma_o \]  

(7)

where as before we identify the applied creep stress with our steady state flow stress \( \sigma_s \), and \( \sigma_o \) is a back stress associated with precipitate strengthening. The effective stress is calculated for each test so that the
extrapolation becomes shifted to agree with the actual creep data. The idea behind the use of an effective stress is that as the precipitate structure develops during a test, one imagines that dislocations are held back by these precipitates. This process creates a back stress that must be overcome for plastic flow to continue. For strong obstacles, this back stress can be estimated by the Orowan bowing formula

\[ \sigma = \alpha \mu b / L \]  

(8)

where \( L \) is the mean precipitate spacing, \( \mu \) is the shear modulus, \( b \) is the magnitude of the Burgers vector of dislocations, and \( \alpha \) is a constant of order unity.

Using Eq. (8), we can calculate values of \( L \) for each test. At a given temperature, tests performed at lower stresses will have longer characteristic durations. From an examination of the data [3] used in Fig. 2, we define this characteristic duration \( t_c \) as the time it takes to achieve a strain of 0.001 if the sample deforms at the minimum creep rate, i.e.

\[ t_c = 0.001 / \dot{\varepsilon}_{p(min)} \]  

(9)

In Fig. 4, we plot the calculated mean precipitate spacing at each temperature as a function of this characteristic time. The result is essentially a linear relationship, with the slope \( (\Gamma) \) increasing with increasing temperature. If we view these curves as representing the precipitation kinetics, and make an Arrhenius plot of the growth rate, \( \Gamma \), as in Fig. 5, we obtain an activation energy for growth of \( Q_g / k = 25484 \) Kelvins.

![Figure 4](image_url)

*Figure 4 - The mean precipitate spacing calculated from the creep data (Fig. 1) as a function of characteristic time (Eq. (9)) at the various creep-test temperatures.*
The growth behavior can therefore be described by the linear relation

\[ L = L_0 + \Gamma \cdot t \]  

(10)

\[ \Gamma = \Gamma_0 \exp(-Q_g/kT), \]  

(11)

where \( \Gamma = 1.824 \times 10^{-2} \text{ m/s} \). We should note that the minimum value approached by \( L \), which is about 0.2 \( \mu \)m, is not unreasonable with regard to microstructural observation [1]. In fact, we have used Eqs. (10) and (11) as a crude guide to estimating aging parameters that might produce an observable precipitate distribution (\( L = 1 \mu \)m) in an optical microscope. Time was limited, and we wanted to guarantee that we would obtain resolvable precipitates within thirty days. We calculated an aging temperature range of from 700°C to 850°C. Not wanting to exceed the tempering temperature, we chose 740°C as an aging temperature. Figure 6 shows scanning electron micrographs of three samples. Figures 6A and B are micrographs of samples aged for one day and thirty days, respectively, after austenitizing and tempering. Both samples show chromium rich carbide precipitates as indicated. We were unable to find these precipitates in the as-heat-treated unaged material (Fig. 6C). Even though the activation energy in Eq. (11) was obtained by very indirect means, we point out that it agrees within about 10% with the activation energy for chromium diffusion in \( \alpha \)-iron/chromium alloys [13].

* Scanning electron microscopy, and energy dispersive and wavelength dispersive x-ray spectrometry were performed by McCrone Associates, Inc., Westmont IL.
Figure 6 - Scanning electron micrographs of HT-9 samples austenitized, tempered and aged for (a) one day, (b) 30 days, (c) unaged. The light colored features (a) and (b) are Cr-rich carbide precipitates, not found in (c).
Effects of Precipitation on Mechanical Properties

In the previous section, we extracted a reasonable kinetic law for carbide precipitation behavior by invoking the effective stress concept to account for apparent increased strength during long time creep testing. Guided by its parameters, we were able to produce these precipitates via appropriate aging treatment. We would like to use the derived precipitation kinetic equation in conjunction with our deformation model to make predictions regarding the effect of carbide precipitation on the high temperature mechanical behavior of HT-9. Obviously, we cannot test the verity of these models using the same creep data that we used to develop them. Instead, within the context of these models, we will in this section examine other creep data obtained generally at lower temperatures than the data discussed earlier. This places them in the higher normalized-rate transition range between creep and tensile behavior. We will also use the deformation and precipitation models to help understand the differences in rupture behavior reported for short and long-time tests.

