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EFFECT OF SODIUM ON THE CREEP-RUPTURE BEHAVIOR OF TYPE 304 STAINLESS STEEL

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EFFECT OF SODIUM ON THE CREEP-RUPTURE BEHAVIOR OF TYPE 304 STAINLESS STEEL

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ABSTRACT

Uniaxial creep-rupture data have been obtained for Type 304 stainless steel in the solution-annealed condition and after exposure to a flowing sodium environment at temperatures of 700, 650, and 600°C. The specimens were exposed to sodium for time periods between 120 and 5012 h to produce carbon penetration depths of ∿0.010, 0.020, and 0.038 cm in the steel. The results showed that, as the depth of carbon penetration and the average carbon concentration in the steel increase, the rupture life increases and the minimum creep rate decreases. Creep correlations that relate rupture life, minimum creep rate, and time-to-tertiary creep have been developed for the steel in both the solution-annealed and sodium-exposed conditions. Isochronous stress-creep strain curves and results on the calculations of the stress levels for 1 percent creep strain and long-term rupture life are also presented.

INTRODUCTION

The austenitic stainless steels used for the fuel cladding, in-core structural components, piping, valves, and intermediate heat exchanger in Liquid-metal Fast-breeder Reactors (LMFBRs) are subjected to a flowing sodium environment at elevated temperatures, which can result in compositional and microstructural changes as well as time dependent (creep) deformation in the materials. In the case of out-of-core components that have a design life of 20 to 30 y, the influence of the sodium environment, namely the time- and temperature-dependent migration of carbon and nitrogen, on the mechanical behavior of the materials must be considered.[(1)]

Nonmetallic elements such as carbon and nitrogen migrate in sodium heat-transport systems as a result of chemical activity differences. Transfer of these elements occurs in monometallic austenitic stainless steel systems with temperature gradients as well as in systems where combinations of materials of different composition are used. The ASME Boiler and Pressure Vessel Code Case 1592 for elevated-temperature nuclear-component design[(2)] requires consideration of mechanical-property changes that arise from compositional variations in the materials, due to the sodium environment during the service life of a component. Extensive research is being conducted at Argonne National Laboratory to establish quantitatively the influence of the sodium environment on the tensile, creep-rupture, and low-cycle fatigue behavior of austenitic stainless steels.

Limited data are available for the creep-rupture properties of austenitic stainless steels under carburizing conditions in liquid sodium. The creep-rupture strength of Type 304 stainless steel in flowing sodium at 650°C was reported[(3)] to be the same as that in helium; however, the carburization in these experiments was confined to a 50- to 75-μm surface region of the 0.15-cm-thick specimens for exposure times of ≲1000 h. If thinner specimens or longer exposure times were used, the alloys would have carburized throughout their entire cross section, and significant property changes, when compared with the tests in helium, would have been observed. Furthermore, in these experiments the carbon concentrations in the sodium were considerably higher than can reasonably be expected[(4)] in reactor heat-transport systems. Figure 1 shows the regions of carburization and decarburization for austenitic stainless steels with a nominal carbon concentration of 0.06 wt%. Presently, the carbon concentration in the primary sodium of the U.S. Experimental Breeder Reactor II (EBR-II) is in the range of 0.16-0.19 ppm.[(5)] Under such conditions, the stainless steels with an initial carbon content of 0.06 wt% would almost be in thermodynamic equilibrium with a carbon concentration in sodium of ∿0.17 ppm at ∿625°C, would tend to carburize at temperatures below 625°C, and would decarburize above 625°C. The extent to which the steels can undergo carburization or decarburization upon exposure to a sodium environment can be calculated from the carbon activity-concentration relationships developed as a function of temperature for these steels[(6)] and the carbon solubility values in sodium.[(7)] Figure 2 shows the equilibrium carbon concentration values for Type 304 stainless steel calculated as a function of carbon concentration in sodium at various temperatures. The predictions based upon

