

# Thermally Activated Deformation in Dilute Zirconium/Oxygen Alloys

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The effect of temperature and strain-rate on the yield and flow stress of zirconium, containing oxygen in the range of 0.09 to about 2.5 at. % has been examined at temperatures between 77 and 700° K. The above measurements were coupled with strain-rate change tests and stress-relaxation experiments, so that all the deformation parameters associated with thermal activation could be evaluated.

The results of these measurements showed that the thermal component of flow stress increases with increasing oxygen content of the alloy. Two stages of activation were found to occur for all these alloys. The first stage was associated with the unpinning of dislocation loops from impurity pinning points. At higher temperatures, because of the unpinning of many impurity pinning points, a second stage of activation associated with a different mechanism was found to occur. The variation of certain parameters associated with this stage of deformation strongly suggests the Peierls-Nabarro force as the controlling criterion.

## 1. Introduction

The strong temperature-dependence of flow stress of many "hard"\* metals is well known, and has been the subject of numerous investigations. This dependence has been attributed to the presence of short-range obstacles which can be overcome at finite temperatures with the help of thermal fluctuations, even though the force on glide dislocations is smaller than the force exerted by these obstacles. The temperature-independent part, or to be more accurate, the mildly temperature-dependent part of the flow stress is due to overcoming of long-range elastic interactions between dislocations.

Many investigations have been carried out to study this temperature-dependence of flow stress by precision tensile experiments which involve temperature changes, strain-rate changes, and relaxation techniques during tests. But almost all these investigations were limited to bcc metals which exhibit the strongest temperature-dependence of all. Results of these experiments have been summarised in an excellent review by Conrad [1].

These experiments have suggested that a large

Peierls-Nabarro force (P-N force) present in crystal structures of this type may possibly be responsible for the strong temperature dependence. However, there is still some controversy as to the role of interstitials in determining the temperature-dependent part of the flow stress [2-4]. The possibility that very fine precipitates might be the main obstacles was first suggested by Mordike and Haasen [5]. This suggestion has been reinforced by recent experiments on iron crystals with accurately controlled carbon contents. Results of these experiments by Stein [6] suggest that at least more than a single thermally activated mechanism influenced by impurities (either as precipitates, or in the form of impurity atmosphere) could be operative in some specific temperature ranges.

Unlike bcc metals, no systematic investigations on the temperature-dependence of the flow stress have been carried out for the "hard" group of hcp metals until recently. Single-crystal deformation studies on zirconium by Rappoport and Hartley [7], and recently on titanium by Levine [8] have shown that there exists a strong temperature-dependence of flow

\*By "hard" hcp metals we mean those which slip predominantly on prismatic and pyramidal planes.

stress in these metals also. Conrad and his co-workers [9] have recently calculated all the activation parameters for deformation in polycrystalline, commercially pure, titanium, and have shown that interstitial impurities raise the temperature-dependent part of the flow stress significantly.

It is the purpose of the present experiments to evaluate various activation parameters associated with deformation in zirconium at different temperatures, and more specifically, to study the role of oxygen in increasing the temperature-dependent flow stress. This has been achieved by studying various zirconium alloys containing controlled additions of oxygen. Because of the large solubility of oxygen in zirconium, no second-phase precipitation is likely to affect the experimental results.

## 2. Experimental Procedure

### 2.1. Preparation of Alloys

Three types of alloys were prepared for this investigation. For preparing specimens with minimum oxygen content, iodide zirconium bars were melted in an electron beam furnace, and were then cold-rolled to the required thickness before the tensile samples were machined out.

Reactor grade sponge zirconium itself could be used for preparing specimens containing about 1 at. % of oxygen, without adding any further alloying additions. Specimens of this composition were prepared by non-consumable arc-melting, using purified argon. These ingots were then hot- and cold-rolled to produce tensile samples. For preparing alloys with high oxygen concentration, sponge zirconium was melted together with calculated amounts of pure  $ZrO_2$  in an arc-furnace under purified argon. The melting pro-

cedure was repeated several times to produce well homogenised buttons. Sheets for preparing tensile samples were produced by hot-rolling the buttons. Tensile specimens were then machined from these sheets, and were then annealed at the required temperatures to produce well recrystallised samples of the same grain size. The exact chemical analyses of these samples are shown in table I. For estimating the amounts of oxygen accurately, the precision lattice parameter method suggested by Lichter [10] was adopted. As the lattice parameter of zirconium is highly sensitive to the oxygen content, this method could be used with great accuracy. Results of these analyses are shown in table I.

### 2.2. Tensile Testing

Well polished tensile specimens,  $13 \times 3 \times 0.8$  mm, were tested in a floor-model Instron tensile testing machine, at temperatures ranging from 77 to 720° K. The normal strain-rate adopted during these tests was  $6.6 \times 10^{-5}$  sec. For strain-rate change tests, an instantaneous change from  $6.6 \times 10^{-5}$  to  $3.3 \times 10^{-4}$ /sec was used. At least three specimens were used for each test, and there was excellent reproducibility between the results with these specimens. Yield stress variation between duplicate experiments was always found to be less than 5%.

