

Diffusion Creep in Zirconium and Certain Zirconium Alloys

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The steady-state creep behavior of zirconium and zircaloy-2 was examined in the temperature range 520° to 620°C. At low stresses the creep rates were characterized by a linear stress dependence; at higher stresses the stress dependence was much more pronounced. Temperature-cycling tests yielded values for the activation energy for creep. Various theories were examined in the light of the experimental results and it was concluded that the low-stress creep behavior is the result of the stress-directed diffusion of vacancies along grain boundaries.

IT has been observed,^{1,2} usually under conditions of high temperature and low stress, that creep deformation can occur for which the steady-state creep rate is linearly dependent on the applied stress.

For magnesium and certain magnesium alloys, Harris and Jones¹ and Jones² have argued that this type of creep occurs by mass transfer as a result of the stress-induced generation and migration of vacancies, along a gradient defined by the stress direction. Jones² demonstrated that the rate-controlling diffusion path is sensitive to grain size and temperature, and that by suitable control of these variables creep could occur by vacancy diffusion either predominately along grain boundaries or through the lattice.

Recently, Jones³ suggested from an examination of limited high-stress data for zircaloy-2, composition in Table I, that significant diffusion creep could occur at low stresses, at least between 375° and 500°C, controlled by grain boundary vacancy diffusion. This process could have an important implication in assessing the role of zirconium alloys as a structural or cladding material in certain classes of nuclear reactors, since it predicts creep deformation far in excess of any estimates based on extrapolating slip creep data from higher stress levels.

If the diffusion creep process occurs it should be possible to describe the total steady-state creep rate of zirconium and its alloys as the sum of two terms, Eq. [1]; the first term relates to a slip creep process important at high stresses and which is manifested by a much more pronounced dependence of creep rate on stress⁴ than diffusion creep and the second to a process controlled by mass transfer,^{5,6} dominant at low stresses:

$$\dot{\epsilon}_s = A_1 \sigma^n \exp(-Q_1/RT) + \frac{B_1 \sigma}{T} \exp(-Q_2/RT) \quad [1]$$

where A_1 and B_1 are parameters which can depend on structure, Q_1 and Q_2 are the activation energies for

the particular creep process occurring, and n describes the sensitivity of the creep rate on stress.

It is the purpose of this paper to present some direct experimental evidence in support of this view. It is recognized that other analytical approaches have been proposed to explain data of this kind and these will also be discussed.

1) EXPERIMENTAL PROCEDURE

Flat creep specimens (gage length 1 by 0.25 by 0.02 in. approx) were prepared from cold-rolled, argon-remelted, crystal bar zirconium and cold-rolled commercial-grade zircaloy-2, the analyses of which are given in Table I. The specimens were annealed at a pressure of $<10^{-5}$ Torr at temperatures from 625° to 675°C for 2 hr and slow-cooled. This treatment produced stable grains of average size (defined here by the average linear intercept) of $\sim 2 \times 10^{-3}$ in. ($\sim 50 \mu$) for zirconium and $\sim 4 \times 10^{-4}$ in. ($\sim 10 \mu$) for zircaloy-2. The specimens were tested in a dead load tensile creep rig. The stress was maintained constant by adjusting the applied load after approximately each 1 pct of strain. The specimen temperature was controlled to better than $\pm 1^\circ\text{C}$. This system had a small thermal lag, so that rapid temperature changes were possible. To minimize corrosion, the specimens were tested in high-purity (99.95 pct) argon, further dried,

Table I. Analyses of Zirconium and Zircaloy-2

Zirconium	
Element	Analyses, ppm
O	30
Hf	100
Ni	200
Unspecified	170
Zircaloy-2	
Element	Analyses*
Sn	1.42 ± 0.07 pct
Fe	0.14 pct
Cr	0.10 pct
Ni	0.05 pct
N ₂	39 ± 5 ppm
Ti	31 ± 2 ppm
Al	52 ± 7 ppm
Hf	79 ppm
H ₂	7 ± 3 ppm

*These are the average of readings taken from the top, middle, and bottom of the original ingot—when no average deviation is given, the three readings were identical.

