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Plastic deformation of Zr–Sn polycrystals at intermediate temperatures

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The yield stress and the activation volume for Zr–Sn alloys with 0.74, 2.85, 4.27 and 6.19 wt% Sn have been measured at temperatures between 400 and 750 K. The temperature dependence of the yield stress exhibits a plateau except for the alloy with the highest content of tin. The yield stress increases with increasing content of tin atoms. A non-monotonic variation of the activation volume with temperature has been observed for pure zirconium and for Zr–Sn alloys with 0.74 and 2.85 wt% Sn. The maximum value of the activation volume (at about 600 K) decreases with increasing content of tin. Dynamic strain ageing is considered to be responsible for the maximum in the temperature dependence of the activation volume. The dislocation structure has been observed. The experimental results are interpreted in terms of a simple model which considers that the flow stress is determined by thermally activated glide of dislocations through obstacles, dynamic strain ageing and a strengthening effect of tin atoms.

1. Introduction

Temperature has a great effect on the deformation behaviour of hexagonal close packed metals. Plastic deformation of polycrystalline alpha zirconium is also strongly influenced by temperature. In previous papers [1, 2] the effect of temperature on the flow stress of alpha zirconium deformed at temperatures between 77 and 900 K has been investigated. The yield stress, defined as the flow stress at plastic true strain of 0.2%, decreases with increasing temperature. The decrease is interrupted in the temperature ranges 300–400 K and 500–700 K, where the yield stress is independent of temperature; so-called athermal (or plateau regions) are observed. Above this, the yield stress again becomes dependent on temperature. The temperature dependence of the yield stress indicates that the mechanisms controlling the rate of deformation of alpha zirconium polycrystals may be different in different temperature ranges.

In order to identify the thermally activated mechanism responsible for slip, the activation volume should be determined. If we know the dependence of the flow stress, σ, on strain rate, $\dot{\varepsilon}$, the activation volume, V_a, can be evaluated from the experiments according to the following equation

$$V_a = MkT\left(\frac{\partial \ln \dot{\varepsilon}}{\partial \sigma}\right)_T \qquad (1)$$

where k is the Boltzmann constant, T is the absolute test temperature and M is the Taylor factor. The values of the activation volume for pure alpha zirconium estimated with the help of Equation 1, using $M = 2$, at the beginning of deformation, are plotted versus temperature in Fig. 1 (taken from [2]). It can be seen that the variation of the activation volume with temperature is non-monotonic in the intermediate temperature range from about 450–700 K. The temperature dependence of V_a exhibits a local maximum at about 600 K. Yin *et al.* [3] have measured the activation volume as a function of temperature for Ti–50A (0.5 at% O_{eq}). They have shown that an abrupt increase in the value of the activation volume occurs above 500 K and a maximum value occurs at about 650 K.

It is interesting to note that the deformation of alpha zirconium after stress relaxation started at a stress which was higher than that at the beginning of the stress relaxation, when the specimens were deformed at temperatures between 450 and 600 K [4]. The material hardens on ageing. The effects of strain ageing depend on strain and temperature for a constant time of relaxation [4]. Ramaswami and Craig [5] have reported that at temperatures between 520 and 650 K, a yield point occurred on changing the strain rate during deformation. The above-mentioned effects and the appearance of serrations along the stress–strain curves at about 600 K may be explained as a result of dynamic strain ageing associated with the oxygen atoms [4–6].

Hong [7] has explained a peak in the activation volume measured by Yin *et al.* [3] by assuming that the flow stress is the sum of the stress increment due to dynamic strain ageing, σ_a, and the stress of the basic

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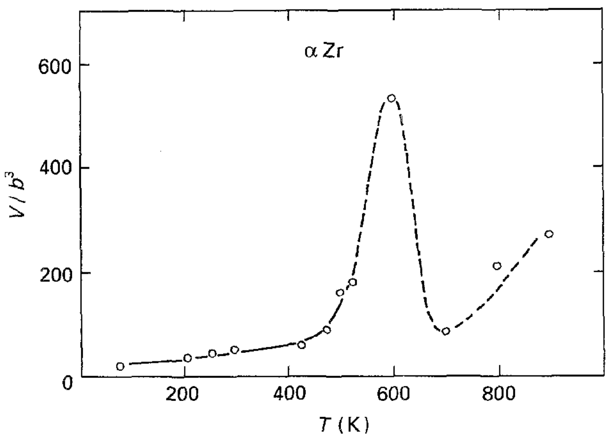


Figure 1 The temperature dependence of the activation volume for pure α-zirconium.