Stress-relaxation experiments were also carried out during tensile tests by stopping the tensile machine at various stress levels, and allowing the stress to decay as a function of time. Relaxation studies were carried out for periods ranging from 15 to about 100 min.

## 3. Results

### 3.1. Evaluation of Experimental Data

Conrad and Wiedersich [11] have presented methods for evaluating both activation energy and activation volume for thermal activation from the well-known strain-rate equation

$$\dot{\gamma} = NAbv^* \exp - \frac{H(\tau^*)}{kT}$$

In this equation,  $N$  is the number of dislocations per unit volume,  $b$  the Burgers vector, and  $A$  the area swept out by the dislocation during one activation jump.  $k$  and  $T$  have their usual significance.  $v^*$  is the atomic vibrational frequency factor.  $H(\tau^*)$  is the activation enthalpy for this thermally activated process and is dependent only on the effective shear stress. Following

TABLE I Chemical analysis of zirconium alloys.

Element	Concentration in ppm (by weight)		
	Zr/0.09 at. % O	Zr/1.0 at. % O	Zr/2.5 at. % O
Hf	200	200	200
W	140	140	140
Fe	100	100	100
Al	32	32	25
Si	60	110	55
Cu	25	25	25
C (nominal)	100	500	500
N (nominal)	30	50	50
O	150	1800	4500
Vickers hardness number	72	160	310

Seeger [12], this thermal component of stress,  $\tau^*$ , is related to the applied stress by

$$\tau^* = \tau - \tau\mu$$

where  $\tau$  is the total applied stress, and  $\tau\mu$  is the athermal stress, dependent on temperature only through the variation of shear modulus.

Assuming that the temperature variation of  $\tau\mu$  can be neglected, Conrad has shown that both the activation energy  $H$  and the activation volume  $V^*$ † can be determined from the deformation partials  $(\partial \ln \dot{\gamma} / \partial \tau)_T$  and  $(\partial \tau^* / \partial T)_{\dot{\gamma}}$ . Activation parameters can then be calculated using the following relations

$$H = -kT^2 \left( \frac{\partial \tau^*}{\partial T} \right)_{\dot{\gamma}} \left( \frac{\partial \ln \dot{\gamma}}{\partial \tau^*} \right)_T$$

and

$$V^* = kT \left( \frac{\partial \ln \dot{\gamma}}{\partial \tau^*} \right)_T$$

These partials can be evaluated from strain-rate change tests, and also by measuring the difference in flow stress between various temperatures at a constant strain-rate. Data for the partial  $(\partial \tau^* / \partial T)_{\dot{\gamma}}$  were obtained from independent stress/strain curves measured at different temperatures at a constant strain-rate. Corrections were not made for the shear modulus variation with temperature, as it has been shown to be small for zirconium.

Feltham [13] has developed an alternative method for determining the activation volume by using stress-relaxation experiments and this procedure is being increasingly adopted to determine  $V^*$  [14, 15]. Relaxation methods were also adopted in the present experiments to determine  $V^*$  independent of strain-rate change experiments. This method has an additional advantage, in that it provides data for specimens where the percentage elongation would be small, and hence the strain rate change experiments would be limited.

### 3.2. Stress/Temperature Curves

Fig. 1 shows the 0.2% yield stress of zirconium/oxygen alloys as a function of temperature. In this figure, the yield stress variation with temperature is also shown for 5 at. % O alloy. Because of the inherent brittleness of the alloys containing high oxygen, detailed investigations

were limited only up to 2.5 at. % O concentration. The variation of  $\tau^*$  with temperature for these alloys are shown in fig. 2. In spite of the apparently good experimental fit with the linear plots, a certain amount of scatter is apparent around 300° K for all these alloys. As this scatter is of the order of the experimental accuracy of measurements, a single linear plot has been drawn for each alloy throughout the entire temperature range. This, however, does not overrule the possibility of a discontinuity existing at these temperatures. Linearity of  $\tau^*$  against temperature is best observed below 300° K. Though Conrad [9] suggests plotting  $\tau^*$  against the square root of absolute temperature, the present fit of experimental results appear as faithful as when plotted against the square root of temperature. Results on the temperature variation of CRSS of zirconium by Rappoport and Hartley [7] also show that the linear variation of  $\tau^*$  with temperature is more faithful.

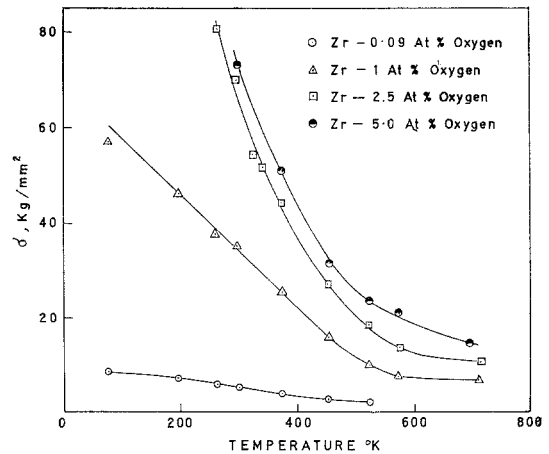


Figure 1 0.2% yield stress of zirconium/oxygen alloys as a function of temperature.

