Viscous creep in metals*

P. Rama Rao

In several high technology applications, stressed components are exposed to elevated temperatures. More often, the resulting creep deformation rate is a function of stress raised to a power 4 to 6. When stresses are below about $10^{-5} \, G$, where $G$ is shear modulus of the material, viscous creep processes, characterized by a linear dependence on stress of creep rate, usually in the range $10^{-7}$ to $10^{-11} \, s^{-1}$, dominate over power-law creep. Two such creep processes, the Nabarro-Herring creep and the Coble creep, are grain boundary-related while the third, the Harper-Dorn creep is not. This paper describes viscous creep phenomena, experimentally investigated using spring specimens, in reactive materials Ti, Zr and the nuclear fuel-cladding zircaloy. Experience with the two-phase superplastic Zn–22 Al alloy, in which stage I deformation has been seen to have viscous characteristics, is also presented. Current interest in Zr–2.5 Nb alloy is indicated in the context of not only its present usage, in replacement of zircaloy, in nuclear reactors but also as a candidate two-phase material in which superplasticity has been observed.

The proportionality relation ($\dot{\varepsilon} \propto \sigma^4$) between applied stress ($\sigma$) and the resulting strain rate ($\dot{\varepsilon}$) is one of the most elegant relationships in the mechanical properties of matter. Not only elegant but also one of the most useful relationships in terms of which one can distinguish between a solid and a fluid, the constant of proportionality being orders of magnitude different for the two states of matter. If we express $\dot{\varepsilon} = \alpha \sigma$, it will be the Newtonian law of viscous flow. $\alpha$ is fluidity, the inverse of dynamical viscosity ($\eta$). The work discussed in this paper is concerned with Newtonian viscous flow.

Viscosity of a metallic liquid is about $10^{-3}$ to $10^{-2}$ poises at melting and rises rapidly on cooling. Crystallization increases viscosity by several orders of magnitude to about $10^8$ poises and this value increases further as the crystallizing solid cools. If the metallic liquid fails to crystallize, which happens during rapid solidification by splat-quenching, viscosity would still be high and the product is known as metaglass. One can discuss a variety of substances like polymers and rubbers or sols and gels in terms of fluidity and viscosity. We deal here with the viscous flow behaviour exhibited by metals and alloys under certain conditions of loading at high temperatures.

It is not uncommon for metallic components to be exposed during actual service to temperatures of the order of $0.5 \, T_m$, where $T_m$ is the melting temperature expressed in Kelvin. If at such elevated temperatures, the component is loaded to stresses of the order of $10^{-4} \, G$, where $G$ is the shear modulus of the material, the component would undergo slow, time-dependent deformation at strain rates of the order of $10^{-6}$ to $10^{-10}$ per sec. The phenomenon is called viscous creep and has been a subject of our research interest for quite a few years. This is the subject that we shall present and discuss here.

Cottrell creep

An event of historical significance is the commencement, in 1955, of operation of the Calder Hall nuclear reactor in England which heralded the era of civilian nuclear reactor programme. The added significance as relevant to our present subject matter arises from the discovery of viscous creep of one particular kind. Calder Hall was a gas-cooled reactor. The fuel was uranium.

Alan Cottrell, one of the greatest contemporary materials scientists, was sitting in his office cogitating upon the state of the Calder Hall fuel. Orthorhombic uranium displays anisotropic thermal expansion. By then the irradiation growth process had been reported whereby, under neutron irradiation, creep rate of uranium is enhanced. It occurred to Cottrell that the growth stresses in individual grains of polycrystalline uranium would build up stresses at grain boundaries. His simplified calculation showed that these stresses would be higher than the yield stress of the material. Cottrell argued that, in such an internally-stressed material, a small external load could cause considerable plastic strain. In the stack of fuel elements, a given fuel element has to withstand the weight of those above it. If one considered only thermal creep, as had been assumed, there would have

P. Rama Rao is in the Atomic Energy Regulatory Board, Anushaktinagar, Mumbai 400 094, India and Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India.

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been no serious problem (because of marginal U thermal creep under these conditions). However, Cottrell visualized a new important phenomenon arising from the stack behaving like a viscous material. Cottrell derived an expression for viscous creep which would occur in this situation (known ever since as the Cottrell creep) and showed that the strains would be considerable. Consequently, in a constrained assembly, the fuel stack would buckle and undergo bowing. On his advice, some of the fuel elements were prematurely discharged when it was found that the fuel elements had indeed buckled and the extent of sag matched with his model predictions. Several engineering modifications had to be carried out before operation of the reactor was resumed. This is an outstanding piece of purely basic research, but attempted when a major system like a nuclear reactor had gone on to the stage of full scale operation. It should therefore be regarded as a memorable instance of a seamless border between basic research and operating technology. In this case, Cottrell's research led not only to the discovery of a new form of creep but also contained information of considerable engineering significance.