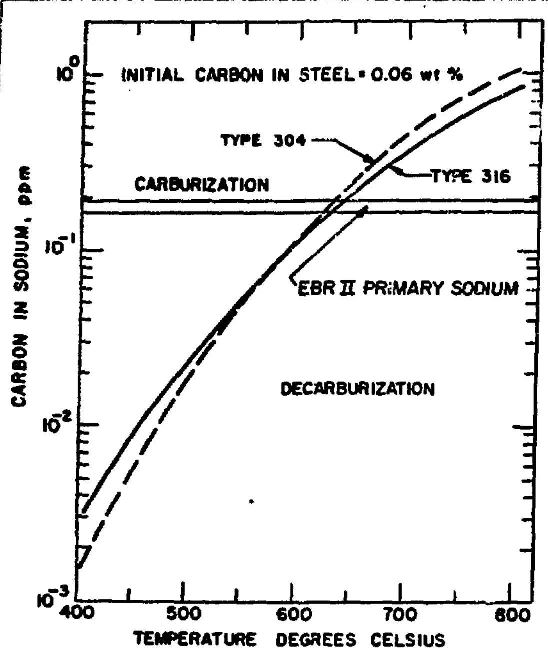

Fig. 1. Carburization-Decarburization Behavior of Austenitic Stainless Steels in a Sodium Environment.

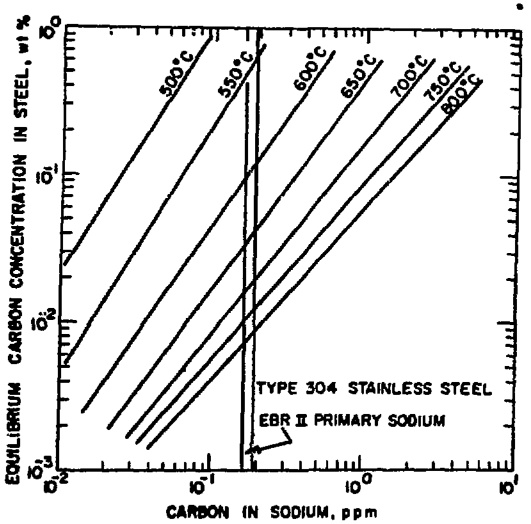

Fig. 2. Equilibrium Carbon Concentration in Type 304 Stainless Steel as a Function of Carbon in Sodium and Temperature.

these curves are that the steel in contact with primary sodium in EBR-II would carburize to ~0.60 wt% carbon at 550°C and decarburize to ~0.04 and ~0.02 wt% at 650 and 700°C, respectively. The sodium-exposure time required for the steel to attain these equilibrium carbon concentrations depends upon the diffusion coefficient for carbon in the steel and the thermal-mechanical history that influences the microstructure of the material. A mathematical analysis has been developed(4) to obtain carbon concentration-distance profiles as a function of time, temperature, and carbon concentration in sodium. Because of the relatively low operating temperatures and the large thickness of the materials in structural components, carbon concentration profiles rather than a uniform equilibrium carbon distribution will result in the steels during the service life of the reactor. Thus, it is essential to obtain mechanical-property data on materials with specific carbon penetration depths and to correlate the property changes with the penetration depth and surface carbon concentration in the material. In the present paper, data are presented on the effect of carburization on the creep behavior of Type 304 stainless steel for temperatures between 600 and 700°C.

EXPERIMENTAL PROCEDURE

The Type 304 stainless steel, identified as heat 9T2796, that is used extensively in breeder-reactor research programs, had the following chemical composition (in wt%): 0.046 C; 0.038 N; 17.7 Cr; 9.3 Ni; 1.17 Mn; 0.47 Si; 0.33 Mo; 0.20 Cu; 0.012 S; and 0.026 P. The steel was cold rolled to 0.0375-cm-thick flat stock, solution annealed for 30 min in argon at 1025°C, and water quenched. The grain size of the material was ~25 μm. Uniaxial creep-rupture specimens were fabricated with a gauge length of 2.22 cm and a width of 0.559 cm. The creep tests were conducted on conventional constant-load creep-rupture machines in an argon environment at temperatures of 600, 650, and 700°C over a stress range of 55 to 243 MPa (8 to 35 ksi). The creep strain in the specimens was measured by a linear-variable-differential transducer, in which displacements of 5×10^{-4} cm could be accurately determined.