### 3.3. Activation Volume Measurements

The calculated activation volume for these alloys is shown as function of  $\tau^*$  in fig. 3. The standard deviation calculated for these results is around 2%. Average values obtained from both strain-rate change and relaxation methods are shown in this figure. Both these methods gave almost identical values of  $V^*$ . More than the

†The activation volume  $V^*$  is equivalent to  $bd^*l^*$  where  $b$  is the Burgers vector of the gliding dislocations,  $d^*$  is the width of the obstacle measured parallel to the Burgers vector, and  $l^*$  is the length of dislocation segment involved in the activated jump across the obstacle.

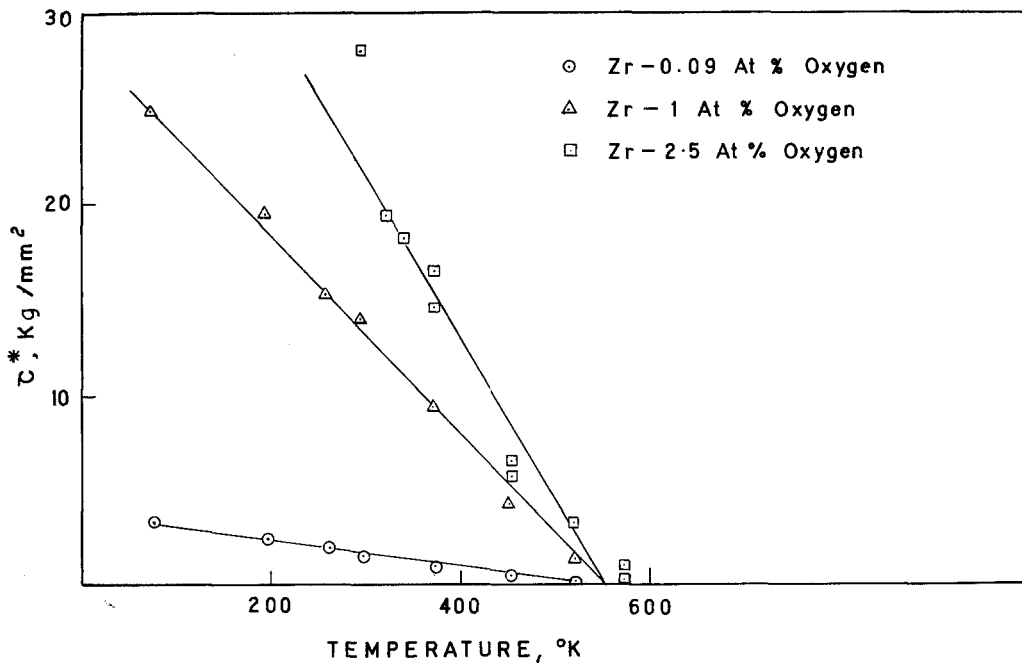


Figure 2 Variation of thermal component of yield stress  $\tau^*$ , with temperature  $T$ .

actual value, the trend of the curves is identical in both the measurements, at least up to  $400^\circ\text{K}$ . Above this temperature, values from the relaxation measurements were found to be higher than those from strain-rate measurements (fig. 4). This trend is to be expected if strain-ageing is active during relaxation. This would tend to increase  $\tau\mu$ , resulting in a decrease of  $\tau^*$ . Activation volume measurements then would show a larger value of  $V^*$ , as the relaxation rate would be decreased. Perhaps because of the low interstitial concentration, this behaviour has not been observed for Zr/0.09 at. % alloy.

The values of activation volume were found to be independent of strain after yielding, and typical values measured for all these alloys at various strain-levels at room temperature are shown in fig. 5. The variation of  $V^*$  with effective shear stress for these alloys (fig. 6) is markedly different from that of bcc metals, which exhibit an almost parabolic variation of  $V^*$  with  $\tau^*$ . At high stress values,  $V^*$  becomes almost constant, and it is difficult to draw a single smooth curve. A truer representation would be to draw two smooth curves, shown as dotted curves in the figure. This would explain satisfactorily the apparent near constancy of activation volume at high  $\tau^*$ . Because of the presence of more than one rate-controlling

mechanism at these temperature ranges, the activation volume measurements tend to show this anomaly. Similar breaks in activation volume/stress curves (or in strain-rate sensitivity/temperature curves) have also been observed by Levine [8], Harris [16] and Koss [17].

In order to check whether drawing of two curves is a truer representation, stress-relaxation experiments were conducted to provide activation volume data for different  $\tau^*$  at the same temperature. This could be accomplished by unloading the specimen to a load corresponding to an almost athermal stress, and then reloading to different  $\tau^*$ , smaller than the  $\tau^*$  characteristic of the temperature at which these tests were conducted. By this method, it is possible to establish whether  $V^*$  is a unique function of  $\tau^*$ , or whether it also depends directly on temperature. If only one specific mechanism is rate-controlling throughout the temperature range, then the values of activation volume for different  $\tau^*$  obtained from stress-relaxation experiments at any *single* temperature would superimpose smoothly with the data obtained from tests conducted at different temperatures. This would not be possible when different mechanisms are rate-controlling. Such stress-relaxation experiments were conducted at  $300$  and  $423^\circ\text{K}$ , for 1 at. % alloy, and the results obtained are