There are other forms of viscous creep which we shall now describe as it is these with which we shall mostly be concerned.

**Diffusion creep**

When creep of solid materials occurs by diffusional processes involving transport of matter, rather than by dislocation flow, Newtonian viscous flow is observed. The earliest observations of diffusional creep were from experiments on thin wire specimens having only one grain per cross-section, called bamboo structures which were used to measure surface energies. The zero creep technique involves balancing the tendency of thin specimens to shrink under the action of surface tension by application of a tensile load. The experiments were performed at temperatures close to the melting point. Jones analyzed the data and showed that the creep behaviour corresponded to diffusion creep. For several years later, diffusion creep was considered merely to be of academic significance as it was thought to occur only at temperatures close to the melting point. However, this notion changed as a result of further significant findings.

The simple principle underlying diffusion creep is that the energy of vacancy formation $E_1$ at the tensile facets of a polycrystal (Figure 1) is reduced by an amount $\sigma \Omega$, where $\sigma$ is the normal stress experienced by the grain facet and $\Omega$, the atomic volume. The equilibrium concentration of vacancies near these facets is thus enhanced by an amount $\sigma \Omega kT$, where $k$ is the Boltzmann constant.

![Figure 1. Vacancy fluxes in a stressed polycrystal.](image)

![Figure 2. a. Formation of zones denuded of particles due to diffusional creep (after Squires et al.). b. Marker offsets as evidence of grain boundary sliding accommodating diffusion creep (after Langdon).](image)

On the other hand, the energy of formation of a vacancy is enhanced by an amount equal to $\sigma \Omega$ near the facets experiencing compressive stress. Consequently, the equilibrium concentration of vacancies at these facets is reduced by $\sigma \Omega kT$.

Thus arises a chemical potential gradient providing the driving force for transport of matter in a direction counter to that of the vacancy flux, i.e. towards the
tensile facets. This leads to the Nabarro Herring (N–H) creep formula:

$$\dot{\epsilon}_{\text{NH}} = (A_{\text{NH}} \Omega D_v \sigma) / d^2 kT,$$

(1)

where $D_v$ is diffusion coefficient; $d$, the grain size and $A_{\text{NH}}$ is a constant. It is useful to note that the N–H creep rate is inversely related to the square of the grain size as the grain dimension would be related to the diffusion distance.

In a somewhat analogous formulation, Coble assumed that migration of matter from facets experiencing compressive stress to those under tensile stress would occur circumgranularly, i.e. along the grain boundaries (rather than through the lattice as in the treatment developed by N–H). Coble derived the following expression

$$\dot{\epsilon}_{\text{C}} = (A_{\text{C}} D_B W \Omega \sigma) / d^3 kT,$$

(2)

where $D_B$ is the grain boundary diffusion coefficient, $W$, the grain boundary width and $A_{\text{C}}$ is a constant. Coble creep has the viscous characteristic, since $\dot{\epsilon}_{\text{C}}$ is linearly related to the applied stress $\sigma$, but the creep rate in this instance varies inversely as (grain size)$^3$, a far stronger dependence on grain size compared with the N–H process.

The theoretical treatments of N–H, carried out in 1948 and of Coble in 1963 constitute a rare instance in physical metallurgy where theory preceded experiment. A dramatic piece of evidence for diffusion creep came in 1963, again from a nuclear reactor operation. Squires et al. observed, for the first time, in a magnesium alloy strengthened by zirconium hydride precipitate particles, zones denuded of precipitates at grain boundaries oriented at right angles to the tensile stress axis. Their micrograph (Figure 2 a) provided dramatic proof of stress-directed creep diffusion with ZrH$_2$ precipitates acting as markers in the diffusion creep process.

When a polycrystal undergoes diffusion creep, causing transfer of matter from grain boundaries under compression to those under tension, individual grains will undergo change of shape. To accommodate the shape change of individual grains, the relative movement of grains in the polycrystal must occur (Figure 2 b). Thus, grain boundary sliding (GBS) is associated, as an accompanying process, with diffusion creep. Recently, the celebrated micrograph of Squires et al. was reexamined by Langdon who pointed out that there are offsets in the hydride particles crossing from one grain to another (Figure 2). This has largely removed doubts expressed about the inference of diffusion creep by Squires et al. It is interesting to note that while the initial formulation of N–H theory was in 1948, it took 15 years for physical evidence to be obtained and another more than 20 years for an observation to be advanced substantiating that piece of evidence.