Creep Deformation. There exists additional creep data [11] that was not used in the creep-deformation model development primarily because it was from a different heat and was obtained at temperatures below half the absolute melting point of the alloy (850 K). We believed that at these temperatures it would not be sufficiently well-behaved in the context of creep. This omission turns out to be fortuitous because this data can now be used in conjunction with our models to help understand behavior in the transition range between creep and tensile flow. We re-plot the "original" creep data from Fig. 1 along with the tensile-flow correlation in Fig. 7, where we have reversed the axes and plotted normalized stress on a linear scale. We use the original data and curve as references from which to view the new data.

![Graph](image)

**Figure 7** - The creep data [3] for all the temperatures shown in Fig. 1 and the tensile correlation (solid line) normalized as in Fig. 2, with the normalized stress plotted on a linear scale.
The new data was obtained from differently fabricated material that was given a slightly different heat treatment. It was tempered for 2.5 hours instead of 30 minutes at 780° C after austenitizing (at 1052° C as discussed before. In Fig. 8, we have added the new data, taken at 425, 480, 540, and 595° C. A number of interesting observations can be made from this plot. The lowest temperature (425° C) creep data appears to align itself with the tensile correlation, as though the precipitation strengthening discussed earlier could not occur at this temperature for the time scale of this test. As the creep test temperature increases the data shift closer to the original creep data, suggesting the occurrence of the same strengthening phenomenon postulated in the previous section. Also, at higher stresses, each set of data appear to display a transition behavior that brings it closer to the tensile flow correlation. This transition occurs at a slightly higher stress for lower temperature tests. It is, in a natural way, accompanied by a decrease in rate sensitivity from that observed at lower stresses. The data that approach the tensile correlation, as the stress is further increased, exhibit a higher rate sensitivity again and appear to be in conformance with the correlation.

![Figure 8 - The same as Fig. 7, but with additional creep data from a different heat of material.](image)

The behavior of the new data can to some extent be explained within the framework that we have developed. Earlier, we postulated that the apparent difference in strength between the high-temperature tensile-tested material and the creep-tested material is a real effect caused by precipitation. This strengthening is represented by a shift from the extrapolated tensile correlation to the creep data without changing slope (stress exponent, n = 2.3). This construction and the maintenance of a constant stress exponent necessitates that the calculated back stress be proportional to the applied stress, as can be seen in Fig. 9. The new creep
data display shifts to lower rate from the tensile correlation. We have just suggested that at 425°C there is insufficient time during the test for the precipitation to occur. At higher temperatures, the kinetics are such that it can occur during the test so these data are shifted from the tensile correlation. As the applied stress is increased along one of these shifted curves, a stress level is reached where the back stress produced by precipitation can no longer increase proportionately with the applied stress. When this happens, further increases in stress are accompanied by greater increments in normalized rate than would be dictated by a stress-dependence of n = 2.3. That is, the stress dependence of the rate increases and the slope in Fig. 8 decreases as the data undergo a transition to conformance with the tensile correlation, which itself reflects the intrinsic flow behavior independent of the carbide precipitation. The stress level where this transition occurs appears to be lower at higher temperatures reflecting a coarser microstructure under these conditions. The magnitude of the shift along the rate axis of the lower portion of these curves should be dictated by the kinetics of precipitation as determined earlier. Taking the 425°C curve as a base line, and shifting the new creep data by the factor $\exp(Q_0/kT)$, we see in Fig. 10 that all of the data fall in alignment with the tensile correlation. We have left the original creep data unshifted, as a reference, but since they were used to determine $Q_0$, they would of course also fall along this line. We have also eliminated the transition portions of the shifted curves for clarity. All of these results help us better understand the mechanical behavior of HT-9 in the transition region between high temperature tensile deformation and high stress creep flow. The results for the creep tests imply that if constant rate tensile tests were done at lower rates or higher temperatures than we have thus far analyzed, they might exhibit the same precipitation-strengthening effects displayed during creep.