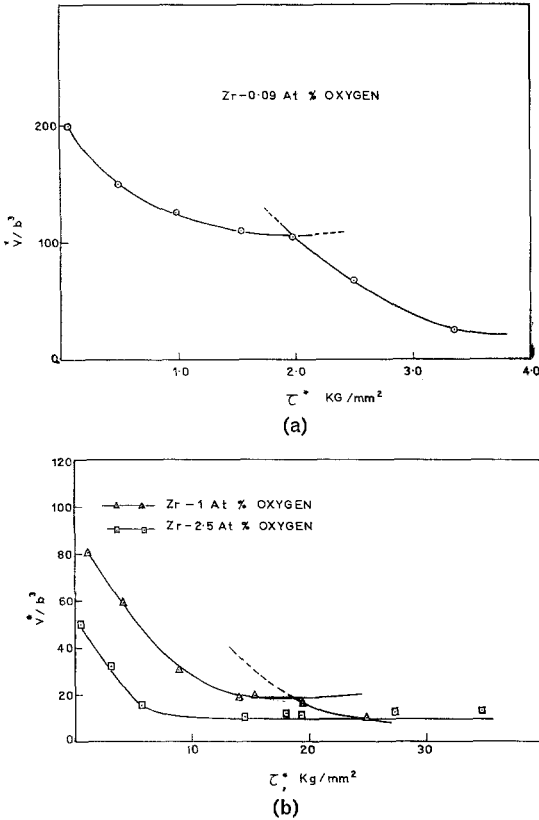


Figure 3 Activation volume  $V^*$  as a function of  $\tau^*$  for zirconium/oxygen alloys. Data from both strain-rate cycling and stress-relaxation tests have been used. (a) Zr/0.09 at. % O; (b) Zr/1.0 at. % O and Zr/2.5 at. % O.

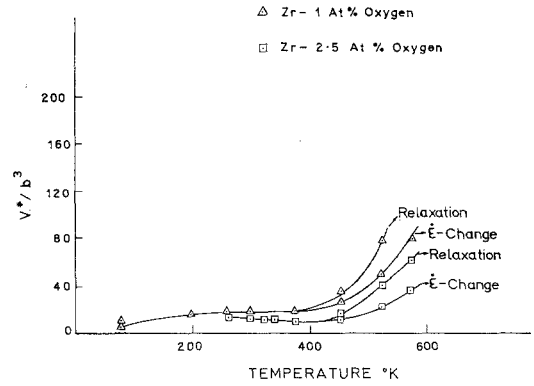


Figure 4 Activation volume as a function of temperature. Values from both strain-rate change tests and relaxation tests are shown.

shown with those obtained at different temperatures in fig. 6. This confirms the possibility that at least two specific mechanisms are rate-controlling, and that they overlap between 200 and 300° K.

### 3.4. Activation Energy Calculations

Figs. 7a-c show plots of activation energy calculated as function of temperature for all compositions. The general behaviour for all these alloys is similar in that they clearly exhibit

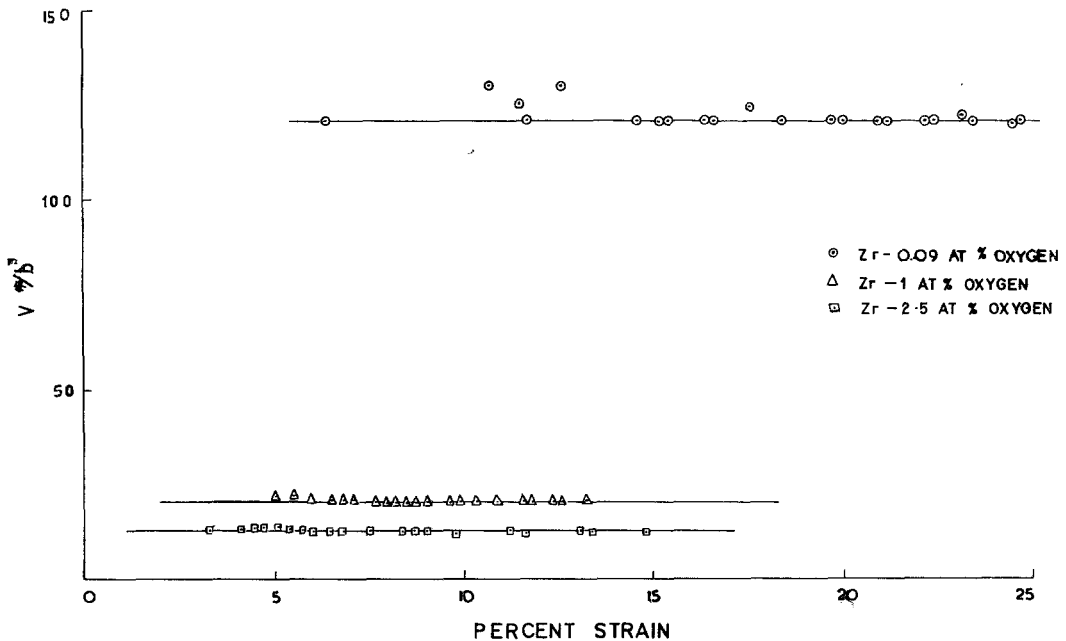


Figure 5 Activation volume  $V^*$  as a function of strain at 298° K for all zirconium/oxygen alloys.