**Power-law creep**

Creep deformation, as is well known, can also be brought out by movement of dislocations. At relatively lower temperatures, the dominant mode of dislocation movement is glide, i.e. dislocations traversing the slip plane. At elevated temperatures (around 0.5 $T_m$ or higher), dislocations would also be capable of climb movement, i.e. perpendicular to the slip plane, often necessary to overcome obstacles on the glide plane. Climb is aided by the presence and migration of vacancies and the controlling mechanism would be self-diffusion, which is the governing process in N–H creep. However, there is a difference. If creep deformation occurs by the glide-climb process, the creep rate would not be linearly dependent on applied stress $\sigma$, but $\sigma^2$ or so. This form of creep is, therefore, referred to as power-law creep.

**Harper–Dorn creep**

Figure 3 is a sketch depicting four different modes of creep. Reference has been made to the two forms of diffusion creep, N–H and Coble creep, and the power-law creep. Although we have mentioned power-law creep for the sake of completeness, the focus of our present discussion is on viscous modes of creep characterized by a linear dependence of $\dot{\epsilon}$ on $\sigma$. The fourth process shown in the sketch is yet another form of viscous flow going by the name of the original discoverers, Harper and Dorn.

Under conditions of exposure to high temperatures and low stresses, Harper–Dorn (H–D) creep can occur and, unlike N–H and Coble creep processes, is not a grain boundary process. H–D creep was found to be governed by a dislocation-based mechanism. The question, then, is, if power law creep and H–D creep are
both dislocation-related, where does the distinction lie which results in power law dependence of creep rate in one case and linear dependence in another. The answer, based on the present understanding is that, during power-law creep, dislocation density varies with stress while in the H–D process dislocation density remains constant, i.e. the H–D process operates under saturated conditions. Harper and Dorn explained in these terms the low stress creep behaviour of Al observed by them at temperatures close to its melting point when the applied stress, as was to be pointed out later, was lower than the lattice friction stress, also known as the Peierls stress. Peierls stress is one of the fundamental concepts in dislocation theory and is based on the idea that the crystalline lattice offers resistance to the passage of dislocations. The resistance arises from a force (Peierls–Nabarro force) exerted by the lattice on the dislocation (Figure 4). On this basis, then, there should be a crystal structure dependence. And this is so. FCC metals have a low Peierls stress while BCC metals higher Peierls stress. H–D creep is a mode driven by dislocation movement overcoming lattice friction. Since H–D creep is not a grain boundary-related process, the creep rate in this case is not a function of grain size.

Previous laboratory observations

The characteristic parametric dependences of the four different creep processes have been assembled in Table 1. The different dependences are experimentally verifiable and therefore constitute an aid in determining which of them is the dominant process in a given situation.

While inference about the occurrence of diffusion creep was first drawn from zero creep experimental data obtained at temperatures close to the melting point, the first set of laboratory experiments at lower temperatures was performed during 1965–70. Jones performed the first set of such experiments on magnesium in 1965 and his data (and those on other metals) showed agreement (Figure 5) with N–H creep theory in respect of all the parametric dependences listed in Table 1. The observed and theoretically predicted creep rates also agreed quite well.

The work of Burton and Greenwood on copper was particularly striking in that it brought out for the first time the switching of creep process from one governed by lattice diffusion to that dictated by grain boundary diffusion. When creep of fine-grained copper was investigated as a function of temperature (Figure 6), coarsening of the microstructure was seen to lower the creep rates as well as to shift the temperature at which transition occurred from N–H to Coble creep at lower temperatures. It may be noted from Figure 6 that the stress applied was in the region of 5 MPa, i.e. about $10^{-5}$ of the shear modulus of the metals studied.

Experimental method

The creep rates at such low stresses of the order of a few kg/mm², depending on the material and the specimen section size, will be in the range of $10^{-7}$ to $10^{-10}$ per sec or so. Laboratory experiments aimed at measuring such low strain rates would need a very long time, maybe several years. If one is to use straight specimens, these would necessarily have to be very long, several
metres in length. These problems are overcome if experiments are carried out on spring specimens which were used by Jones"15, as well as by Burton and Greenwood"16 in their studies.

The springs are coiled. They are self-heated by passing a current through the specimen. They are self-loaded. The load varies from coil to coil, as the load on any given spiral is dictated by the number of spirals beneath it. The top-most spiral experiences the maximum load and the bottom-most nearly no load and so in one specimen run, one can get a wealth of data over a number of stresses at a given temperature.