![Figure 9](image_url)

**Figure 9** - The value of the back stress calculated to cause the extrapolated tensile correlation (Fig. 2) to fit the creep data [3] plotted as a function of the applied stress. The solid line is a least squares fit.
Rupture Behavior. We conclude our discussion with some comments on reported rupture behavior in connection with our findings in this work. It has been observed that for HT-9 measured rupture-life parameters are substantially different when obtained from short-time transient tests than when they are gotten from long-time stress-rupture experiments [10]. The concern over this must be viewed from the perspective that for many other alloys considerable success has been experienced through the use of a Larson-Miller [14] or Dorn Parameter [15] to extrapolate rupture life from one regime to another. In many engineering applications, such as nuclear reactor technology, there is a need to be able to predict rupture life outside of a test-data base. Though empirical in nature, these extrapolation parameters often involve a connection between the high-temperature deformation process and the fracture process, such as via the activation energy for creep flow. This connection is reflected in what is termed the Monkman-Grant relation [16] that the product of the minimum creep rate and the rupture time $t_r$ is constant. This implies that the rupture life has the same stress and temperature dependences as the creep rate, as expressed for example through the stress exponent $n$ and the activation energy $Q_c$, i.e.

$$
\dot{\varepsilon}_{(\text{min})} t_r = C_1
$$

$$
t_r = C_2 \sigma^{-n} \exp(Q_c/kT).
$$

This relationship has been observed many times and put to great use over the years. Its validity can best be justified when there is no microstructural change of the kind we have been discussing.
Even when they are related to each other, the minimum creep rate is a very different mechanical property than rupture life. The former is an event that occurs during the test, the latter is in fact the duration of the entire test. The rupture life in effect probes the kinetics of each event that occurs during the test, e.g. every delay in the flow or fracture process. In Eq.(1), if we replace the applied stress with the effective stress, we get

$$\dot{\epsilon}_p = A_o (\sigma - \sigma_o)^n \exp(-Q_c/kT), \quad (14)$$

and the back stress dictates the magnitude of the minimum creep rate. In Eq.(13) the $A_o$ is a combined constant, and we have removed the subscript s for convenience. We maintain the same intrinsic stress and temperature dependences as before by keeping $n$ and $Q_c$ the same in Eq.(14) as they are in Eq.(1). We imply that these quantities represent the mechanism that controls plastic flow, i.e. controls the rate of dislocation motion once the back stress is overcome. We have pointed out that if the minimum creep rate is produced by a back stress that is proportional to the applied stress, independent of test temperature, then the measured stress exponent has the same value as it does when no precipitation occurs and the back stress is zero. The measured stress exponent is defined by the relation:

$$n_m = (d \log \dot{\epsilon}_p / d \log \sigma)_T$$

$$= [n \sigma/(\sigma - \sigma_o)] d(\sigma - \sigma_o)/d \sigma \quad (15)$$

When $\sigma_o$ is proportional to $\sigma$, as we showed earlier, then the measured stress exponent $n_m = n = 2.3$. On the other hand, when $\sigma_o$ is independent of $\sigma$, then $n_m \geq n$, as we indicated for the transition region between creep and tensile flow in Fig. 7. In this case, when the applied stress is only slightly greater than the back stress, the measured stress exponent is much greater than $n$. As $\sigma$ increases much beyond $\sigma_o$, $n_m$ approaches the value of $n$. Similarly, the measured activation energy is defined mathematically by:

$$Q_{cm} = [d \log e \dot{\epsilon}_p / d (1/T)](\sigma/E)$$

$$- Q_c/k - n [d \log e (\sigma - \sigma_o)/d(1/T)] \quad (16)$$

If, at constant normalized stress, the back stress is independent of temperature (as we observed) then $Q_{cm} = Q_c$, which itself is the activation energy of the intrinsic flow mechanism (i.e. self-diffusion). If $\sigma_o$ decreases with increasing temperature, then $Q_{cm} \geq Q_c$.

Over the duration of the entire creep test, the back stress may start out at zero, then increase to achieve its maximum value after some time in accordance with precipitation kinetics. This value would correspond to a minimum in the creep rate. As the test proceeds, $\sigma_o$ may, via coarsening, reduce to a magnitude insignificant relative to the intrinsic flow stress. The kinetics of this entire process is going to affect what one measures as the activation energy and stress dependence of the rupture life. These quantities are at the heart of prediction tools like the Dorn parameter. In a test of short duration, the back stress may be zero throughout, depending
on temperature. In this case, the measured rupture life should exhibit the same temperature and stress dependences as observed for high temperature flow.

