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HIGH-TEMPERATURE INTERNAL FRICTION IN POLYCRYSTALLINE ZIRCONIUM AND ZIRCALOY-4

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The data on the high-temperature internal friction of zirconium and zirconium alloys are reviewed and new results on zirconium and Zircaloy-4, measured at low and at intermediate frequencies, are presented. It is shown that the damping spectrum of pure zirconium, for annealed polycrystals, shows a peak probably related to relaxation of grain or subgrain boundaries. The data on Zircaloy-4 show two peaks: one near the grain-boundary peak in the pure metal and another one at a higher temperature. Possible mechanisms for these peaks are discussed. Finally, the high-temperature internal friction background of zirconium and zirconium alloys is analyzed and, for Zircaloy-4, the apparent activation enthalpy is found to be related to the grain size.

1. Introduction

Internal friction measurements have been used to obtain information on the interaction between point defects and between dislocations and impurity atoms. This information is very useful for understanding strain-aging phenomena in metals and alloys.

Several peaks on the high-temperatures internal friction (HTIF) of zirconium and zirconium alloys have been reported. Some of these maxima are produced by stress-induced reorientation of interstitial and interstitial–substitutional complexes. Mishra and Asundi [1,2], studied the influence of O and N substitutional impurity atom complexes on the HTIF of Zr. For all the alloying elements, O gave two peaks, the relative intensity depending upon the concentration of O. In the case of N, only alloying elements larger in atomic size than Zr gave internal friction peaks. Furthermore, aging experiments, at 833 K in Zr–0.25 at% Gd, indicated that the high temperature nitrogen peak increased with increasing aging time. This might occur by replacement of O atoms, around the substitutional atom, by N. Similar effects were also noticed in Zr–Sn alloys. In addition, various authors [3–7] have reported internal friction peaks produced by the stress-induced diffusion of O in the Zr lattice and these results have been reviewed by Ritchie and Atrens [8]. Bungardt et al. [9], studied the HTIF of Zr–N alloys. It was found that the introduction of N into the Zr wires reduced the HTIF and small humps were observed between room temperature and 973 K.

Additional maxima, produced by various mechanisms, have been also observed on the HTIF of zirconium and zirconium alloys: a maximum attributed to the allotropic transformation [10,11], a second one attributed to grain-boundary relaxation [1–3,5,12] and a third one attributed to thermally assisted unpinning of dislocations from 0 interstitials [12,13]. The location and magnitude of the last peak is strongly amplitude-dependent and the grain-boundary peak was found to be dependent on the grain size [10,11], the impurity content [1–3,9–11,14] and the structure of the specimens [1,2].

The amplitude dependence of HTIF of iodide-refined Zr(2.4% Hf) and Zr–O was studied by Browne [4]. At all temperatures, oxidized Zr specimens exibited amplitude-dependent internal friction, which was not removed by further annealing. This internal friction was also time-dependent. Ritchie et al. [6] found an anomalous time-dependent and strain-amplitude-dependent

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damping, in a Zr single crystal with low oxygen content, in the temperature range from ambient to 623 K. Atrens [15–17], reported some damping versus strain data in Zr–O alloys, between 300 and approximately 700 K. The validity of the interpretation given by the author to these results has been discussed by Povolo [18,19]. Fernandez and Povolo [13], studied the amplitude-dependent damping and modulus defect of high-purity polycrystalline zirconium and Zircaloy-4, between room temperature and approximately 800 K. The damping versus strain curves could be described by the superposition of three mechanisms acting at low, intermediate and high strains respectively. Ritchie and Sprungmann [12], have studied recently the amplitude and temperature dependence of the HTIF of α-Zr single and polycrystals. The damping spectra were resolved into five peaks: one peak due to thermally assisted unpinning of dislocations, two peaks associated with longitudinal and transverse redistribution of O interstitials on dislocations, a peak associated with special dislocation structures and a grain-boundary peak. Also a background was observed that increased exponentially with temperature.