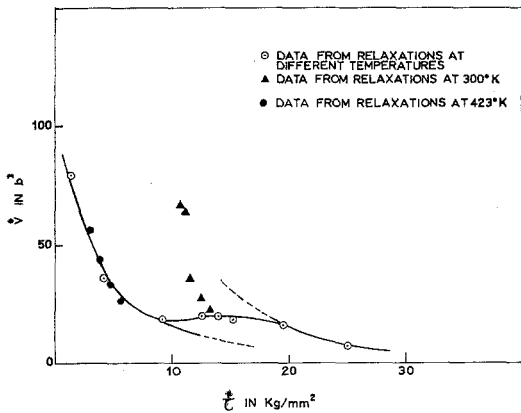


Figure 6 Activation volume  $V^*$  as a function of  $\tau^*$  for Zr/1 at. % O. (Only values from relaxation measurements have been used.)  $V^*$  from single temperature measurements at 300° K and 423° K are also shown.

two distinct stages of activation†; details like the activation energy at the changeover and the frequency factor depend critically on the composition. As a rule, with increasing oxygen content, the transition is shifted to higher activation energies. Except at low temperatures and at high temperatures, where only one rate-controlling mechanism is operative, the activation energy is not linear with temperature and hence a smooth curve is a truer representation. It should be pointed out here that the above activation energy calculations have been made assuming that  $(\partial\tau^*/\partial T)$  is constant as shown in fig. 2. Instead, if  $(\partial\tau^*/\partial T)$  values are taken directly from yield stress curves at every temperature of measurement, then the activation energy peaks near temperatures where the second rate-controlling mechanism takes over. Such peaking in activation energy curves has also been observed by Harris [16] in Nb/W alloys.

Lastly, fig. 8 shows the athermal component  $\tau\mu$  plotted as function of the square root of oxygen concentration. The increase in stress is accurately proportional to the square root of concentration. This is to be expected if the atomic displacements due to the introduction of interstitials do work against the stress field of the dislocation.

**4. Discussion**

Our basic problem in this section is concerned with explaining the following experimental observations: (i) the activation energy for the

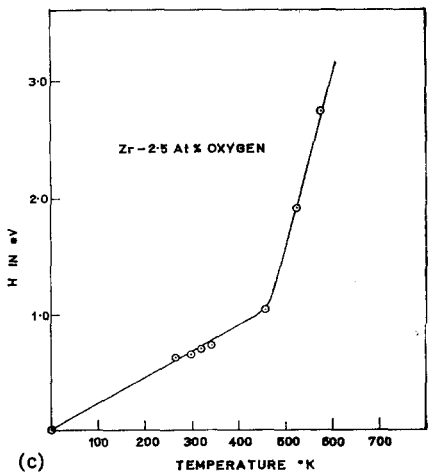
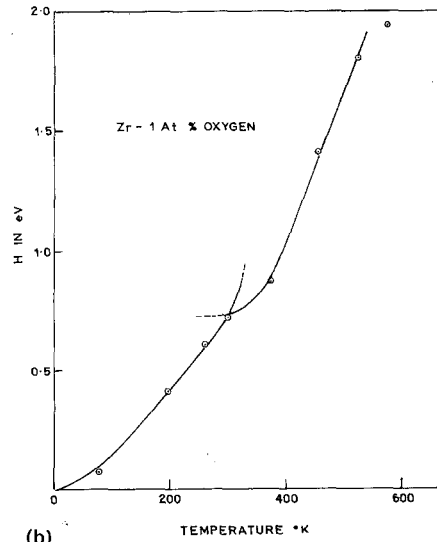
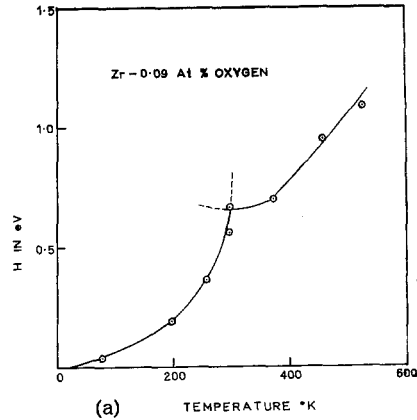


Figure 7 Activation energy as a function of temperature for zirconium/oxygen alloys. (a) 0.09 at. % O; (b) 1.0 at. % O; (c) 2.5 at. % O.

†Note added in proof Two separate stages of activation have also recently been observed during thermally activated deformation of Zr/C alloys [32].

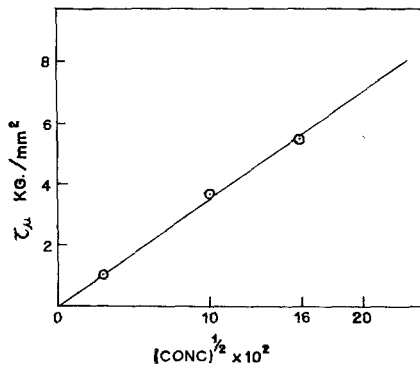


Figure 8 Effect of athermal component of the yield stress  $\tau_{\mu}$  as a function of the square root of the oxygen concentration.

overcoming of short-range obstacles by thermal activation increases as the oxygen content is increased, and (ii) there exists a second rate-controlling process at higher temperatures for all the compositions.