A schematic diagram of the sodium loop used for the exposure of creep specimens, to achieve the desired depths of carbon penetration, is shown in Fig. 3. The loop, which was constructed of nickel, consists of four specimen-exposure vessels, a carbon trap for controlling carbon concentration in sodium, purification system, diffusion-type carbon meter, hydrogen meter, and electrochemical oxygen meters. The volume of sodium in the loop was ~100 liters, and the sodium flow rate was ~1.0 liter/min. The specimen-exposure vessels were connected in series and operated at 700,

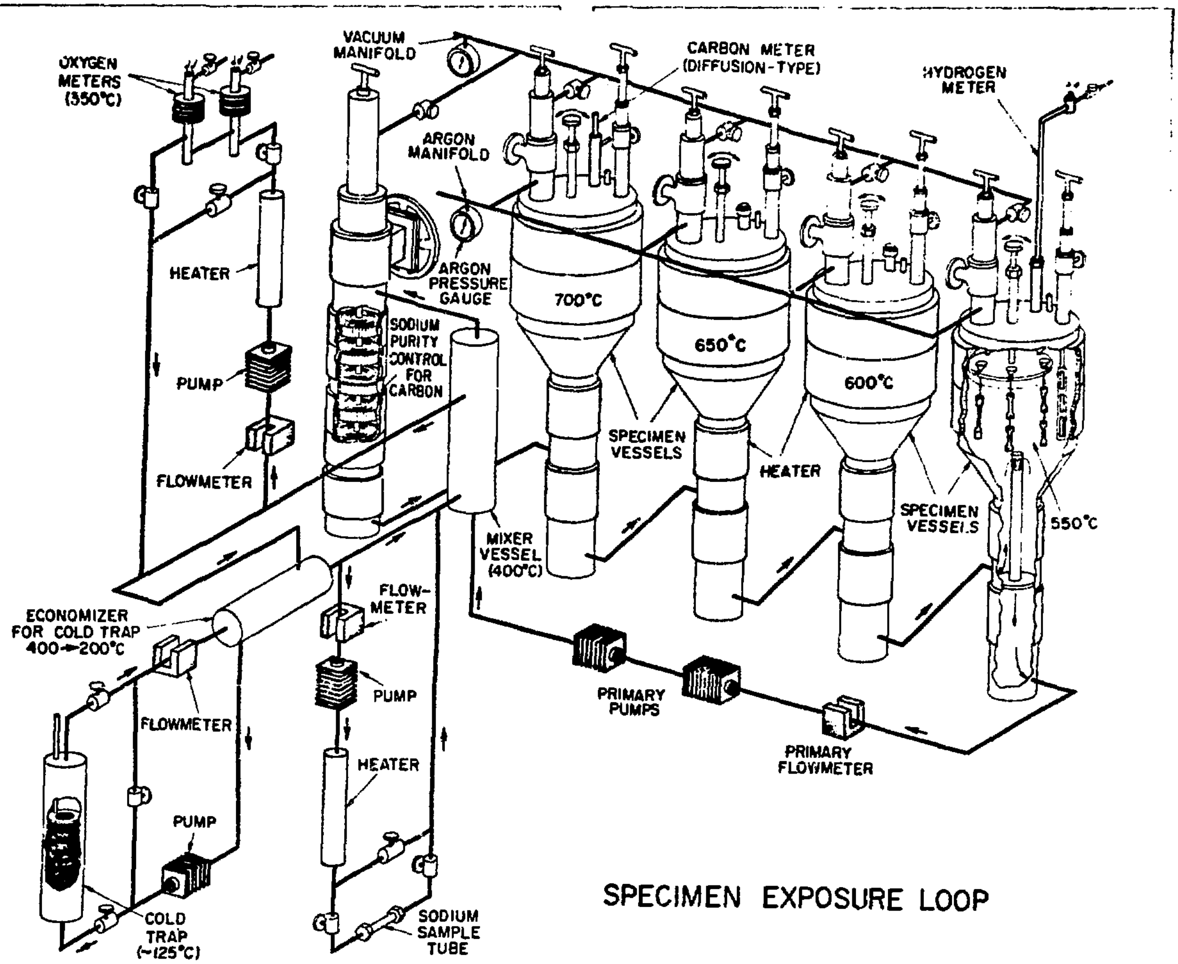

Fig. 3. Schematic of the Sodium Loop Used for Exposure of Mechanical Test Specimens.

650, 600, and 550°C. The sodium flowed successively from the highest to the lowest temperature and subsequently through the carbon trap prior to reentering the 700°C vessel. The electrochemical oxygen meters, with Cu/Cu_2O and Na/Na_2O reference electrodes and ThO_2-15 wt% Y_2O_3 solid electrolyte tubes, were used to monitor the oxygen concentration in sodium. The oxygen concentration in sodium was <1 ppm for all experiments. The carbon concentration in sodium was established by equilibrating a high-purity Fe-18 wt%Cr-8 wt%Ni alloy in sodium and using the reported[8] data on the distribution of carbon between this alloy and sodium. The carbon concentration in sodium was in the range 0.4-0.8 ppm for all experiments.