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Manuscript submitted March 15, 1967. IMD

and purified by passing over magnesium perchlorate and heated copper chips. The specimens were surrounded by either a tube or strips of zirconium which acted as a preferential "getter". In spite of these precautions, visible films were invariably found on the specimen surface after long time creep tests. The probable significance of these films on test results will be discussed in the next section.

2) EXPERIMENTAL RESULTS

The creep behavior of both zirconium and zircaloy-2 was characterized by a short period of primary creep followed by a long period of steady-state creep, Fig. 1. The lower stress test illustrates the effect of a surface film on the creep behavior of zirconium. For this steady-state creep rate (below 10^{-4} hr $^{-1}$), the secondary region was not smoothly linear. Metallographic observations indicated that the steps were a result of periodic cracking and subsequent healing of a surface film. Fortunately this stepped curve only occurred in a small percentage of the tests and when it occurred the possible range in the measured creep rates was within the general experimental uncertainty. For zircaloy-2 the effect was not nearly as pronounced and quite smooth curves were obtained even for rates near 10^{-5} hr $^{-1}$. To examine whether the film had a more direct effect on the creep rate, tests on both zirconium and zircaloy-2 were halted as soon as a plot of $\log \dot{\epsilon}$ vs $\log t$ revealed steady-state conditions, i.e., a slope of unity. For these relatively short time tests, there was usually no visible surface film. The fact that the observed steady-state creep rates were the same as for tests run several hundred hours would appear to eliminate the possibility that the measured creep rate is directly controlled by the surface film.

2.1) Stress Increment Tests. The variation of the secondary creep rate with stress at constant temperature was examined by imposing stress increments on individual specimens undergoing creep. In this way the effects of structural variation were avoided. The results of representative tests on zirconium and zircaloy-2 are shown in Fig. 2. On a diagram of $\log \dot{\epsilon}$ vs $\log \sigma$ the slope of the straight line represents the value of the stress exponent n . For zirconium the stress dependence was linear at low stresses (i.e., $n = 1$). For zircaloy-2 a linear stress de-

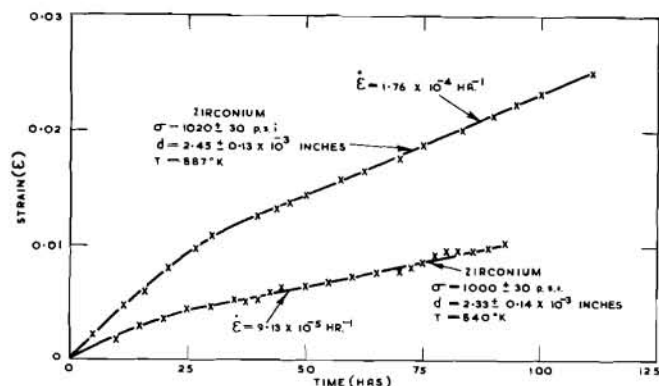


Fig. 1—The creep strain behavior with time for zirconium for two test conditions. The lower strain rate test illustrates the effect of a surface film on the secondary creep rate.

pendence of the creep rate was directly demonstrable over the stress range 1500 to 3000 psi. At 500 psi and 1000 psi the measured rates were higher than the values expected. From a subsequent $\log \dot{\epsilon}$ - $\log t$ plot, it was revealed that these tests had not yet achieved true steady-state conditions. However, the deviation was small, permitting a reasonable extrapolation of the data onto a line of unit slope. When this was done, the estimated true steady-state creep rates at these stresses were in good agreement with the predicted values from Fig. 2. The values of n were 6 to 7 for zirconium above about 2000 psi and 4.5 to 5.5 for zircaloy-2 above about 3000 psi. The fact that n is higher for the pure metal has been observed for other systems.⁸

2.2) Temperature Incremental Tests. If Jones's³ premise is correct, then the activation energy describing the diffusion creep process, Eq. [1], second term, should be that for grain boundary diffusion. While there are no values for this activation energy available for zirconium or zircaloy-2, estimates can be made using the empirical correlation⁹ between