The deflection of each coil of the spring as a function of time can be measured with the help of a simple cathetometer, i.e. a telescope with a vernier, whose position is displaced as creep progresses (Figure 7).

In our work on reactive metals such as Ti, Zr and zircaloy in the past and currently on a Zr-Nb alloy, the problem of the specimens oxidizing looms large. Hence, the spring specimen is housed in a sealed and evacuated chamber with getters to prevent oxidation of samples"17 (Figure 8).

The mechanics of springs is shown in Figure 9. Briefly, let the applied axial force be \( P \). For equilibrium of forces, the moment due to this force \( P \) should be equal and opposite to the torque \( PR \) that is generated. This leads to an expression for shear stress \( \tau \) in terms of \( P \), the radius of the coil \( R \) and the radius of the cross section of the wire specimen (a) (Figure 9). \( P \) can be calculated by the weight acting on any given coil. Each differential length of a given coil can be looked upon as a torsional cylinder and one can get an expression for the shear strain \( \gamma \) (Figure 9).

The shear stress and the shear strain can be converted to normal stress (\( \sigma \)) and normal strain (\( \varepsilon \)). The sensitivity of strain measurement can be gauged from the fact that the deflection of each coil of radius 10 mm would be equivalent to extension of a straight specimen of length 1.6 metres.

**Viscous creep of Ti**

We first investigated Ti. The experimental work was carried out by Malakondaiah"18 and the results obtained by him constituted one of the most comprehensive investigations on a single metal. Grain size was varied by him over one order of magnitude in Ti wires of diameter

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**Table 1a. Theoretically-derived expressions for creep rates**

<table>
<thead>
<tr>
<th>Creep mechanism</th>
<th>N-H Creep</th>
<th>Coble creep</th>
<th>Harper-Dorn creep</th>
<th>Power-law creep</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_{NH} = A_{NH} \frac{\Omega_{h}^{1.0}}{\tau^{3} kT} D_{oh} \exp \left( - \frac{Q_{h}}{RT} \right) )</td>
<td>( t_{C} = A_{C} \frac{\Omega_{C}^{0.1}}{d^{1} kT} D_{oh} \exp \left( - \frac{Q_{c}}{RT} \right) )</td>
<td>( t_{HD} = A_{HD} \frac{b_{0.1}^{0.0}}{kT} D_{ov} \exp \left( - \frac{Q_{o}}{RT} \right) )</td>
<td>( t_{C} = A_{C} \left( \frac{Q_{o}^{0.1}}{G^{0.1}} \right) d^{4} - 6 ) ( D_{ov} \exp \left( - \frac{Q_{o}}{RT} \right) )</td>
<td></td>
</tr>
</tbody>
</table>

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**Table 1b. Parametric dependences in different creep processes**

<table>
<thead>
<tr>
<th>Creep mechanism</th>
<th>Stress dependence</th>
<th>Grain size (d) dependence</th>
<th>Activation energy</th>
<th>Dislocation activity</th>
<th>Substructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nabarro-Herring</td>
<td>( t = \sigma^{1.0} )</td>
<td>( t = d^{-2} )</td>
<td>( Q_{H} )</td>
<td>Only in transient stage</td>
<td>No</td>
</tr>
<tr>
<td>Coble</td>
<td>( t = \sigma^{1.0} )</td>
<td>( t = d^{-3} )</td>
<td>( Q_{H} )</td>
<td>Only in transient stage</td>
<td>No</td>
</tr>
<tr>
<td>Harper-Dorn</td>
<td>( t = \sigma^{1.0} )</td>
<td>Independent</td>
<td>( Q_{H} )</td>
<td>Transient and steady state</td>
<td>Rearrangement of dislocations</td>
</tr>
<tr>
<td>Climb</td>
<td>( t = \sigma^{4.6} )</td>
<td>Independent (d ( \geq 400 \mu m ))</td>
<td>( Q_{H} )</td>
<td>Dominant</td>
<td>Well defined substructure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Independent (d ( \geq 50 \mu m ))</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.5 to 2.0 mm. Temperatures varied between 800 and 1100°C. Stress varied up to 2 MPa. Creep rates were in the range $10^{-9}$ to $10^{-11}$/sec.

Linear dependence of creep rate confirmed viscous creep. That the straight line plot (Figure 10a) passed through the origin indicated absence of a threshold stress, in line with theory. Transition from N–H creep to Coble creep was observed not only from measurement of the activation energy (Figure 10b) but also from $1/d^2$ and $1/d^3$ dependences of the observed creep rates. Further, transition to power law creep from viscous creep, as the stress was raised, was observed (Figure 10a).