Creep specimens were exposed to flowing sodium at temperatures of 600, 650, and 700°C for times between 120 and 5012 h to produce carbon penetration depths of ~0.01, 0.02, and 0.0375 cm, which were calculated from the mathematical analysis in Ref 4. The specimens were subsequently used in creep-rupture tests in an argon environment to obtain the creep curves and creep-rupture times.

RESULTS AND DISCUSSION

A schematic of a creep curve that is obtained from a constant-load creep test is shown in Fig. 4. Strain values ε_1 and ε_2 and times t_1 and t_2 were determined, respectively, from the beginning and end of the secondary creep stage. At rupture, elongation ε_r and rupture time t_r were determined. The minimum creep rate $\dot{\varepsilon}_m$, that is, the slope of the linear portion between t_1 and t_2, was also obtained from the creep-rupture curve. The values for these creep parameters are tabulated elsewhere[9] for specimens tested in the solution-

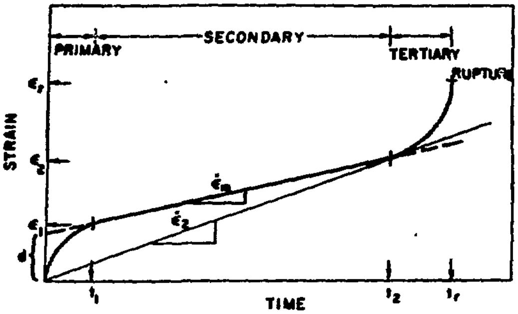

Fig. 4. Schematic of a Creep Curve from a Constant-load Creep Test.

annealed condition and after exposure to a flowing sodium environment. Figure 5 shows the variations in rupture life and minimum creep rate with applied stress at 700, 650, and 600°C for specimens in both the annealed and sodium-exposed conditions. The surface carbon concentrations in the mechanical test specimens were determined from combustion analyses of 50-μm-thick foils of the same material equilibrated in sodium during the specimen-exposure period. The values obtained were ∿0.05 wt% at 700°C, 0.25 wt% at 650°C, and 0.30 wt% at 600°C. The average carbon concentrations in the sodium-exposed specimens ranged from 0.043-0.046 wt% at 700°C, 0.078-0.195 wt% at 650°C, and 0.145-0.25 wt% at 600°C where the larger values correspond to longer exposure times. In general, the creep data show that, for the range of carburization attained in the present investigation, the exposure of the stainless steel to the sodium environment results in an increase in rupture life and a decrease in minimum creep rate when compared with the results for material in the solution-annealed condition. The carbon concentration in sodium is such that Type 304 stainless steel with an initial carbon content of 0.046 wt% is almost in thermodynamic equilibrium with the carbon in sodium at 700°C. As a result, the creep behavior of specimens that were exposed to sodium at 700°C was essentially the same as that of specimens tested in solution-annealed condition. At sodium-exposure temperatures of 650 and 600°C, the steel carburizes; the amount depends on the time of exposure. The creep tests results at these temperatures clearly show the beneficial effect of carburization in the stress range of our invastigation.

The microstructures of the sodium-exposed specimens (in the axial direction) before and after creep testing showed that the specimens with larger rupture strain have grains elongated significantly in the axial direction. It was observed that in Type 304 stainless steel the carbide particles preferentially precipitate at the grain boundaries and that the size of the particles in the specimen with longer sodium exposure is larger, which indicates growth of these particles with time. The precipitate morphology in these specimens should inhibit grain-boundary sliding and migration during the testing period. The respective contributions of grain elongation and relative grain movements to the deformation, that were determined in these specimens by evaluating the change in shape of internal grains and computing the intragranular deformation, showed negligible contribution of grain-boundary sliding to the creep strain in the stainless steel.(10) Examination of the fracture surfaces of annealed and sodium-exposed specimens creep tested at different stress levels showed that the fractures are dimpled, which is indicative of a ductile mode, and can be associated with the growth of internal voids or holes.(10)

