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ANELASTIC RELAXATION PEAKS IN SINGLE CRYSTALS OF
ZIRCONIUM-OXYGEN ALLOYS

by

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Abstract - Relaxations of the compliances S_{11} - S_{12} and S_{44} have been observed in single crystals of zirconium-oxygen alloys tested in flexure and in torsion respectively. The relaxations are attributed to the stress-induced reorientation of substitutional impurity atoms (s) paired with interstitial oxygen atoms (i). The results demonstrate that the jump of the interstitial parallel to the basal plane dominates in the reorientation of the s-i pair.

Introduction

The internal friction spectrum of polycrystalline alpha-zirconium containing oxygen in solid solution exhibits an anelastic relaxation peak at about 430°C at low frequencies (1 Hz). If interstitial oxygen is designated by i and substitutional impurities by s, Gacougnolle et al (1) (2) have shown that both s-i and i-i pair reorientations give rise to measurable relaxations at this temperature. They further showed that the strength of these relaxations was such that in zirconium of commercial purity, only the relaxation of s-i pairs is observed for oxygen concentrations less than about 5 atomic %. This work has settled to some extent the controversy which existed in the literature concerning the mechanism responsible for the so-called oxygen peak in polycrystalline zirconium (3)-(7). However, as pointed out by Nowick (8) further insight into the details of the relaxations involved can be obtained only from a study of single crystals of appropriate orientations.

Following (1), (2) we assume that in zirconium of commercial purity containing up to 4 atomic % of oxygen, the observed relaxation will be due to the reorientation of s-i pairs. This paper reports observations of the relaxations of compliances S_{11} - S_{12} and S_{44} isolated by testing a single crystal of $\langle hko \rangle$ orientation in flexure and a single crystal of $\langle 001 \rangle$ orientation in torsion respectively. It is shown that both relaxations are governed by the same atomic jump and that the relaxation time is consistent with diffusion data strain ageing data.

Theory

When an interstitial in an octahedral interstice in the hexagonal lattice is paired to a substitutional atom, the resulting s-i defects is $\langle 100 \rangle$ monoclinic.

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Using the methods of group theory, Povolo and Bisogni (9) and Nowick (8) have shown that the relaxations of S_{44} and $S_{11}-S_{12}$ compliances are possible for this defect. The six nearest neighbour equivalent configurations for the s-i pair are shown in Fig. 1. If it is assumed that the substitutional atom is fixed and reorientation of the pair occurs by jumps of the more mobile interstitial, the two distinct types of jump designated by W_1 (parallel to the basal plane) and W_2 (in the direction of the C-axis) can lead to reorientation. The kinetics of these relaxations have been investigated theoretically (8) (9) and lead to the following relaxation times (8)

$$\tau_{S_{11}-S_{12}}^{-1} = 3 W_1 \quad \text{and} \quad \tau_{S_{44}}^{-1} = 3 W_1 + 2 W_2$$

If these relaxations are of an observable magnitude, both should give rise to an internal friction peak in tests on polycrystalline specimens. Thus the observation of a single peak, which is nearly a single time of relaxation, in polycrystalline samples suggests that W_1 is the rate controlling jump. However, it is possible as favoured by Bisogni et al (10) in their discussion of a peak in hafnium-oxygen alloys, that $W_2 \gg W_1$. In this case the 'Frozen-free-split' discussed by Nowick (8) would occur and the relaxation of $S_{11}-S_{12}$ would be expected to occur at temperatures well above those carried out to date on polycrystalline specimens. Since the s-i peak in polycrystalline alloys in very small and sits on the low temperature tail of a series of large peaks associated with grain boundary phenomena, only measurements on suitably orientated single crystals can be used to distinguish which of the two jumps is rate controlling. This is most easily accomplished by measurement of $G_{\langle 001 \rangle}^{-1}$ (which gives $\tau_{S_{44}}^{-1}$) in a torsion pendulum and $E_{\langle hko \rangle}^{-1}$ (which gives $\tau_{S_{11}-S_{12}}^{-1}$) in a flexure pendulum.

Experimental technique

The single crystals used in this study were grown by the floating zone technique at the University of British Columbia (11) from zirconium of commercial purity. The first, a platelet (4.2 cm x 0.5 cm x 0.1 cm) with the c-axis perpendicular to the plane of the platelet was tested in flexure from ambient to 700°C in a counterbalanced reed pendulum (12)(13) at strain amplitudes $< 10^{-5}$. The second, a needle (2 cm x 0.1 cm x 0.08 cm) with the c-axis parallel to the long dimension was tested in a modified inverted torsion pendulum over the temperature range ambient to 700°C at a strain amplitude of 2×10^{-5} . Testing was carried out in a vacuum of 10^{-6} mm of Hg and the specimen temperature and temperature variation along the length of the specimen was maintained within 1°C during each internal friction measurement.