Various specific short-range mechanisms have been suggested as rate-controlling during thermal activation. The ones often suggested are (a) overcoming the Peierls-Nabarro stress by dislocations forming double kinks [1, 18], (b) dislocations breaking away from the interstitial atmosphere [19-21], (c) dynamic recovery of dislocations by cross-slip [22, 23], (d) dislocations overcoming the stress barrier created by small interstitial precipitates [5], and [l] dislocation intersections [24]. The last two possibilities seem unlikely in the present experiments. For one thing, the amount of interstitial oxygen in these alloys is well within the solubility limit of oxygen in zirconium (about 33 at. % of oxygen); for another, the activation volume is independent of strain (fig. 5). In addition, the small values of activation volume measured are clearly incompatible with any dislocation intersection mechanisms where large values of  $V^*$  ( $\sim 3000 b^3$ ) are usually called for. Hence, serious consideration need only be given to the first three rate-controlling mechanisms.

The Peierls-Nabarro force has often been proposed as rate-controlling for bcc metals. Experimental evidence accumulated until now shows that this indeed is possible. Levine [8] has suggested the operation of the same P-N mechanism for titanium also. A rigorous mathematical formulation for this mechanism has been proposed by Dorn and Rajnak [25]. With this formulation, it is possible to distinguish whether

or not this mechanism is operative in zirconium.

An equation of the type  $H = A - B \ln(\tau^*/\tau_p)$  where A, B and  $\tau_p$  are constants, has often been assumed for the P-N force and cross-slip models. In order to test whether this equation is valid during any particular stage in thermal activation, it is usual to plot  $1/V^*$  against  $\tau^*$  [18, 26]. In the present experiment as shown in fig. 9, moderately good agreement with the expected straight line relation is obtained only at low  $\tau^*$  values. This suggests that at low temperatures (high  $\tau^*$ ) a mechanism other than the P-N force may be operative.

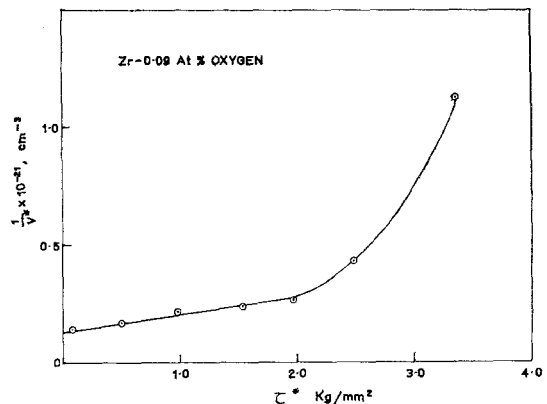


Figure 9 Variation of reciprocal of  $V^*$  as a function of  $\tau^*$  for Zr/0.09 at. % O alloy.

A much more rigorous test can be made by comparing experimental values of  $\tau^*/\tau_p$  against  $H/2E_k$  where  $\tau_p$  is the Peierls stress at absolute zero,  $H$  the activation energy needed to nucleate a kink pair, and  $E_k$  is the energy of a single stable kink. Dorn and Rajnak have given universal curves for  $H/2E_k$  against  $\tau^*/\tau_p$  for different modifications of a sinusoidal P-N barrier. The term  $H/2E_k$  can be calculated by knowing some temperature  $T_0$  above which plastic deformation can take place without the assistance of  $\tau^*$ . It then follows that  $H/2E_k = T/T_0$  for  $T < T_0$ . Because of the two stages of activation observed, it is difficult to choose a unique  $T_0$ . It can be either the end of the first activation stage ( $T_{01}$ ), or the end of the second activation stage ( $T_{02}$ ). Further, it is difficult to determine  $T_{01}$  accurately, as there is always an overlap of the second stage. Even with such approximations, when values of  $\tau^*/\tau_0^*$  (where  $\tau_0^*$  is the value of  $\tau^*$  at absolute zero) are plotted against  $T/T_0$  for Zr/1 at. % O alloy, the

large scatter of these results (fig. 10) shows that the P-N force is not the exclusive operating mechanism. At high temperatures however, the experimental results tend to approach the theoretical curves. It is not known whether this is significant, or is simply due to inherent inaccuracies present in low stress regions. It is further questionable whether Dorn and Rajnak's theory can be applied to these experiments without any modifications that would take into consideration the effect of interstitials. They may very well account for the observed discrepancies. The influence of impurities on  $\tau^*$  can manifest itself in two ways: One, the direct interaction between impurities and dislocations may give a temperature-dependent component for flow stress, additional to the P-N force. Alternatively, a P-N force sensitive to impurity content may modify  $\tau^*$  as the interstitial concentration is increased. The second possibility is less direct and is not well understood, though there have been some attempts by Arsenault [27] to calculate the P-N stress for substitutional alloys. In the absence of a quantitative theory it is therefore worthwhile considering in detail the direct interaction between dislocations and impurities.