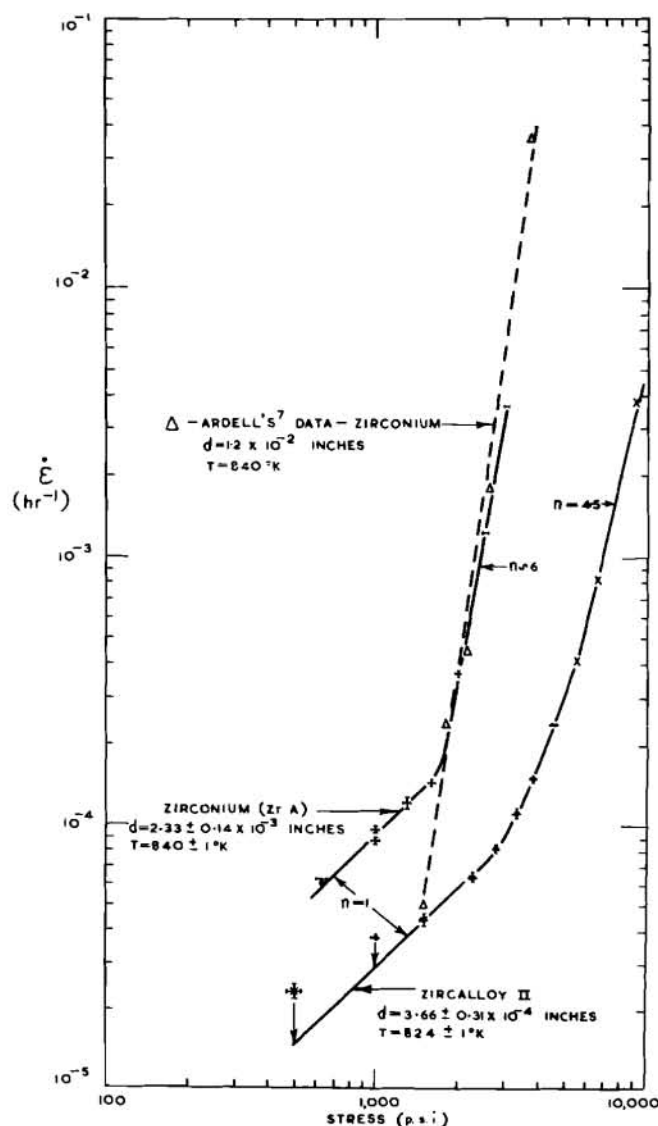


Fig. 2—The effect of stress on the steady-state creep rate for zirconium and zircaloy-2.

grain boundary activation energies and known values for self-diffusion energies.¹⁰ The activation energy obtained in the high stress range where slip creep is dominant should be more comparable with self-diffusion.⁴

Assuming that Eq. [1] describes the total creep rate, values for the two activation energies concerned can be obtained from temperature cycling experiments at different stress levels where the processes are individually dominant. Such experiments were performed on specimens of zirconium and zircaloy-2 and on the zirconium-base alloy ATR (which contains approximately 0.5 pct Cu and 0.5 pct Mo). For ATR stress incremental tests were also performed to determine the stress range where a linear stress dependence existed. Whenever possible tests were performed by reducing the temperature. This was particularly necessary for zirconium in the linear stress dependency region, where increasing the temperature resulted in small structural changes and an unstable creep rate. Fig. 3 illustrates the results for the condition $\eta = 1$. In these circumstances, according to Eq. [1], plotting $\log \dot{\epsilon} T$ vs $1/T$ at constant stress should produce straight lines of slope $-Q_2/2.303R$.

The slopes were determined from a least mean squares analysis of the data and yielded activation energies, for the temperature ranges employed, of 29.7 ± 1.5 kcal per mole for zirconium at 1500 psi, 41.3 ± 2.2 kcal per mole for zircaloy-2 at 1815 psi, and 39.2 ± 2.9 kcal per mole for ATR at 2175 psi. The activation energy was also determined for zirconium at 1000 psi and a value of 28.6 ± 2.2 kcal per mole was obtained, indicating that there is no significant stress dependence of Q in the low stress range. At higher stresses where $\eta > 1$, Q for the creep of zirconium was found to be ~ 56 kcal per mole (broadly in agreement with Ardell's⁷ results); for zircaloy-2 a value of ~ 68.5 kcal per mole was obtained. Both of these values were somewhat stress-

dependent, but the exact form of this dependency was not investigated. Clearly, in both stress ranges alloying increased the activation energy for the creep process. The values in the high-stress region are of the same magnitude though rather higher than the best available tracer results for self-diffusion in zirconium (45.5 kcal per mole)¹⁰ and zircaloy-2 (~ 62 kcal per mole which was actually determined for a Zr-1.3 pct Sn alloy).¹⁰