(dislocation) rate-controlling mechanism, σ_d (in the absence of dynamic strain ageing). Then the flow stress is given by

$$\sigma = \sigma_d + \sigma_a \tag{2}$$

According to Hong [7], σ_a has the form of the statistical distribution and its temperature dependence may be expressed by the following equation

$$\sigma_a = \sigma_{ao} \exp\left[-(T - T_1)^2/B \right] \tag{3}$$

where σ_{ao} is the maximum value of σ_a, T_1 is the temperature at which this maximum occurs and B measures the width of the distribution about T_1. B is a function of strain rate. Then the apparent activation volume can be determined from the following equation

$$V_a = MkT \left[\frac{\partial \ln \dot{\varepsilon}}{\partial(\sigma_d + \sigma_a)} \right]_T \tag{4}$$

Using the expression for σ_a in Equation 3, we have

$$V_a = \frac{V_d}{1 + K_a V_d} \tag{5}$$

where

$$K_a = \frac{1}{MkT} \left[\frac{\partial \sigma_a}{\partial \ln \dot{\varepsilon}} \right]_T \tag{6}$$

and V_d is the activation volume without dynamic strain ageing. Because K_a depends on temperature, Equation 5 indicates that the activation volume can change with temperature in the dynamic strain ageing region. The maximum value of V_a is observed in the temperature region where $K_a < 0$. The values of the activation volume calculated by Hong [7] are in good agreement with those obtained experimentally for Ti–50 A (0.5 at % O_{eq}) by Yin *et al.* [3].

Malygin [8] has presented a theoretical analysis dealing with the influence of impurity atmospheres on dislocations formed during deformation on the activation parameters. Assuming that the impurity concentration on dislocations changes with temperature and strain rate, he has shown that the temperature dependence of the activation volume can be described by

$$V_a = \frac{V_d}{1 - (V_d \Delta\sigma_{am}/MkT)\,\varphi(q)} \tag{7}$$

where $\varphi(q) = (2/3)q^{2/3} \exp(-q^{2/3})$ and $q = KD/\dot{\varepsilon}$. In Equation 7, $\Delta\sigma_{am}$ is the maximum value of the stress increment due to dislocation pinning by impurities, D is the diffusion coefficient and K is a parameter which depends on the mobile dislocation density, the mean spacing between the obstacles, the concentration of impurity atoms in the solid solution, and the interaction energy between dislocations and impurities. Taking into account the temperature dependence of q ($\sim \exp(-U_m/kT)$, where U_m is the activation energy for the impurity migration), from Equation 7 it follows that at the constant strain rate the variation of the test temperature should cause a sharp increase in the activation volume at a certain temperature.

The mechanical behaviour of materials is also influenced by the presence of substitutional solute atoms. It may be expected that substitutional solute atoms will affect the material properties that also govern plastic deformation of alpha zirconium.

The aim of this work was to investigate a possible influence of solute tin atoms on the yield stress, the activation volume and the temperature dependence of these quantities for Zr–Sn alloy polycrystals deformed in the intermediate temperature range from about 400–750 K. Some results of investigation of the dislocation structure by TEM are reported. The results give the basic features of changes in the density and arrangement of dislocations after a certain strain as a function of tin concentration and/or temperature.

2. Experimental procedure

Designations and the chemical compositions of four Zr–Sn alloys are given in Table I. The preparation of samples is described elsewhere [9]. The test specimens of 80 mm × 9 mm × 3.3 mm gauge dimensions were annealed in vacuum at 583 K for 8 h. The resulting grain size was determined by optical metallography to be about 28 μm.

The specimens were deformed in tension in an Instron testing machine (type 1195) at temperatures between 400 and 750 K at a constant crosshead speed giving an initial strain rate, $\dot{\varepsilon}$, of $6.7 \times 10^{-5}\,\mathrm{s}^{-1}$. All the tests were conducted in a flowing atmosphere of dry argon. A temperature-controlling chamber was used to adjust the temperatures. The yield stress, σ_{02}, was defined as the flow stress at a plastic true strain of 0.2%. The stress relaxation tests were used to estimate the activation volume, V_a, stress relaxation was allowed to occur for 300 s.