Oxygen occupies octahedral interstitial sites in zirconium. These octahedral sites are spherically symmetric when the axial ratio is ideal. In zirconium, as  $c/a$  is less than the ideal value, the

stress induced by the presence of oxygen will be spherically symmetric only to a crude approximation. The increase of oxygen in the lattice does not alter this situation radically, since  $c/a$  remains almost constant even with increasing alloying additions. In spite of this almost symmetrical distortion, the volume change produced by the insertion of oxygen should be interacting strongly with the stress field of dislocation, and from the high value of activation energy measured, it is likely that they pin the dislocations strongly. To make dislocations break away from these pinning points at absolute zero, a high enough stress must be obtained so that the energy barrier is overcome. Once the temperature is increased, the dislocation can overcome the energy barrier by thermal activation at much lower stresses. Considerations on these lines were first put forward by Lücke and his co-workers [28], to explain low-temperature damping phenomena. Friedel [20] has extended this to unpinning of dislocations during tensile deformation at low temperatures.

Following Friedel, the strain-rate equation discussed in an earlier section can be approximated to

$$\sigma \approx \sigma_i + (\sigma_c - \sigma_i) (1 - T/T_c)^n \text{ for } T \ll T_c$$

and

$$\sigma \approx \sigma_i \text{ for } T \gg T_c$$

where  $\sigma_i$  is the tensile stress at the temperature

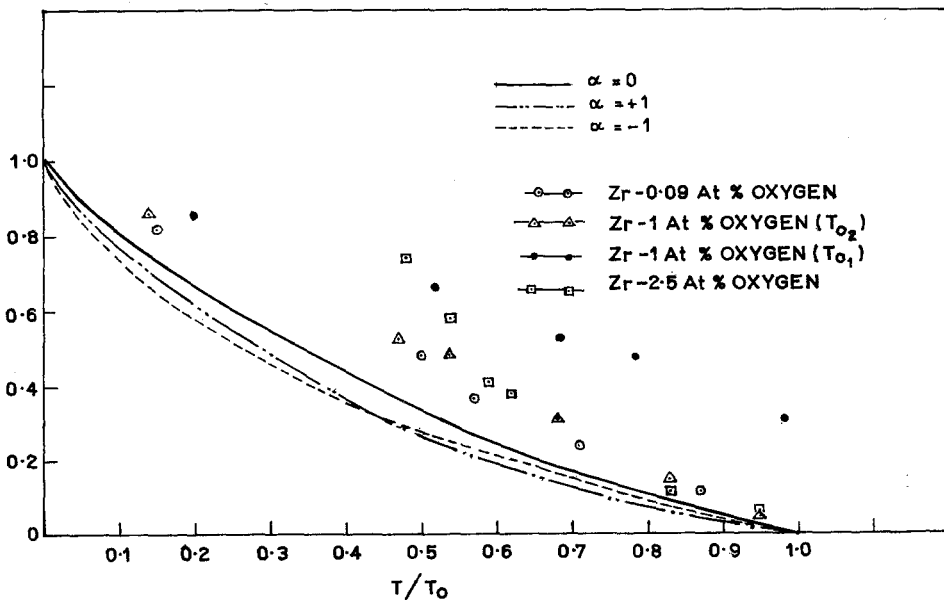


Figure 10 Theoretical curves of  $\tau^*/\tau^*_0$  against  $T/T_0$  given by Dorn and Rajnak's theory compared with experimental data of zirconium/oxygen alloys.  $\alpha$  is a disposable parameter in the theory, associated with the P-N barrier.



$T_c$  at which the rate-controlling mechanism ceases to operate, and  $\sigma_c$  is the stress at  $0^\circ$  K. Impurity concentrations at two extreme levels have been considered by Friedel. For not too dilute solutions ( $c > 10^{-4}$ , Mott's case),  $n$  has been approximated to unity and for reasonable experimental conditions ( $\dot{\epsilon} = 10^{-4}/\text{sec}$ ,  $c = 10^{-4}$  to  $10^{-1}$ ) the interaction energy comes to about  $1/25 kT_c$ . For dilute solutions, the value of  $n$  is about 1.5, and the interaction energy is about  $1/15 kT_c$ .

The implications of the above approximations are the following. The thermal component of the flow stress should be linear with  $T$  up to  $T_c$ , and the activation energy should increase linearly with temperature. In addition, the activation volume should be independent of stress and temperature for concentrated solutions, and is given by  $V^* \approx \alpha b^3/2c$ , where  $\alpha$  is a constant ranging from  $\frac{1}{2}$  to  $\frac{1}{3}$ , and  $c$  is the concentration. For dilute solutions, however,  $V^*$  increases moderately with temperature.

Fleischer [21] has considered the problem of impurity pinning on the basis of elastic interaction between solute atoms and dislocations. He has found that for asymmetrical distortions, the interaction energy is large, resulting in a maximum effectiveness of hardening. Though calculations for interstitials in hcp crystals have not been carried out, the results obtained for alkali halide crystals by Fleischer can be used without much loss of generality. For "rapid" hardening due to interstitials,  $\tau^{*\frac{1}{2}}$  is linear when plotted against  $T^{\frac{1}{2}}$ . The activation volume  $V^*$  is not constant, but varies with  $\tau^*$ , obeying the relation

$$V^* = b^3(\sqrt{\tau^*_0/\tau^*} - 1)/\sqrt{3c}$$

where  $\tau^*_0$  is the zero temperature intercept in the stress versus temperature curve. As a rough approximation,  $V^*$  should be about  $b^3/\sqrt{3c}$ .