Bedford et al. [20] reported internal friction and electron microscope studies in high-purity Zr (50 ppm O) and Zr–500 ppm O, at temperatures between 290 and 873 K. A transition from logarithmic to nonlogarithmic decay of the torsional vibrations was found, at all temperatures, for special dislocation structures. These changes in the damping could not be attributed to grain-boundary relaxation since the grain size was large compared with the diameter of the wire. It would appear that the kind of subgrain boundaries which undergo stress-relaxation are dislocations in tangled walls. For fully polygonized boundaries the damping is strongly reduced and no relaxation is observed.

An analysis of the results on the HTIF of zirconium and zirconium alloys, reported in the literature, shows that the interpretation of the observed behavior is still controversial. Some new data, taken in zirconium and Zircaloy-4 at low and at intermediate frequencies, will be presented. The results will be discussed in the framework of current theories for high-temperature damping.

2. Experimental procedure

The specimens were prepared from zirconium and nuclear grade Zircaloy-4, supplied by Teledyne Wah Chang, Albany. The chemical compositions supplied by the manufacturer are given in tables 1 and 2. Prior to the internal friction measurements, all the specimens were annealed for 1 h at 1023 K in high vacuum. A strain-annealing treatment was given to some of the Zircaloy-4 specimens to increase the grain size. This treatment consisted of pre-straining the specimens by different amounts at room temperature and a subsequent annealing for ten days at 1063 K in argon atmosphere to avoid contamination. This treatment will be indicated as "grain growth".

Two types of pendulum were used for the internal friction measurements:

(a) A low-frequency Ke's type inverted pendulum with a frequency of the order of 1 s^{-1}. The internal friction was obtained from the decay of the oscillations, registered by means of a photodiode on the screen of an oscilloscope with memory. Typically, maximum strain amplitudes between 3×10^{-5} and 8×10^{-6} were ob-

Table 1
Main impurities in zirconium (in ppm)

Al	< 35
C	75
Cr	63
Hf	53
Fe	490
O	1050
Mn	< 25
Ni	< 35
N	45
Si	< 40
Ti	< 25
W	< 25

Table 2
Composition of Zircaloy-4 (in %)

Sn	1.41
Fe	0.19
Cr	0.1

Main impurities (in ppm)

C	135
Hf	60
N	45
Al	35
Ni	19
Si	28
Ti	18
W	< 25
O	980

tained on the surface of the specimens during free decay.

(b) An automatic pendulum working at intermediate frequencies, of the order of 70 s^{-1}. This equipment allows measurements of the damping at constant maximum strain amplitude and the internal friction versus temperature is recorded automatically. In this type of pendulum, the internal friction is recorded in terms of the energy required to maintain a given oscillation amplitude. Since this energy is proportional to f^{-2} the recorded internal friction versus temperature can be distorted if the oscillation frequency changes considerably with the temperature. A special feature of the pendulum used is that this effect is corrected automatically so that an undistorted recording of the damping versus temperature is obtained. The details of the pendulum are given elsewhere [21].

Finally, two types of specimen were used for the measurements at low frequencies: wires of 1 mm diameter and sheets 0.4 mm thick and 4 mm wide. Wires with 2 mm diameter were used for the measurements at intermediate frequencies.

3. Results

Fig. 1 shows the HTIF obtained in Zr wires at low and at intermediate frequencies. It is seen that a well-defined peak, which shifts with a change in frequency, is present. The average grain size of the as-received material was of the order of 20 μm (measured according to ASTM E 112 standards). For the curve obtained at low frequencies, after the annealing treatment, the specimen was located into the pendulum and heated at a rate of 275 K h^{-1}. The internal friction curve was measured on cooling at an average rate of 68 K h^{-1}. The final grain size was found to be inhomogeneous, with an average size of 40 μm at the center of the cross-section of the wire and 150 μm at the periphery.