The dislocation structure was studied by TEM. The specimens for TEM were prepared by the usual procedure. Thin slices were spark-planed to a thickness of

TABLE I Chemical composition of tin in alloys

Alloy	Sn (wt %)	Sn (at %)
Zr–0.8 Sn	0.74	0.57
Zr–3.0 Sn	2.85	2.20
Zr–4.5 Sn	4.27	3.31
Zr–6.0 Sn	6.19	4.98

0.3–0.4 mm and then thinned using a standard jet electropolishing technique. Foil preparation is described elsewhere [10, 11]. Foils prepared from the slightly deformed specimens ($\varepsilon < 0.02$) represent the beginning of the deformation process. The specimens for the TEM observations were cooled under stress after interruption of straining. The electron microscope was a Tesla BS 540 instrument.

3. Results

The temperature dependence of the yield stress, σ_{02}, obtained for various concentrations of tin is presented in Fig. 2. It is evident that each curve, except for the highest concentration of tin, exhibits a region where the stress is independent of temperature (i.e. a plateau region). Fig. 2 illustrates also the influence of tin content on the yield stress: the yield stress increases with increasing tin concentration.

The temperature dependence of the activation volume V_a ($M = 1$) for four Zr–Sn alloys is shown in Fig. 3. It is seen that the values of activation volume decrease with increasing tin concentration at all temperatures investigated, with the exception of $T = 750$ K. From Fig. 3 it follows that the maximum in the temperature dependence of V_a decreases with increasing tin concentration and it vanishes for alloys with higher tin concentrations.

In our experiments the dislocation structure formed by long wavy dislocation lines was relatively often observed, especially at higher temperatures. This is illustrated in Fig. 4, showing the dislocation structure of Zr–4.5 Sn alloy deformed at 750 K to $\varepsilon = 0.5\%$. Dislocations in Fig. 4 very probably have a screw character with a Burgers vector of the type $\boldsymbol{b} = \frac{a}{3}\langle 2\bar{1}\bar{1}0\rangle$, so-called $\langle a\rangle$ dislocations. Many jogs in these dislocations have always been found. The height, h, of jogs was determined from stereo-pictures and it depends on tin concentration and temperature. In the case shown, h was estimated to be about 100 $\boldsymbol{b}$. Part of that dislocation line with a jog for $\boldsymbol{b} = \frac{a}{3}\langle 2\bar{1}\bar{1}0\rangle$ is shown schematically in Fig. 5. Similar dislocation structures (after deformation) with long screw dislocations have been observed in α-zirconium [12] and in zirconium-based alloys [13]. The dipoles of the screw dislocation arrangement are seen in Fig. 6. Screw dislocations of opposite sign form pairs and dislocation details. In the lower left part, annihilation of screw dislocations by cross-slipping is visible.

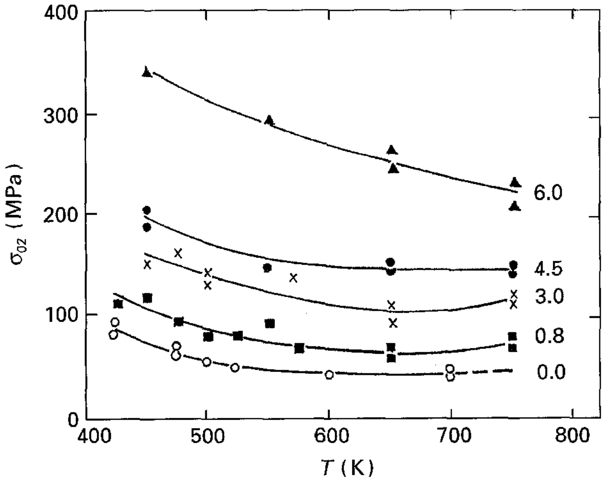


Figure 2 The temperature dependence of the yield stress, σ_{02}, for various Zr–Sn alloys.