In our present experiments, though it is difficult to say unequivocally that activation volume remains constant during the first stage, the general trend is for the activation volume to increase with decreasing  $\tau^*$ .

If impurities form main obstacles for dislocations, as has been assumed in both the models, then we can calculate the free loop length of dislocations,  $l^*$ , touching the nearest neighbouring pinning points. If we approximate  $d \approx b$ , then the activation volume should be  $l^* b^2$ . For instance, in 1 at. % O alloy,  $V^*$  can be calculated to be about  $25b^3$  using Friedel's

model, while Fleischer's model gives about  $6b^3$ . Within the experimental accuracy of measurements, the second value fits in well with the measured activation volume of about  $7b^3$  at liquid  $N_2$  temperatures. This is also true for 0.09 at. % O oxygen alloys, where the calculated values of  $300b^3$  and  $19b^3$  are compared with the measured value of  $25b^3$  at  $77^\circ$  K. At higher temperatures, this ceases to be valid, as many pinning points may not be active and a larger  $l^*$ , different from the calculated values, might be operating. With increasing temperature, and with the onset of the second stage, the linear relationship between  $V^*$  and  $c^{-\frac{1}{2}}$  is not maintained. Both these models, however, imply a dependence of  $V^*$  on  $c$ , and this has been found to be true only during the first stage of activation.

We consider next the problem of a second rate-controlling mechanism, coming into operation at high temperatures. This phenomenon manifests itself in the form of breaks in the activation energy/temperature, and activation volume/flow stress, curves. With increasing concentration of impurities, the onset of this second stage is pushed into higher  $H$  values, suggesting higher energy barriers. If, as we have assumed, thermal breakaway from impurity pinning points and the corresponding activation energy controls the first activation process, it is quite likely that for short loops (i.e. those containing larger number of impurity pinning points) a higher activation energy is needed. With increasing temperature, it is possible that dislocations get unpinned from some pinning centres by thermal activation alone, and then we have the case of dislocations having larger free loop-lengths. These loop-lengths can be further thermally activated in two different ways: they may get unpinned from the remaining pinning points, or they may move by forming double kinks within the free loop-lengths. The first calls for a rather large activation energy extending over long distances, while the second is energetically more attractive. This mechanism is the same as has been suggested for the overcoming of the P-N force. Earlier in this section we have already noted that at low  $\tau^*$ , a linear relationship exists between  $1/V^*$  and  $\tau^*$ , suggesting the operation of the P-N force. Comparison with the universal curves of Dorn and Rajnak (fig. 10) has also suggested this possibility at low  $\tau^*$  values. An order of magnitude calculation for existing loop-lengths can be performed from the values of activation volume at temperatures where the

transition takes place with the assumption that  $d^* \approx b^\dagger$ . This can then be compared with the calculated equilibrium distance existing between two kinks. Such calculations can be made by using Seeger's [29] formulation. The results of these calculations in the present experiments show that Seeger's theory gives values for  $l^*$  that are about twice as high as those calculated from  $V^*$ . This may very well be due to the many approximations that are present in Seeger's model, or it may just be due to  $d^*$  being significantly smaller than  $b$  when the P-N force commences to be rate-controlling. In the absence of a force/distance relationship, it is difficult to account for this discrepancy quantitatively. In spite of this apparent difficulty, it is quite likely that the P-N force is rate-controlling at these higher temperatures. The variation of  $1/V^*$  with  $\tau^*$ , and the absence of any relationship between  $V^*$  and  $(c)^{-\frac{1}{2}}$  at these temperatures strongly suggests such a possibility. Though the P-N force is often assumed to be rate-controlling only at low temperatures, it is possible that when impurities are present the effect of the P-N force may be shifted to high temperatures, when dislocations are relatively free to move by forming kinks.

It is quite unlikely that cross-slip can be the activating mechanism during the second stage. The stacking fault energy of zirconium has been deduced to be high from studies on the stacking fault probability of zirconium [30, 31] and hence it is less probable that dislocations will dissociate into partials in the basal plane while cross-slipping. Moreover, attempts to calculate the recombination energy of the partials ( $R_c$ ) and the constriction energy ( $U_c$ ) from the experimental results, as has been done by Dorn and his co-workers [23], proved unsuccessful as both quantities were found to vary strongly with temperature.

## Conclusions

There is a large temperature-dependent flow stress in zirconium when oxygen is added as an interstitial impurity. Both the temperature-dependent and the temperature-independent flow stress components increase with increase in the interstitial oxygen content.

Impurity depinning seems to be rate-controlling at low temperatures until thermal activation removes a sufficient number of pins to make the

P-N force operative. During this first stage of activation, the activation energy increases linearly with temperature only at temperatures where there is no overlap, and the activation volume is proportional to the square root of the interstitial concentration.

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<sup>†</sup>Unlike in impurity mechanism, this approximation is crude;  $d^* \approx b/2$  has been shown to be more realistic for lattice-hardening.

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