3) DISCUSSION

The experimental results firmly establish the existence of a linear stress exponent for zirconium and zircaloy-2 at low stresses. It has been suggested^{7,11,12} that such behavior might be explainable on the basis of a general creep equation, applicable over a wide range of stress, of the form:

$$\dot{\epsilon}_s = A (\sinh k\sigma) D_0 \exp(-Q/RT) \quad [2]$$

where A and k are terms that may depend on stress and temperature. Harper and Dorn^{11,12} have used such an equation to explain a linear stress dependence in aluminum at low stresses. They concluded that a dislocation climb mechanism was rate-controlling for all stresses. More recently Barrett and Nix¹³ have proposed a model for steady-state creep based on the motion of jogged screw dislocations. Their relationship was of the same form as Eq. [2] with k dependent on temperature and with a stress-dependent mobile screw dislocation density as part of the preexponential constant A . If the mobile screw dislocation density becomes independent of stress at low stresses, then a linear stress dependence could result.⁷ The alternate approach favored in this paper is the one presented in the introduction, based on the concept of grain boundary diffusion creep as formulated by Coble.⁶ For this case the second term of Eq. [1] has the form:

$$\dot{\epsilon}_s = \frac{B}{d^3} \frac{\Omega \sigma}{kT} w D_{0gb} \exp(-Q_{gb}/RT) \quad [3]$$

where

B is a geometrical factor,

Ω is the atomic volume of a unit cell,

σ is the applied stress,

d is the diameter of a spherical grain,

w is the effective width of the grain boundary,

D_{0gb} is the frequency factor for grain boundary diffusion, and

Q_{gb} is the activation energy for grain boundary diffusion.

An examination of Eqs. [1], [2], and [3] make it possible to distinguish between these two theories by the following comparisons.

a) The creep rate is a very sensitive function of grain size for diffusion creep while there is no obvious grain size dependence for the slip creep process described by Eq. [2] though an inverse linear grain size dependence might be expected at high creep temperatures¹⁴ and a (grain size)² dependence at low temperatures.^{4,14}

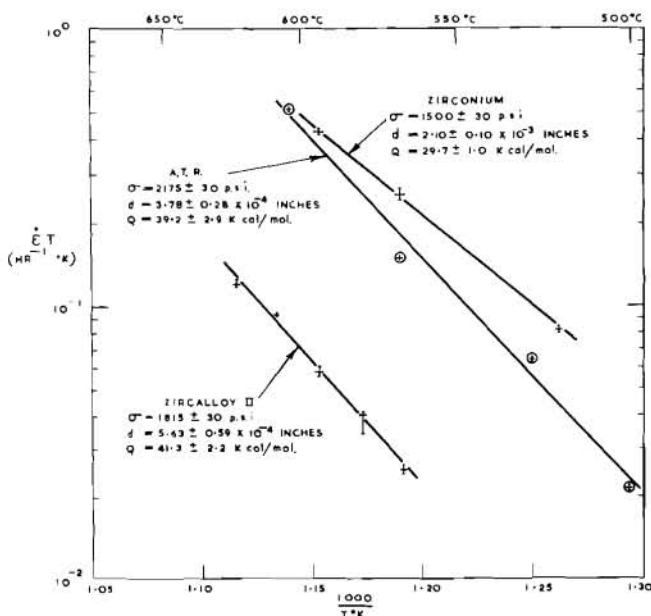


Fig. 3—The effect of temperature on the temperature-compensated steady-state creep rate for zirconium, zircaloy-2, and ATR, each tested at constant stress. The calculated creep activation energies are shown.

b) For diffusion creep the slope of $\log \dot{\epsilon}T$ vs $1/T$ yields a direct measure of the grain boundary diffusion energy, which is not a function of the applied stress. If slip creep is controlling a plot of $\log \dot{\epsilon}$ vs $1/T$ yields an apparent activation energy whose significance depends on the exact form of Eq. [2]. The self-diffusion energy is often obtained if the preexponential terms are temperature-independent. If this is not the case, the experimental activation energy is expected to decrease with increasing stress.⁷

c) Eq. [2] defines the condition where a single process is rate-controlling over the entire stress and temperature range. The variation in stress dependence with stress arises from the form of the $(\sinh \sigma)$ term. However if grain boundary diffusion creep is dominant at low stresses, two distinct processes acting in parallel are involved.