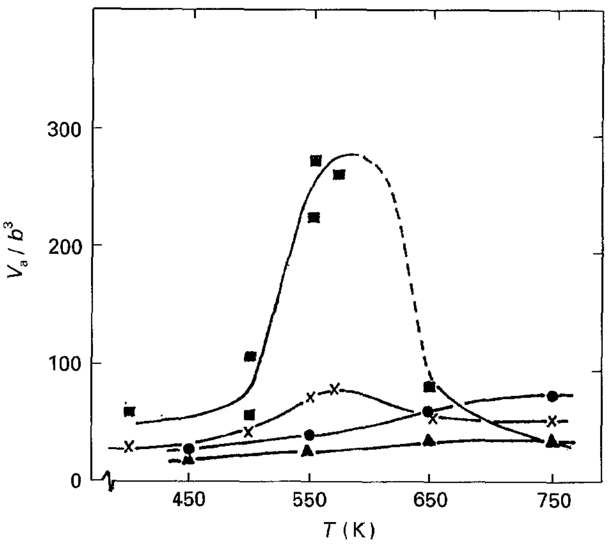


Figure 3 The temperature dependence of the activation volume for Zr–Sn alloys: (■) 0.8, (×) 3.0, (●) 4.5, (▲) 6.0 Sn.

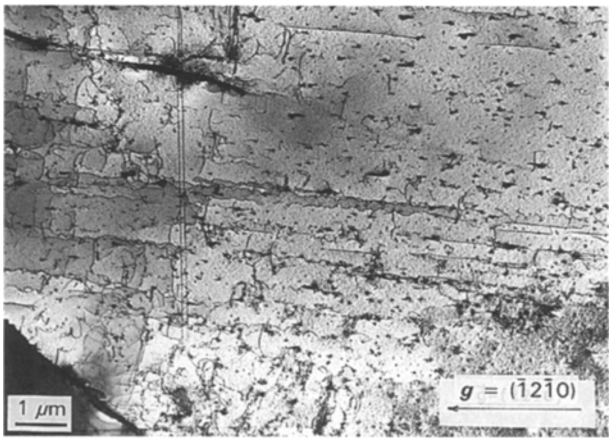


Figure 4 Wavy $\langle a\rangle$–dislocations (very probably of screw character) in Zr–4.5 Sn alloy deformed at 750 K to $\varepsilon = 0.005$.

The dislocation structure with a subgrain is shown in Fig. 7. Walls of subgrains are formed by $\langle c + a\rangle$ dislocations with the Burgers vector of type $\boldsymbol{b} = \frac{a}{3}\langle 11\bar{2}3\rangle$. Most of the dislocations are out of contrast under given diffraction conditions (e.g. $\langle a\rangle$ dislocations). A relatively high density of the free screw dislocation segments with a Burgers vector of type $\boldsymbol{b} = \frac{a}{3}\langle 2\bar{1}\bar{1}0\rangle$ was determined in samples with higher tin content. The edge dislocations were observed only as tangles (Fig. 8). A similar situation with an abundance of screw dislocations has also been observed in pure zirconium after high-temperature creep deformation [12]. For a higher stage of deformation there is characteristic subgrain structure, as can be seen in Fig. 9. Within the subgrains, the majority of dislocations are mutually intersecting $\langle a\rangle$ dislocations.

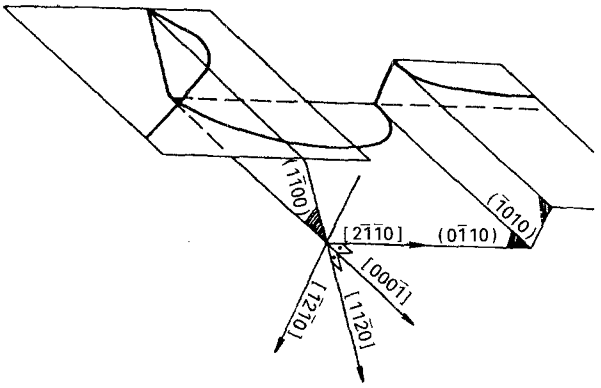
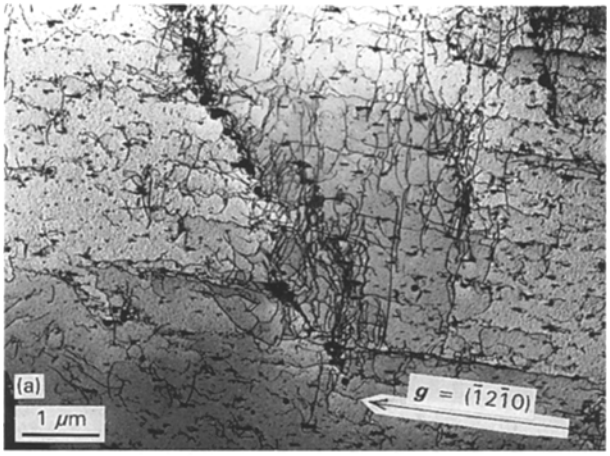