For the curve at intermediate frequencies, the specimen had an additional annealing treatment at 1073 K for $\frac{1}{2}$ h. After this, it was located into the pendulum, heated at 240 K h^{-1} and the internal friction curve was measured on cooling at a rate of 75 K h^{-1}. The final grain size, measured at the cross-section of the wire, was found to be uniform with an average size of 90 μm.

Fig. 2 shows the HTIF of a Zircaloy-4 wire measured at intermediate frequencies. The data were obtained on heating and on cooling, at a rate of 80 K h^{-1}. The damping spectra were reproducible either on heating or on cooling and the average grain size remained stable, either during the annealing or during the internal friction measurements, at 19 μm.

Fig. 3 shows the influence of the grain size on the HTIF spectra of Zircaloy-4 wires at low frequencies. Curve (a) was obtained from an as-received specimen, with an average grain size of 13 μm. Curves (b) and (c) were measured on specimens subjected to a grain growth treatment. The average grain size of the specimen for curve (b) was 34 μm and that for curve (c) 88 μm. All the data were obtained on cooling, at a rate of 70 K h^{-1}.

On improving the sensitivity of the pendulum, two small peaks could be resolved in the HTIF spectra of Zircaloy-4 at low frequencies. This is shown in fig. 4 for

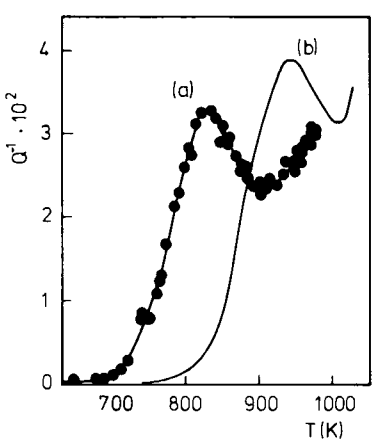

Fig. 1. HTIF of zirconium wires: (a) low, and (b) intermediate frequencies. Both curves were obtained on cooling.

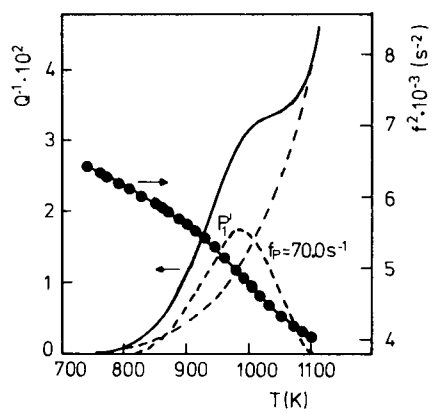

Fig. 2 HTIF of a Zircaloy-4 wire at intermediate frequency. The changes in the resonant frequency of the pendulum with temperature and the resonant frequency at the peak location, f_p, are also indicated.

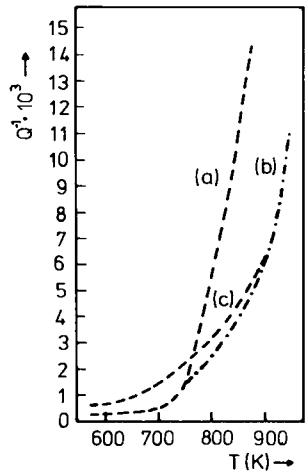

Fig. 3. HTIF of Zircaloy-4 wires at low frequencies, for different grain sizes, d: (a) $d = 13$ μm, (b) $d = 34$ μm, and (c) $d = 88$ μm.

a sheet cut with the axis parallel to the rolling direction. This sheet was annealed at 1013 K for 1 h, located into the pendulum and measured on cooling at a rate of 70 K h^{-1}. The average grain size after the measurement was 33 μm. Similar results were obtained on wires measured at the same frequency.