CREEP-RUPTURE CORRELATIONS

To understand creep-rupture behavior more fully, various correlations between rupture life and other quantities determined from the creep curves were attempted. Relationships between rupture life t_r and minimum creep rate $\dot{\varepsilon}_m$ or time for onset of tertiary creep t_2 are useful if they describe the creep behavior of the material over a wide range of temperatures and applied stresses. Furthermore, such relationships, if developed, can be used to evaluate the necessary creep quantities from standard stress-rupture tests. Current elevated-temperature design rules(2) require not only a knowledge of rupture behavior but also information on the time to the onset of tertiary creep and time to reach a specified strain. Tertiary creep is generally indicative of material cracking and void formation, and therefore is metallurgically related to material damage. Also, tertiary creep results in material instability, since an increase in strain rate occurs with an increase in strain and strain concentrations induced by creep are accelerated. As a result, a correlation between the rupture life and the time-to-tertiary creep will be useful to establish the onset of instability in design studies.

The variation of t_r as a function of $\dot{\varepsilon}_m$ can be written as

$$t_r = C\left(\dot{\varepsilon}_m\right)^{-\alpha} \qquad (1)$$

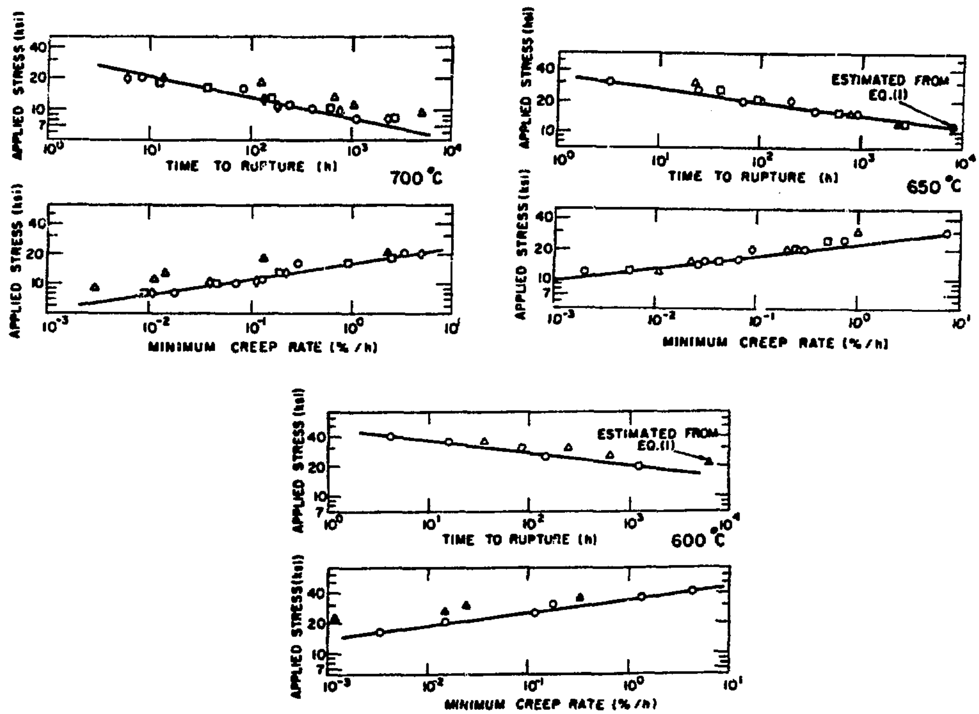

Fig. 5. Variation of Time to Rupture and Minimum Creep Rate with Applied Stress at 700, 650, and 600°C. Solution annealed: ○, Carburization depths: Δ = 100 μm, □ = 200 μm, and ◊ = 375 μm. Conversion factor: 1 ksi = 6.894 MPa.

where C and α are constants. Figure 6 shows a plot of $\ln t_r$ versus $\ln \dot{\varepsilon}_m$ for specimens tested in the solution-annealed condition and after exposure to flowing sodium