Figure 5 The geometry of wavy $\langle a \rangle$ dislocations shown schematically.



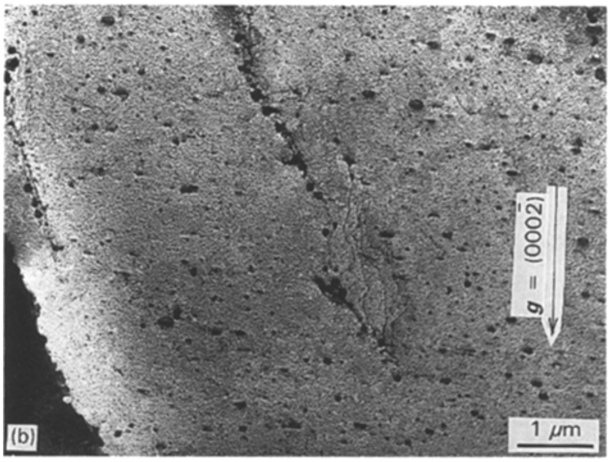


Figure 8(a) Tangles of $\langle a \rangle$ dislocations in Zr–4.5 Sn alloy deformed at 750 K to $\varepsilon = 0.05$. (b) In the same place (for different ***g***), the visible dislocations have very probably a Burgers vector with non-zero $\langle c \rangle$ component.

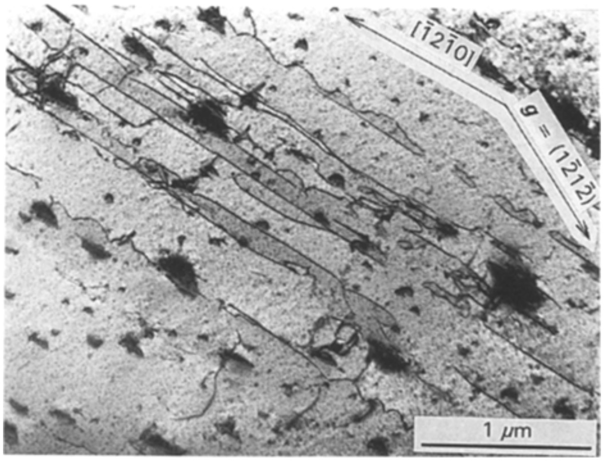


Figure 6 Electron micrograph of Zr–4.5 Sn alloy deformed at 750 K to $\varepsilon = 0.005$. An annihilation of dislocations is visible at the bottom left.

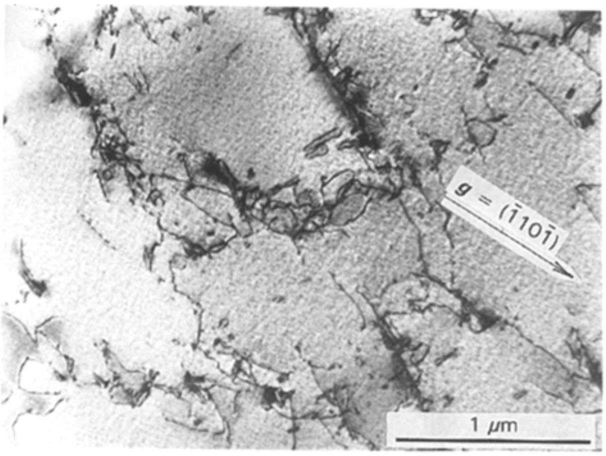


Figure 7 Tangles of $\langle a \rangle$ dislocations in Zr–4.5 Sn alloy deformed at 750 K to $\varepsilon = 0.01$.