The most important part of the results is shown in Figure 11 which is a plot of the data in terms of temperature and diffusion compensated creep rate as a function of grain size which showed a transition from $1/d^2$ dependence to grain size-independent viscous creep. This is the first ever experimental result pointing to the occurrence of H–D creep at lower temperatures (significantly lower than the melting temperature) of the order of $0.5 \, T_m$, which means a temperature of practical interest.

With wide ranging results available, it became possible to draw experimental creep mechanism maps (Figure 12) in stress-temperature space, as was suggested by Ashby, or in grain-size-stress space, as was suggested by Mohamed and Langdon. One can superimpose constant strain rate contours on these maps and use them for component design. These maps are also useful in the design of experiments aimed at studying a single mechanism of interest.

**H–D creep at 0.5 $T_m$**

The findings of H–D creep in coarse-grained Ti at about 0.5 $T_m$ led us to investigate Co (ref. 23) under similar conditions where also II–D creep was observed. Since then, H–D creep has been accepted as possible at temperatures like 0.5 $T_m$. And this is noticeable in the subsequent literature concerning H–D creep. There is a revival of interest in H–D creep thanks to the work of Wang. In the context of recent Wang's theoretical treatment, there is also a fresh assessment of the constant $A_{H-D}$ in the creep rate equation (Table 1).

STRESS
\[ \tau = \frac{2PR}{\pi a^3} \]
\[ \sigma = \sqrt{3} \tau \]

STRAIN
\[ \varepsilon = \frac{\delta a}{2 \pi R^2} \]
\[ \varepsilon = \gamma / \sqrt{3} \]

SPRING SENSITIVITY
\[ \delta = \sqrt{3} \frac{R}{a} x \]

IF \[ \frac{R}{a} = 15, \; \delta = 26 x \]

WITH R = 10 mm ONE COIL IS
AS SENSITIVE AS A STRAIGHT
WIRE OF LENGTH 1.6 m

Figure 9. Sectional view and mechanics of spring specimen.
Figure 10. (a) Strain rate against stress showing transition from viscous to power-law creep at a stress ~ 1.0 MN/m² in alpha-titanium; (ii) Present power law data correlated to published results; (ii) Variation of temperature compensated deflection rate with reciprocal test temperature for alpha titanium showing a transition from N-H creep to Coble creep at lower temperatures.

Table 2. Constant $A_{HD}$ in Harper-Dorn creep expression

<table>
<thead>
<tr>
<th>Material</th>
<th>$T/T_m$</th>
<th>$A_{HD}$</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>&gt;0.9</td>
<td>$17 \times 10^{-11}$</td>
<td>Harper and Dorn$^{12}$</td>
<td></td>
</tr>
<tr>
<td>Al-Mg</td>
<td>&gt;0.9</td>
<td>$1.2 \times 10^{-11}$</td>
<td>Marty et al.$^{26}$</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>&gt;0.9</td>
<td>$9.6 \times 10^{-12}$</td>
<td>Mohamed et al.$^{37}$</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>&gt;0.9</td>
<td>$2.4 \times 10^{-11}$</td>
<td>Mohamed et al.$^{37}$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Ti</td>
<td>0.52</td>
<td>$1.0 \times 10^{-9}$</td>
<td>Malakondaiah and Rama Rao$^{18}$</td>
<td>Implicitly $A_{HD}$ constant</td>
</tr>
<tr>
<td>$\beta$-Co</td>
<td>0.61</td>
<td>$7.4 \times 10^{-11}$</td>
<td>Malakondaiah and Rama Rao$^{23}$</td>
<td>Considered variable</td>
</tr>
</tbody>
</table>

In the earlier work at temperatures close to the melting point, $A_{HD}$ was assumed to be constant, independent of the material and test conditions. A value of $10^{-11}$ was commonly assigned to $A_{HD}$ (Table 2). In our work on H-D creep of Ti (ref. 18), we obtained reasonable agreement between the experimentally-observed and the theoretically-estimated creep rates by assigning a value $A_{HD} = 1.0 \times 10^{-11}$. We had also surmised that assigning an invariant value to $A_{HD}$ may not be valid. (We had used different $A_{HD}$ values for Ti (ref. 18) and Co (ref. 23) (Table 2)).