An important difference between the HTIF of Zr and Zircaloy-4 is that the damping of the alloy is reproducible either on heating or on cooling. This is not the case for the zirconium specimens where the grain

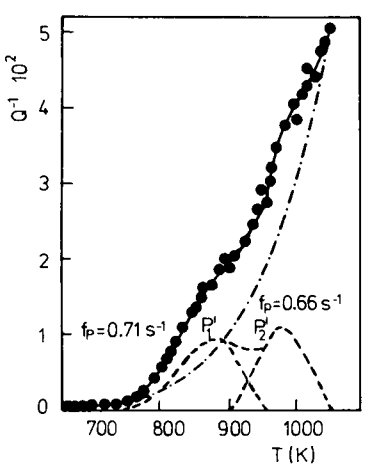

Fig. 4. HTIF of a Zircaloy-4 sheet with an average grain size of 33 μm, measured at low frequencies.

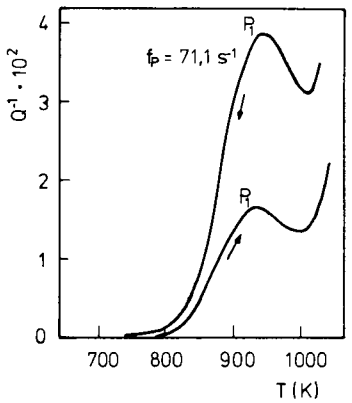

Fig. 5. HTIF of a zirconium wire, at intermediate frequencies, measured on heating and on cooling.

size is changing during the measurement. This is shown in fig. 5 for an annealed zirconium specimen measured on heating and on cooling, at intermediate frequencies.

The different peaks present either in the pure metal or in the alloy, at intermediate or at low frequencies, are summarized in fig. 6. Only one peak, called P_1, is present in zirconium and two peaks, called P_1' and P_2', have been observed in zircaloy-4. The peak at the higher temperature, P_2', could not be detected at intermediate frequencies due to the fact that it is probably masked by the high-temperature background. The peaks were subtracted from the total damping by assuming an exponential increase of the high-temperature background with temperature, i.e. the internal friction was plotted as log Q^{-1} versus $1/T$ and a straight line was drawn through the data below and above the peaks. This is shown, for example, by the increasing broken curves of figs. 2 and 4.

The activation enthalpies and the relaxation times obtained from a shift of the peaks with a change in

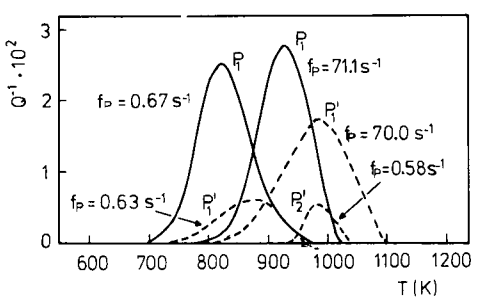

Fig. 6. Internal friction peaks, at intermediate and at low frequencies, on the HTIF of zirconium and Zircaloy-4.

Table 3
Characteristics of the internal friction peaks observed in zirconium and Zircaloy-4. T_p is the peak temperature and f_p the frequency at the peak.

Material	Peak type	T_p (K)	f_p (s^{-1})	ΔH (kJ mol)	τ_0 (s^{-1})
Zr	P_1	822	0.67	280 ± 30	$2.3 \times 10^{-(18 \pm 2)}$
	P_1	926	71.1		
Zircaloy (wire)	P_1'	876	0.632	320 ± 30	$1.3 \times 10^{-(19 \pm 2)}$
	P_1'	982	70.0		
	P_2'	977	0.582		
Zircaloy-4 (sheet)	P_1'	874	0.714		
	P_2'	969	0.665		

frequency are given in table 3. It was not possible to measure the activation enthalpy and the relaxation time for peak P_2' in Zircaloy-4 due to the fact that it could not be resolved at intermediate frequencies.

Finally, it must be pointed out that some small and reproducible peaks could be observed in Zircaloy-4 below about 700 K. These are probably due to interstitial substitutional or interstitial-interstitial complexes and will not be discussed in this paper.

3. Discussion

As shown in fig. 6, the HTIF of zirconium reveals one internal friction peak, P_1, both at low and at intermediate frequencies, which has been reported by several authors. The peak has been generally attributed to grain-boundary relaxation, since it is strongly reduced by increasing the grain size of the specimens. In fact, Bungardt and Preisendanz [11] have shown that the peak disappeares at large grain sizes.