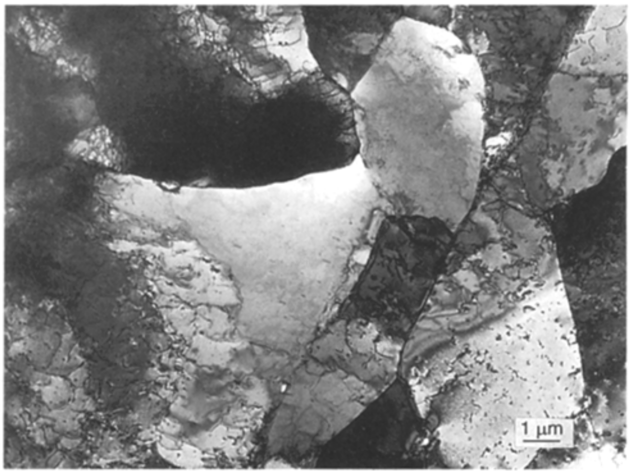


Figure 9 Subgrain structure in Zr–0.8Sn deformed at 750 C to $\varepsilon = 0.07$.

Very recent results [14] indicate that samples of Zr–Sn alloys contain a fine dispersion of Zr_4Sn particles. The precipitates are present both in grain boundaries and inside grains. The diameter of these precipitates (dark spots in Fig. 8b) increases with increasing tin content. The mean diameter of Zr_4Sn precipitates in Zr–6Sn is about 10^{-1} μm.

4. Discussion

The high-temperature plateau region in the temperature dependence of the yield stress of α-zirconium has been studied in more detail by Heritier *et al.* [15]. They have observed that for temperatures above about 750 K, the yield stress decreases with increasing temperature. The plateau region has been interpreted as a thermally non-activated interaction of glide dislocations with obstacles (for example, forest dislocations) which are overcome only by the applied stress. The effect of tin as solute element on the deformation behaviour of zirconium has been investigated by Luton and Jonas [16] at high temperatures. They have shown that the strengthening effect of tin could be due to an increase in the density of local obstacles. The plateau region in the yield stress of Zr–Sn polycrystals has been observed. Athermal mechanisms have also been used to explain yield stress plateaus [16]. A temperature-independent component of the yield stress is considered to dominate the macroscopic behaviour of Zr–Sn polycrystals at intermediate temperatures and therefore a yield stress plateau is produced. However, Luton and Jonas [16] have found a local maximum (a hump) in the temperature dependencies of the yield stress at temperatures between 700 and 800 K. An indication of a hump in the temperature dependence of σ_{02} is also observed in our results at 750 K, namely for Zr–0.8 Sn and Zr–3 Sn alloys. The athermal approach cannot explain humps (peaks) in the temperature dependence of the stress. These peaks are very probably connected with dynamic strain ageing. At elevated temperatures, solute atoms are mobile and can interact with moving dislocations.

According to experimental results published by many authors [4–6, 15, 17–19] we can assume that oxygen atoms move to dislocations at elevated temperatures. Within a certain temperature region, an increase in temperature causes an increase in the magnitude of the interaction between moving dislocations and mobile solute (oxygen) atoms. This increase produces an additional strengthening component. The dislocation velocity decreases due to solute drag and hence the stress must increase to maintain the imposed strain rate. The strain-rate sensitivity of the flow stress, $S = (\partial\sigma/\partial \ln \dot{\varepsilon})_T$, is decreasing and therefore the activation volume (see Equation 1) should increase within a limited temperature range, which is observed (Fig. 1). In this connection, it is interesting to note that James and Davies [19], investigating the stress relaxation behaviour of polycrystalline Zr–8.5 at % O alloy at temperatures between 573 and 773 K, have found that the temperature dependence of the activation volume (in the temperature range investigated) exhibits a local minimum at about 670 K. The activation volume increases with decreasing temperature for $670\,\text{K} > T > 573\,\text{K}$ and increases with increasing temperature for $670\,\text{K} < T < 773\,\text{K}$. The course of a plot of the activation volume versus temperature is similar to that given in Fig. 1. However the values of V_a obtained by James and Davies [19], ranged from 24–30 $\boldsymbol{b}^3$, and are much lower than those presented in Fig. 1. The difference can be explained by the fact that the content of solute oxygen in our samples is several times smaller than that in the alloy used by James and Davies [19].