We have mentioned that there is a reported discrepancy between long-time and short-time rupture parameters in HT-9. During short-time transient testing the activation energy for rupture is found [10] to be close to the creep activation energy \( Q_c/k = 36,739 \) K that we denoted earlier, but its stress exponent is somewhat greater. Higher stress dependences can occur at higher stresses even for intrinsic flow unaffected by precipitation (see Fig. 2). However, the long-time creep rupture data [10] exhibited stress exponents with values ranging from 6 to 14, and activation energies \( Q_c/k \) ranging from 60,000 K to 90,000 K. During a test like this, the back stress is not always proportional to the applied stress. It evolves along with the microstructure (precipitation), so one would expect its presence to cause an increase in the measured stress exponent. Also, during the test, the evolution of the magnitude of the back stress is not independent of temperature. One would expect its varying magnitude over time to cause a difference in the measured value of the activation energy for rupture relative to that for creep. As we have stated, the rupture time as a test parameter probes both the kinetics of deformation and fracture processes (e.g. self-diffusion and plasticity), and that of the precipitation process as well. This can be expressed crudely in a modified Monkman-Grant relation allowing us to estimate the effects of precipitation on these rupture parameters. We express the rupture time as

\[
 t_r = C (\sigma - \sigma_o)^{-n} \exp(Q_c/kT) \tag{17}
\]

where \( \sigma \) is a function of time and temperature according to Eqs.(8), (10) and (11). The measured stress exponent and activation energy can be obtained mathematically from equations analogous to Eqs.(14) and (15). The back stress varies over time, but if we assume its value to be that given in Fig. 8 ( \( \sigma_b = 0.82 \sigma \) ), then we estimate a stress exponent as high as 13. Also, if we assume that a precipitate distribution having a mean spacing \( L = 0.5 \) \( \mu m \) forms at 600 °C after 1000 hours during deformation at a modulus-normalized stress of \( 5 \times 10^4 \), then we calculate an effective activation energy for rupture of \( Q_c/k = 56,000 \) K. These estimates are in reasonable agreement with observed high values from stress-rupture tests discussed above. More importantly though, the concepts and results we have been discussing might help in the development of a more basic understanding of the mechanical behavior of HT-9 leading to a predictive capability with regard to such properties as rupture life.

Summary

In this paper, we develop a model for the deformation behavior of the martensitic-ferritic alloy HT-9. This alloy is a prime candidate for long-time service in advanced fast reactor designs. In these kinds of applications, it is desirable for models to describe correctly the response to a wide range of loading conditions and to reflect the physics of plastic flow. It is hoped that this will lead to an ability to predict important mechanical properties over the range of interest. We base our model on a Dorn-type power-law creep equation and a Voce-type strain-hardening law. These are both well-established phenomenological laws that have a physical basis. They in effect reflect and embody the evolution of the microstructure associated with certain intrinsic aspects of plastic flow, and have exhibited considerable general applicability. These models are
employed here in a way that anticipates that the high temperature tensile data would be directly compatible with the high stress creep data. However, when creep and tensile data for HT-9 are plotted in accordance with this model, the high-temperature tensile data appear to represent a weaker material than that displayed by the creep data even though both sets of data are obtained from the same heat of material given the same heat-treatment. We postulate that this is a real strength difference caused by a change in the microstructure, namely secondary carbide precipitation, that occurs over time at high temperature during creep. We quantify this effect by calculating a back stress that when substituted into the tensile flow correlation causes it to predict the observed creep rate. We estimate the precipitate density using the Orowan bowing formula and extract a kinetic law for the precipitation process from the observed strength differences for different temperatures and characteristic times of the creep tests. The kinetic equation allowed us to prescribe an aging treatment that produced a microscopically observable precipitate distribution. The activation energy for the precipitation process is found to appropriately reconcile with the model additional low-temperature creep data obtained from a different heat of material. These results make it apparent that as creep tests are performed for longer times at higher temperatures, the creep strength shifts to higher values. It also appears possible that if constant-rate high-temperature tensile tests were performed at low enough rate, they might exhibit the same strengthening phenomenon. Finally, it is shown how these strengthening effects can cause observed differences between short-time and long-time rupture behavior. This is important, as it relates to the prediction of rupture life over a range of possible service conditions. With regard to fast reactor applications, service conditions of interest include normal operation as well as overpower and/or undercooling accident transients.

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References


10. F.R. Shoher, private communication.