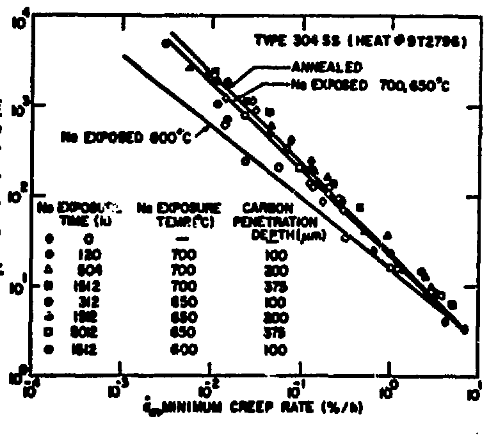

Fig. 6. A Plot of Rupture Life versus Minimum Creep Rate for Specimens in Solution-annealed and Sodium-exposed Conditions.

at 700, 650, and 600°C. In general, the results indicate that, for a given rupture time, the minimum creep rate decreases as the amount of carburization increases. The evaluations of constants C and α, for different sets of data in Fig. 6, are given in Table I. The correlations developed here are used to estimate the rupture lives of specimens for tests terminated prior to fracture. The calculated values, i.e., the solid symbols in Fig. 5, are in excellent agreement with extrapolations based on data obtained at the higher stresses.

The time for the onset of tertiary creep can be correlated with rupture life by the expression

$$t_2 = B\left(t_r\right)^{\beta} \qquad (2)$$

where B and β are constants. Figure 7 shows a plot of $\ln t_2$ versus $\ln t_r$ for specimens tested in the solution-annealed condition and after exposure to flowing sodium at 700, 650, and 600°C. The constants B and β, evaluated for different sets of data, are given in Table I. The results show that the time to initiation of tertiary creep is a fixed fraction of the time to rupture for the annealed and carburized conditions in the temperature range 600-700°C. The rate of coalescence of voids and growth of cracks during tertiary creep should

Table I. Creep Correlations

$$t_r = C\left(\dot{\varepsilon}_m\right)^{-\alpha}$$

Treatment	α	C
Solution Annealed	0.99	22.16
Na Exposed at 650 and 700°C	0.95	22.45
Na Exposed at 600°C	0.79	17.90

$$t_2 = B\left(t_r\right)^{\beta}$$

Treatment	β	B
Solution Annealed	1.025	0.558
Na Exposed (All Temperatures)	1.061	0.475
All Data	1.05	0.501

$$\dot{\varepsilon}_2 = D\left(\dot{\varepsilon}_m\right)^{\gamma}$$

Treatment	γ	D
Solution Annealed	0.987	1.072
Na Exposed at 650 and 700°C	0.972	1.079
Na Exposed at 600°C	0.918	1.075

$$\dot{\varepsilon}_m = A(\sigma)^n$$

Treatment	Temperature, °C	n	A
Solution Annealed	700	5.60	1.53×10^{-7}
Solution Annealed	650	5.90	5.33×10^{-9}
Solution Annealed	600	6.40	7.31×10^{-11}
Na Exposed	700	6.23	2.74×10^{-8}
Na Exposed	650	6.48	5.26×10^{-10}
Na Exposed	600	10.71	9.22×10^{-18}

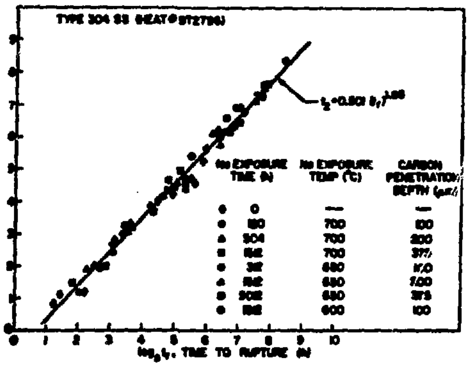

Fig. 7. A Plot of Rupture Life versus Time-to-tertiary Creep for Specimens in Solution-annealed and Sodium-exposed Conditions.

be related to quantity B in Eq. (2). Since β is almost unity, $B = t_2/t_r$. From the values of B reported in Table I for specimens in the solution-annealed condition and after exposure to *sodium*, it can be concluded that the void coalescence rates in the carburized specimens are slower than in the annealed specimens.