We believe that the observed maximum in the temperature dependence of the activation volume for pure zirconium and for alloys with a small concentration of tin is very probably the consequence of dynamic strain ageing. From Fig. 3 it follows that the maximum value of V_a decreases with increasing concentration of tin. Thus the influence of the migrating interstitial solute atoms on glide of dislocations is, in alloys with higher tin concentration, superposed by an interaction with tin atoms. The presence of tin atoms (as single or groups of tin solutes) may affect the mobility of moving interstitials. The addition of tin atoms increases the yield stress (Fig. 2). Then we can write, for the total stress

$$\sigma = \sigma_d + \sigma_a + \sigma_f \tag{8}$$

where a stress component, σ_f, expresses a strengthening effect of tin atoms in Zr–Sn alloys. It is obvious that σ_f increases with increasing concentration of tin atoms. It is possible to use Equation 8 under simplifying assumptions about the dislocation density and strength of obstacles [20].

The effects that the stress component, σ_f, has on the temperature dependence of the activation volume are understood by solving Equation 1 for σ given by Equation 8. We can write

$$\frac{1}{V_a} = \frac{1}{MkT}\left[\frac{\partial(\sigma_d + \sigma_a + \sigma_f)}{\partial \ln \dot{\varepsilon}}\right] \tag{9}$$

or

$$V_a = \frac{V_d}{1 + K_a V_d + K_f V_d} \tag{10}$$

where

$$V_d = MkT\left(\frac{\partial \ln \dot{\varepsilon}}{\partial \sigma_d}\right) \tag{11}$$

and

$$K_f = \frac{1}{MkT}\left(\frac{\partial \sigma_f}{\partial \ln \dot{\varepsilon}}\right) \tag{12}$$

The coefficient K_a is given by Equation 6. From Equation 9 it follows that in the case when dynamic strain ageing is absent and the effect of tin solute atoms can be neglected, i.e. $K_a = 0$, $K_f = 0$, the apparent activation volume corresponds to the thermally activated motion of dislocations in a "pure crystal". This motion of dislocations may be influenced by various types of obstacles. Based on the previous experimental results [1, 2, 17] and our observation of dislocation structures, presented in this work and elsewhere [21], we can conclude that at elevated temperatures the basic micromechanism controlling the rate of plastic deformation may be connected with the non-conservative motion of jogs in screw dislocations.

When dynamic strain ageing takes place in pure zirconium, i.e. $K_f = 0$, $K_a \neq 0$, the maximum in the V_a versus T plot is observed in the temperature region where $K_a < 0$ and the absolute value of K_a is close to $1/V_d$ [7]. If the strain-rate sensitivity of the stress component, σ_f, has a positive value, i.e. $K_f > 0$, then one expects suppression of the maximum in the temperature dependence of V_a with increasing concentration of tin atoms. This is in qualitative agreement with experimental observations.

A qualitative similar explanation of the influence of tin as the substitution-type impurity on the temperature variation of the activation volume, can also be obtained using Equation 7 deduced by Malygin [8] and Equation 8.

Finally, it is important to note that the present investigation represents the complex behaviour of Zr–Sn alloy polycrystals. Tin atoms can change the formation of the dislocation structure, either through changes in the rate of dislocation multiplication or dynamic recovery. The influence of dynamic strain ageing should be considered in the temperature range investigated. Tin atoms can influence these processes either directly or through precipitation.

5. Conclusions

1. The temperature dependence of the yield stress, σ_{02}, obtained for various concentrations of tin, exhibits a plateau region (except for the highest concentration of tin) in the temperature range 450–700 K. The yield stress increases with increasing content of tin at all temperatures.
2. The temperature dependence of the activation volume for α-zirconium and Zr–0.8 Sn and Zr–3Sn alloys has a non-monotonic character with a maximum in the vicinity of 600 K. The maximum of the activation volume decreases with increasing content of tin.
3. Dynamic strain ageing is considered to be responsible for the maximum value in the temperature dependence of the activation volume. Based on the experimental results, a simple phenomenological explanation has been outlined. It emphasizes the effect of substitutional tin atoms on the mobility of interstitial oxygen atoms.
4. Long wavy screw dislocations with jogs are a significant feature of the dislocation structure formed at the beginning of deformation at elevated temperatures.

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