Thus these points indicate ready methods of distinguishing experimentally between the two mechanisms. The experimental results show that, in the low-stress region where $n = 1$, the rate-controlling process is characterized by a low activation energy (*i.e.*, 29.7 kcal per mole for zirconium, 41.3 kcal per mole for zircaloy-2, and 39.2 kcal per mole for ATR). However, at higher stresses when n is in the range 6 to 7 for zirconium and 4.5 to 5.5 for zircaloy-2, the activation energies are significantly larger (~56 kcal per mole for zirconium and ~68.5 kcal per mole for zircaloy-2). This clearly demonstrates that different processes are rate-controlling in the two stress regions. Support for the premise that grain boundary diffusion creep is controlling when $n = 1$ is afforded by the ratios of the creep activation energies to self-diffusion energies. This ratio is 0.65 for zirconium and 0.67 for zircaloy-2, in good agreement with the empirical correlation of 0.5 to 0.7 for the ratio of these energies.⁹ The fact that the high-stress region is characterized for both cases by an activation energy which is greater than the self-diffusion values is in agreement with the results of Ardell.⁷

As far as the effect of grain size on creep is concerned, the results of this investigation are less conclusive as it proved impossible to produce a wide

range of stable grain sizes in the two materials. However the results of Ardell⁷ provide a graphic demonstration of the effect of grain size on creep rate. Extrapolation of his results down to 870°K allows comparison with specimen ZrA, Fig. 2. The creep rates were similar for the two series of tests when $n > 1$, even though the grain size of Ardell's samples was about six times larger than the grain size of ZrA. However, at low stresses the coarse-grained material is a good deal stronger, suggesting that in this range the effect of grain size is much more significant. To discover the actual grain size dependence of the creep rate when $n = 1$, attempts were made to correlate results from different specimens using realistic grain size dependence corrections (*e.g.*, d^{-1} , d^{-2} , and d^{-3}). It was found that by far the best correlation resulted from the application of an inverse cube grain size correction. Accordingly all the results in this region were plotted using the parameter $\log \dot{\epsilon}(Td^3/\sigma)$ vs $1/T$ which takes into account the variation in both grain size and stress between samples, see Fig. 4. This comprehensive display of the experimental data yielded the best values for the activation energy for low-stress creep in both materials (26.7 ± 3.3 kcal per mole for zirconium and 42.5 ± 3.9 kcal per mole for zircaloy-2).

While the available evidence points strongly towards grain boundary diffusion creep being the rate-controlling process at low stresses in zirconium and zircaloy-2, it might still be possible, at least analytically, to devise a dislocation mechanism that could rationalize the experimental results. However, if this is attempted it is very difficult to envisage a process which must fulfill the requirements of a linear stress exponent and an activation energy lower than that for self-diffusion, and which only operates at low stresses. This low activation energy restricts the type of mechanism that could be invoked to explain this high-temperature, low-stress creep behavior. The stress independence of the activation energy must rule out any model which depends on the stress-assisted thermal activation of dislocations over Peierls barriers. Feltham and Meakin¹⁵ and Barrett and Sherby¹⁶ have examined the creep of copper in a temperature range where the activation energy was found to be substantially less than that for self-diffusion. The low value of Q was attributed by the former authors to a process controlled by the motion of vacancies along dislocations. Barrett and Sherby¹⁶ questioned this view, pointing out that the observed activation energy was too large for such a process. They suggested that the low value of Q was a result of high-diffusivity paths around dislocations acting as short-circuit channels for the self-diffusion process. For both mechanisms creep was still considered to be a result of the climb of edge dislocations. However, Barrett and Sherby¹⁶ found no change in n when the activation energy changed (with temperature) from its low value to that describing volume self-diffusion. This is completely different from the present case, where the change in activation energy was associated with the change in stress exponent.