The time to a specified strain limit (currently set at 1 percent total inelastic membrane strain) has been analyzed by the use of isochronous stress-strain curves.[11] This involves analysis of individual strain-time curves from constant-load constant-temperature tests and development of analytical formalisms to describe the strain-time behavior. In the present paper, the experimental strain-time curves were analyzed in terms of the creep equation developed by Booker.[12] The equation is a single rational polynomial and is written as

$$\varepsilon = \frac{dpt}{1 + pt} + \dot{\varepsilon}_m t \tag{3}$$

where ε is the creep strain, d the intercept strain, $\dot{\varepsilon}_m$ the minimum creep rate, and t the time. The parameter p is related to the curvature of the primary portion of the curve. The intercept d was evaluated by the expression

$$d = \varepsilon_2 - \dot{\varepsilon}_m t_2 \tag{4}$$

where ε_2 and t_2 are strain and time that correspond to the onset of tertiary. The parameter p was assigned a value of $49/t_2$ since this value resulted in a good agreement between the experimental strain-time data for Type 304 stainless steel (heat 9T2796) and Booker's analysis.[12] Analytical expressions that relate the minimum creep rate $\dot{\varepsilon}_m$ and applied stress σ were also developed for temperatures of 700, 650, and 600°C from the creep data generated in this program on specimens in both the annealed and sodium-exposed conditions. The expression can be written as

$$\dot{\varepsilon}_m = A(\sigma)^n \tag{5}$$

where A and n are constants, the values of which are also given in Table I.

The correlations given in Table I were used in Eq. (3) to compute the strain-time curves and a comparison of the experimental data with the calculated values for specimens in annealed and sodium-exposed conditions was attempted. Figure 8 shows that the calculated values are in good agreement with the experimental data generated on solution-annealed and sodium-exposed specimens at 600 and 650°C. Generally the agreement was good in the temperature range 600-700°C and stress range of 8 to 35 ksi. Figure 9 shows the isochronous stress-creep strain curves that were generated at temperatures of 700, 650, and 600°C for annealed and sodium-exposed conditions. The results show that the carburization of the steel in the sodium environment in the range of our investigation enhances the creep-rupture properties of the material. The

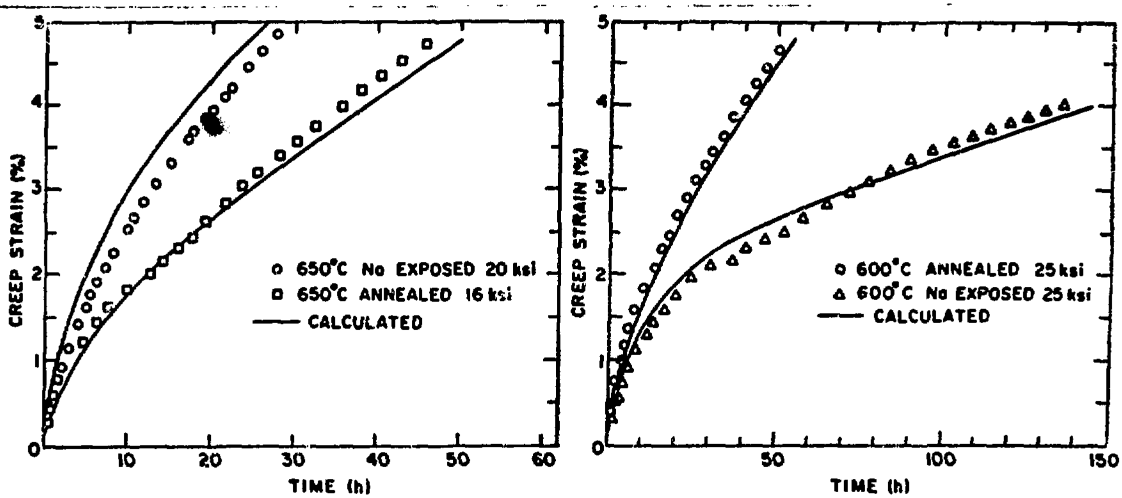

Fig. 8. A Comparison of Experimental Creep Strain-Time Curves with the Calculated Values.