In the microphysical model of H-D creep developed by Wang$^{13}$, it is shown that H-D creep occurs at stresses below the Peierls stress and that $A_{HD}$ is a function of Peierls stress which means a different value for different crystal structures. Wang's theory yielded

$$A_{HD} = 1.4(\tau_pG)^2. \tag{3}$$
Transient stage

There is an aspect which the original theories of N–H or that of Coble did not envisage and this is about the occurrence of a transient stage prior to attainment of steady-state creep. The transient stage is characterized by a decreasing slope, with time, of the deflection versus time plots (Figure 13). In our experiments on spring specimens, the transition stage is invariably observed. We have seen detailed analysis of the steady state data from experiments on Ti. We can now turn to the transient behaviour in the same material.

We performed simple experiments on Ti specimens in which we ensured that the same scale of microstructure was obtained through two different thermomechanical treatments. In one specimen, compared to the other, the amount of cold work was greater and the duration of annealing was less. In the first sample, the transient strain before the onset of steady state was measurably higher, although, noteworthy, the steady state creep rate was the same in both the specimens (Figure 13). This result substantiated the prevalent concept that the transient stage arose from dislocation activity prior to the onset of steady state.

Through several experiments of Malakondiah, a substantial set of data on transient creep in the low stress regime became available and in a way as to allow a study of the parametric dependences of transient strain as well as transient time on stress, grain size and temperature. The data for Ti, Co and α–Zr showed similar trends and were sufficient to encourage an evaluation of the systematics in the dependence of the two transient parameters.

The analysis was carried out with reference to the available models. The experimental behaviour matched with the predictions of only one model, the grain boundary diffusion-based model of Rishi Raj who treated the transient in terms of a stress redistribution necessary to match with the maximum at the centre of the grain.
boundary. He assumed that the redistribution occurred by local climb of dislocations. While our experimental data for transient time was in agreement with Raj's theory (Figure 14) for relatively finer grain size, there was disparity between the model prediction and the experiments on coarse-grained Ti which exhibited H-D creep. Raj's grain boundary diffusion-based model predicted strong grain size dependence of transient time ($\propto d^3$). While our experiments had this feature in Ti of small grain size, the transient time was nearly independent of grain size in the coarse grain size range (Figure 15).

We have, therefore, proposed a modified model, considering that dislocation density decreases with time (conforming to the observation that creep rate decreases with time) and that the dislocation density decrease is due to their mutual annihilation (by dislocations of the opposite sign coming together). This means that $\rho_{\text{final}} < \rho_{\text{initial}}$. When grains are coarse, dislocation annihilation can contribute to reduction in dislocation density without bringing in any action associated with the grain boundary. On this basis, the observed grain size independence of transient time in coarse-grained Ti is understandable. The corresponding expression for $t_u$ is

$$ t_u = (\rho_o - \rho)kTt/2G
$$

and shows grain size independence and the calculated $t_u$ agreed satisfactorily with the experimental values.

The average values of strain, over the duration of $t_u$, can be shown to be equal to

$$ \varepsilon = \left( \frac{2bcp(\rho_0/2 - \rho_1/2)}{(\rho_0 - \rho_1)\rho_0^{1/2} - \rho_1^{1/2}} \right). $$

The above expression explains also the experimental observation, discussed earlier, with regard to the effect
Table 3. Physical properties of titanium and zirconium

<table>
<thead>
<tr>
<th>Property</th>
<th>Ti</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>Crystal structure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hcp(a)</td>
<td>≤ 882°C</td>
<td>≤ 885°C</td>
</tr>
<tr>
<td></td>
<td>c/a = 1.586</td>
<td>c/a = 1.591</td>
</tr>
<tr>
<td>bcc(b)</td>
<td>&gt;882°C</td>
<td>&gt; 865°C</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>4.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Modulus, GPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>120.2</td>
<td>99.3</td>
</tr>
<tr>
<td>G</td>
<td>45.6</td>
<td>36.2</td>
</tr>
<tr>
<td>Cohesive energy, kJ/mol</td>
<td>468</td>
<td>603</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>1667</td>
<td>1852</td>
</tr>
<tr>
<td>Latent heat of fusion, kJ/mol</td>
<td>17.5</td>
<td>19.3</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>3285</td>
<td>4400</td>
</tr>
<tr>
<td>Self diffusivity at 0.52 Tm, m²/s</td>
<td>1.28 × 10⁻¹⁵</td>
<td>2.1 × 10⁻¹⁶</td>
</tr>
</tbody>
</table>

for transient creep in coarse grain Ti, a final dislocation density

\[ \rho_f = 10^6 - 10^7 \text{ lines/cm}^2. \]

At this dislocation density, steady-state creep sets in which, in these cases, has been shown to be H–D creep. If we are to use this value of \( \rho_f \) in the equation for \( A_{H-D} \), we arrive at a magnitude of \( 1 \times 10^9 \) for \( A_{H-D} \). Wang formulation calculates \( \rho_f \) in terms of Peierls stress and calculates a value of \( \rho_f = 5 \times 10^{-6} \text{ cm/lines}^2 \) for \( \alpha - Ti \), matching with what value we had suggested.