The oxygen content of the flexure specimen was 5000 wt ppm (= 2.85 atomic %) and about 7000 wt ppm (~ 4 atomic %) for the torsion specimen. After testing, one of the crystals was analysed and found to contain 80 wt ppm of Fe, 45 wt ppm of Hf and a total of 350 wt ppm of other metallic impurities.

Results and Discussion

In the single crystal of orientation $\langle kho \rangle$ tested in flexure, a small but well defined and reproducible relaxation peak was observed as shown in Fig. 2. Also shown is the shift in peak position obtained by altering the frequency by a factor of ~ 2 . From an analysis of these results (14) it was found that the activation energy from peak shift was 46 ± 2 kcal/mole (2.0 eV), while half width measurements gave 42.0 k/cal/mole for both peaks. The frequency factor, τ_0^{-1} was found to be $1.1 \times 10^{15} \text{ s}^{-1}$. These results are in excellent agreement with the parameters estimated from polycrystalline samples, particularly the work of Gacougnolle et al (7) on their material of commercial purity.

For the single crystal of orientation $\langle 001 \rangle$ tested in torsion, a similar peak was observed in the same temperature range as shown in Fig. 3. After subtraction of an estimated background, this peak can be well represented by a Debye peak with an activation energy of 46 kcal/mole. The frequency for this specimen was also altered by a factor 2.

TABLE 1
SUMMARY OF SINGLE CRYSTAL RESULTS *

	Freq. f(Hz)	Peak Temp. °C	Peak HT $\Delta_M \times 10^3$	Actn. En. Half-width kcal/mol	% Broadening
Torsion $\langle 001 \rangle$	0.671	424 ± 2	2.34	46	4
	1.213	435 ± 2	2.20	44	9
Flexure $\langle hko \rangle$	2.438	450 ± 1	1.23	42	14
	4.554	465 ± 1	1.37	42	14

* From $\ln f$ vs T^{-1} (Fig. 4): Activation Energy 47.9 kcal/mol (2.08 eV)

$$\tau_0 = 2 \times 10^{-16} \text{ s}$$

The results representing two frequencies for each of the two orientations are summarized in Fig. 4 and Table 1. From these results it can be seen that the two relaxations isolated in this study are governed by the same kinetics. The peaks are small (log. dec, Δ_{max} between 1.2×10^{-3} and 2.3×10^{-3}) but only slightly broader than the single time of relaxation parameters obtained from peak shift with frequency. Thus, the basal plane jump W_1 dominates in the reorientation of s-i pairs in zirconium-oxygen alloys. This is a surprising result, since it has been generally assumed that the c-axis jump W_2 is rate controlling in the diffusion of oxygen in zirconium (15). For this reason, in an attempt to estimate diffusion coefficients at relatively low temperatures from internal friction data (16) and strain ageing data (17), the various authors have interpreted their data in terms of c-axis jumps. Because of the results of this paper, we have reanalysed the internal friction and dynamic strain ageing results of various authors (18). The results of this analysis together with a compilation of the most accurate diffusion data for oxygen in zirconium are plotted in Fig. 5.

These results are again surprising because the intersection of the two linear segments occurs at 650°C which is 200°C above the limit of the data estimated from s-i pair reorientation. In fact, Quataert and Coen-Porisini (19) found essentially the same two diffusion equations shown in Fig. 5 in a study of oxygen diffusion over the temperature range 550°C - 910°C. Consequently, it is interesting to speculate that, as in the case of the reorientation of the s-i pair, the basal plane jump is also rate controlling in the diffusion of oxygen at temperatures below 650°C while the c-axis jump does not become important until temperatures above 650°C are reached.

Conclusions

- 1) The basal plane jump W_1 is rate controlling in the reorientation of s-i pairs in zirconium-oxygen alloys.
- 2) The parameters obtained for the relaxation of the s-i pair are consistent with the data in the literature for dynamic strain ageing and oxygen diffusion.

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Figure Captions

- Fig. 1 : The two types of interstitial jump, W_1 parallel to the basal plane and W_2 parallel to the c-axis which produce reorientation of a nearest neighbour s-i pair in zirconium (after Nowick (8)).
- Fig. 2 : The oxygen peak measured at two frequencies in flexure for the single crystal of $\langle hko \rangle$ orientation.
- Fig. 3 : The oxygen peak measured in torsion of the single crystal of $\langle 001 \rangle$ orientation.
- Fig. 4 : $\ln f$ vs $1/T$ Arrhenius plot for the single crystal data.
- Fig. 5 : Plot of the volume diffusion data for oxygen in α -zirconium. Compilation of this data is given in (18).