All the problems of attempting to describe artificially a dislocation model capable of explaining the observed creep behavior of zirconium and zircaloy-2 at low stresses are avoided if the rate-controlling

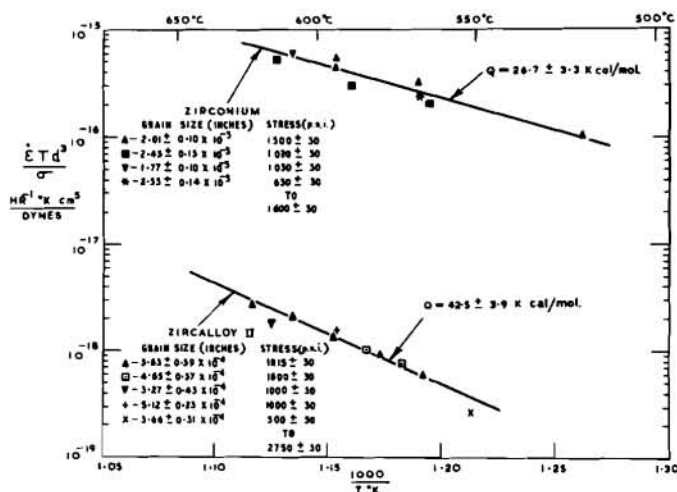


Fig. 4—The effect of temperature on the steady-state creep rate compensated for grain size, stress, and temperature, for zirconium and zircaloy-2. The calculated creep activation energies are shown.

Table II. Estimated Experimental Values of BD_{0gb} and D_{0gb}

	BD_{0gb}	D_{0gb}
Zirconium	37	0.75
Zircaloy-2	526	11
ATR	275	6

process is accepted to be grain boundary diffusion creep, as described by Eq. [3]. While it should then be possible to compare the theoretical predictions of the steady creep rate from Eq. [3] with experimental results, the uncertainty in some of the preexponential terms, in particular D_0 , allows only a qualitative comparison to be made. Alternatively the approach can be to use the experimental steady-state creep rates to estimate values of the terms BD_{0gb} and D_{0gb} (assuming after Coble⁶ that $B = 150/\pi$). The results are given in Table II. The values taken for Ω and w were 2.32×10^{-23} cu cm and 10^{-7} cm, respectively. The fact that D_{0gb} is smaller for zirconium than for zircaloy-2 has also been indicated for the corresponding self-diffusion values in these materials.¹⁰ It is informative that the creep rate for zircaloy-2 at, for example, 500° to 600°C is two to three orders of magnitude less than zirconium (for the same grain size and stress) even though the preexponential term is about an order of magnitude greater. This illustrates the importance of the magnitude of the activation energy in determining the creep rate.

4) CONCLUSIONS

The steady-state creep behavior of zirconium and zircaloy-2 was examined in the temperature range 520° to 620°C, with the following results.

1) Both materials exhibited a linear stress dependency of creep rate at low stresses. At higher stresses zirconium had a stress exponent of 6 to 7 and zircaloy-2 one of 4.5 to 5.5.

2) In the region where $n = 1$, the rate-controlling process was shown to be grain boundary diffusion

creep. Using all test results, a grain boundary activation energy of 26.7 ± 3.3 kcal per mole was found for zirconium, and values of 42.5 ± 3.9 and 39.2 ± 2.9 kcal per mole were found for zircaloy-2 and the zirconium alloy ATR, respectively. These values constitute the first experimental determination of grain boundary activation energies in zirconium and its alloys, and are in good agreement with the empirical correlation $Q_{gb} = (0.5 \text{ to } 0.7)Q_{sd}$.⁹

3) At high stresses activation energies for creep were in qualitative agreement with values for self-diffusion.

4) The very large increase in creep strength for the alloys as compared to pure zirconium in the diffusion creep range is a result of solute additions greatly increasing the grain boundary activation energy.

ACKNOWLEDGMENT

The author wishes to thank Dr. R. B. Jones for many stimulating discussions and Mr. Eric Hoare for experimental assistance.

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