**α-Zr versus α-Ti**

It is interesting to make a comparison of the low stress creep behaviour of two important reactive metals, α-Ti and α-Zr, both of which are used in structural applications requiring high temperature service. α-Zr and α-Ti have both the same HCP structure and comparable physical properties (Table 3), excepting in the case of a few. The higher density of Zr precludes its use in aero-engines for which application Ti is preferred. Zr is a popular nuclear fuel cladding material because, when freed of Hf, Zr has low neutron absorption cross section.

Using the mapping technique, we compared the creep behaviour of these two metals (Figure 16). It is evident, from the strain rate contours corresponding to \( 10^9 \text{ sec}^{-1} \) plotted in the map, that α-Zr is significantly more creep-resistant. Thus, for a given grain size, the stress to cause the same creep rate in Zr is significantly higher. Notable shifts in operating regimes occur when the creep behaviour of the two metals is compared.

The higher creep strength of Zr seems to arise essentially from its higher cohesive energy, which is reflected

![Figure 16. A comparison of creep behaviour of α-Ti and α-Zr.](image)

of prior thermomechanical treatment on transient strain. Since \( \rho_f \) is a steady-state value and, therefore, a constant, the transient strain should vary with \( \rho_0 \), the initial dislocation density. The initial dislocation density can be varied with the amount of cold work or the time of annealing during thermomechanical treatment. Equation (5) suggests higher transient strain for higher \( \rho_0 \).

An important observation can now be made about \( \rho_f \). Our mutual annihilation of dislocation model predicts,

![Figure 17. Deflection–time curves for zirconium and zircaloy-2 obtained under identical test conditions. Transient stage extends to a much longer duration in zircaloy. Transient strain in zircaloy is one-third that of zirconium.](image)
in higher melting and boiling points of Zr (Table 3). These features are supported by the diffusivities that can be derived from our creep experiments on the two metals.

A remark about self-diffusion measurements is in order. The literature values for self-diffusion are usually based on the work that uses radiotracer technique, although the values from this technique can vary widely. The variation is partly because of the state of purity of the base metal employed in radiotracer experiments and partly because the concerned isotope, i.e. Zr$^{95}$, in the case of Zr, has a shorter half-life and therefore can undergo radioactive decay during the course of duration of the experiments. For these reasons, we did not use the literature values and preferred to use the values derived from our own low stress creep experimental data. It is only thus that we are able to rationalize several of our observations that we have discussed. It is gratifying to note that some of the recent work on Ti reported in the literature has tended to use values obtained by us (Table 3).

**Zircaloy versus α-Zr**

Zircaloy is a popular nuclear fuel cladding alloy. With Zr as the base, zircaloy contains about 1.5 wt% Zn, which is added as an agent to fix nitrogen and thereby enhance corrosion resistance. In addition, zircaloy contains small amounts of Fe, Ni and Cr. The data presented in Figures 17, 18 and 19 clearly depict superior low stress creep resistance of zircaloy when compared with Zr.
In regard to the transient stage, it persists over a much longer duration in zircaloy. Transient time extends over several hours for zircaloy while it is only several minutes for Zr (Figure 17). The transient strain of Zr is one-third that of Zr (Figure 17).

Creep rates are lower in zircaloy by about two orders of magnitude under similar conditions (Figure 18a). Remarkably, grain boundary diffusion (characterized by a much lower activation energy) is totally suppressed in zircaloy even at a fine grain size like 20 μm (Figure 18b) (compare 18b(ii) for zircaloy with 18b(i) for zirconium).

The absence of grain boundary diffusion creep is a significant finding and is attributable to the presence of refractory Cr bearing grain boundary precipitates (Figure 19a).