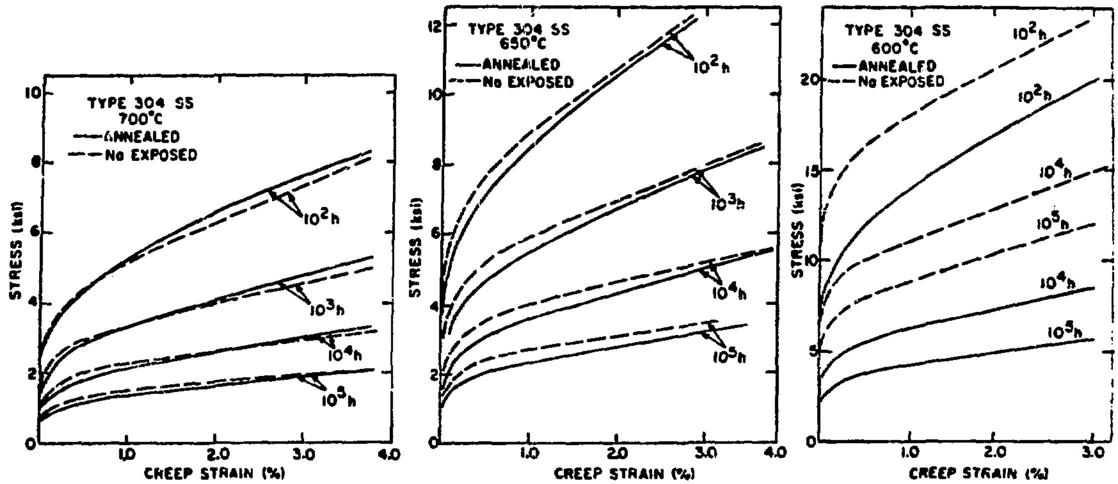

Fig. 9. Isochronous Stress-Creep Strain Curves for Specimens in Solution-annealed and Sodium-exposed Conditions. Conversion factor: 1 ksi = 6.894 MPa.

beneficial effect is more pronounced at 600°C where the material has undergone a larger degree of carburization than at 650 and 700°C.

Figure 10 shows the stress levels calculated for 1 percent strain limit in a specified time as a function of temperature for the steel in the solution-annealed and sodium-exposed conditions. Figure 11 shows the stress levels calculated for 10^4 and 10^5 h rupture strengths as a function of temperature.

SUMMARY

Uniaxial creep-rupture data have been obtained for Type 304 stainless steel in the solution-annealed and sodium-exposed conditions in the temperature range 600-700°C. The creep behavior of the steel carburized in sodium containing 0.4-0.8 ppm carbon, which represents an upper level for the carbon concentration in the sodium of an LMFBR heat-transport system, indicates that an increase in rupture life and a decrease in minimum creep rate will occur in this temperature range. Creep correlations have been developed which aid in the evaluation of creep quantities, such as minimum creep rate and time-to-tertiary creep, from standard stress-rupture tests. Isochronous stress-creep strain curves were generated for the steel in both the solution-annealed and sodium-exposed

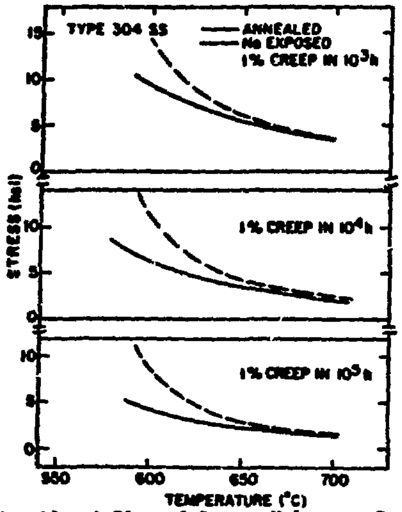

Fig. 10. A Plot of Stress Values to Produce 1 Percent Creep Strain as a Function of Temperature for Solution-annealed and Sodium-exposed Conditions. Conversion factor: 1 ksi = 6.894 MPa.

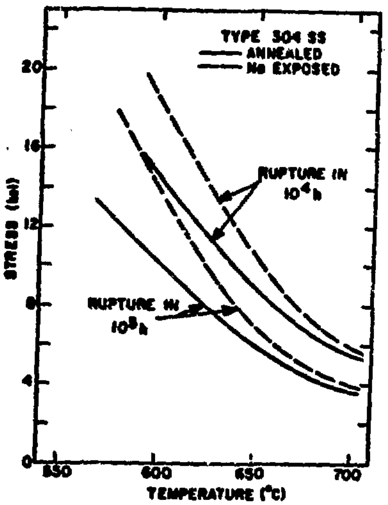

Fig. 11. A Plot of Stress Values for 10^4 and 10^5 h Rupture Strengths as a Function of Temperature for Solution-annealed and Sodium-exposed Conditions. Conversion factor: 1 ksi = 6.894 MPa.

conditions, with the use of a single polynomial creep equation. Results on the calculations of the stress levels for 1 percent creep strain and for long-term rupture life are also presented.

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