Zircaloy, unlike Zr, exhibits a threshold stress (Figure 19b) below which diffusion creep is not activated. The appearance of a threshold stress again is relatable to the interaction of grain boundary dislocations with the particles or precipitates at the grain boundary which in this case is evident in the higher resolution micrographs (Figure 19a).
Zircaloy and Zr–Nb alloy

Zircaloy has now been replaced by a new alloy of Zr containing 2–5 wt% Nb. Reactor components out of the new Zr–Nb alloy are now regularly fabricated by the Nuclear Fuel Complex at Hyderabad. The coolant channels recently replaced in the Rajasthan Atomic Power Plant-II, hailed as an outstanding DAE achievement, are made of the new alloy. Zr–2.5 Nb alloy is a two-phase material, somewhat like zircaloy but with a major difference (Figure 20). While the second phase in zircaloy is an intermetallic precipitate, the two phases in the Zr–2.5 Nb alloy are both solid solutions. The α-phase, which is the matrix, is a solid solution of Nb in HCP Zr while the grain boundary β-phase is a solid solution of Nb in BCC Zr. In zircaloy, intermetallic particles, constituting the second phase, are much harder and far more brittle compared with the general matrix. On the other hand, Zr–2.5 Nb alloy is characterized by two phases of somewhat comparable mechanical properties. Investigation of the low stress creep behaviour of Zr–2.5 Nb alloy has been presently undertaken, at Bhabha Atomic Research Centre, to make a comparative assessment with the results that we have on zircaloy.

The comparable mechanical properties of the two phases in Zr–2.5 Nb alloy can render the alloy amenable to superplasticity which has been found and investigated by Singh et al. The feature provides further motivation to study the low stress creep behaviour of Zr–2.5 Nb alloy, which is related to our experience with the two-phase superplastic Zn–22% Al alloy which will be briefly described now.

Superplastic alloys are characterized by a sigmoidal stress–strain rate relationship (Figure 21). There is usually difficulty in characterizing the stress–strain rate behaviour in the regime of the lowest strain rates (early part of stage-I superplasticity, Figure 21), where the strain rates are of the order of $10^{-7}$ to $10^{-9}$/sec which are difficult to register in conventional machines. However, this is the range of strain rates that is conventionally studied with the use of spring specimens. We chose Zn–22Al superplastic alloy for the investigation of stage-I creep because of considerable conflict reported in the literature, in regard to whether stage-I conforms to diffusional creep flow or an altogether different kind of creep behaviour with a rate dependence on stress of a higher order magnitude. We had hoped to clarify the contentious issue related to stage-I through precise measurements possible by resorting to the spring geometry for the specimens.

The data obtained by us (Figure 22a) confirm the operation of a viscous flow process with a linear strain...
rate dependence of stress. However, when the dependence of the creep rate on other variables, notably grain size, was examined, the known dependence of creep rate (Figure 22a) was not fulfilled for any one of the known mechanisms of low stress creep. Subsequently, electron microscopy was carried out but without any pointer being obtained. The observed complication in this case is traceable to the very fine, odd-shaped Zn-rich precipitates detected (Figure 22b) at the phase boundaries and the influence of three types of interfaces α-α', α-β' and β/β'.

The work in progress on Zr-2.5 Nb alloy is expected to provide valuable results which may prove helpful in more clearly characterizing the low stress creep behaviour of two-phase alloys. The data shown in Figure 23 are typical of the first results with promise of interesting further research.

Figure 23. Deflection versus time curves for Zr-2.5 Nb (Kishore, unpublished work).

Review of acid rain potential in India: Future threats and remedial measures

Manju Mohan* and Sanjay Kumar

Centre for Atmospheric Sciences, Indian Institute of Technology, New Delhi 110 016, India

Acid rain is a necessary fall-out of rapid industrialization, urbanization and other developmental activities in India. Acidic deposition is a complex process and can be felt hundreds of kilometers away. Tropical climatic conditions, alkaline-rich soil, desert and sea-derived aerosols, low sulphur content in fuels, etc. coupled with the relatively low industrial growth rate are the foremost favourable factors in preventing acid rain problem in the country as also indicated by several studies in the past. This is in spite of the fact that India is the second largest country, next to China in the Asian continent producing sulphur dioxide emissions. However, the pace of current developmental activities has overtaken these natural favourable factors and as a result, many metropolitan cities are now showing decreasing pH or acidic trends in the precipitation. This paper overviews the present trend, its likely effect, outlines factors contributing to acid rain and suggests possible preventive measures to stop the trend. Projections were made on the basis of RAINS ASIA model to identify areas of potential impact on the ecosystem and identify steps to mitigate the stress factors.

Over the last few years, there have been important advances in our understanding of the steps which link the emissions of acidic gases such as SO₂, NOₓ and HCl to their subsequent deposition and its fall outs. The major contribution to acid rain is reported to be due to sulphur component (= 70%) and oxides of nitrogen (= 30%)

*For correspondence. (e-mail: mmanju@cs.iitd.ernet.in)