Ritchie and Sprungmann [12], however, have interpreted peak P_1 (named P_2 by them) as due to the stress-assisted redistribution of oxygen interstitials along dislocations, by longitudinal core diffusion. Their conclusion is based mainly on two arguments: first, that a small peak was detected in a slightly deformed zirconium single crystal, so that grain-boundary relaxation is not involved and, second, that the peak can be qualitatively and quantitatively explained by the Winkler-Gniewek et al. [22] theory of stress-assisted thermally activated core redistribution of point defects.

It must be pointed out that Ritchie and Sprungmann observed generally only one maximum, above about 673 K, on the HTIF of zirconium, with location and shape strongly dependent on the thermomechanical treatment given to the specimens. Sometimes, a second maximum, also observed by Gacougnolle and associates [3,5,23], could be partially resolved from the HTIF spectrum.

The five internal friction peaks reported by Ritchie and Sprungmann were obtained by decomposing graphically the total damping and the analysis of the amplitude dependence of the HTIF, and consequently for the P_1/P_2 complex, has been performed on damping versus strain data measured by free decay, at various temperatures.

As discussed by Povolo [24], when the internal friction is amplitude-dependent the logarithmic decrement can give a severely distorted image of the real damping behavior of the material. Furthermore, it was shown that peak P_1 is not described quantitatively by the Winkler-Gniewek et al. theory, as admitted by Ritchie and Sprungmann. These seem to invalidate the interpretation of the HTIF of zirconium suggested by Ritchie and Sprungmann.

In summary, one can safely state that, besides the peaks due to interstitials or interstitial–substitutionals or interstitial–interstitial complexes, reported in Refs. [1–4] and [5–7], two main peaks seem to be present on the HTIF of zirconium: a peak due to thermally assisted unpinning of dislocations from oxygen atoms, reported for the first time by Fernandez and Povolo [13] and named P_0 by Ritchie and Sprungmann [12].

A second peak, i.e. P_1 of figs. 1, 5 and 6, occurs at higher temperatures, which is strongly dependent on the thermomechanical treatment given to the specimens and on composition. This peak seems to be amplitude-dependent and in pure zirconium the peak height and

location are not reproducible during successive measurements.

The activation enthalpy and particularly the relaxation time, for this peak, vary according to the different authors. The values reported in table 3 were obtained by a change in frequency of two orders of magnitude. This reduces the errors introduced in the determination of ΔH and τ_0, since only changes in the oscillation frequency lower than one order of magnitude were used previously in the literature. Furthermore, a plot of $\log f_p$ versus T_p^{-1} inluding the data of refs. [3] and [11] and those for peak P_1 shown in fig. 6, give a straight line. A least-squares fitting to the experimental points leads to

$$\Delta H = (270 \pm 30)\ \text{kJ mol}^{-1}, \qquad \tau_0 = 1.5 \times 10^{-(18 \pm 2)}\text{s} \tag{1}$$

with a correlation coefficient of 0.995. These values are of the order of those given in table 3, within experimental errors.

Eq. (1) gives the more reliable parameters for peak P_1 in annealed zirconium polycrystals. It must be pointed out, however, that these values should be taken with caution since the HTIF spectrum of zirconium is amplitude-dependent, as shown by the internal friction versus strain amplitude curves reported by Fernandez and Povolo [13] and Ritchie and Sprungmann [12]. We believe that peak P_1, generally attributed to grain-boundary relaxation, is produced by dislocation movements occurring at the grain or subgrain boundaries. This would explain the fact that the peak shape and location are strongly dependent on the morphology of the grains or subgrains, as reported by Mishra and Asundi [2], and that a small peak was detected in slightly deformed single crystals [12].

One interesting point is that the activation enthalpy given by eq. (1) is similar to the apparent activation enthalpy measured during creep experiments in zirconium and zirconium alloys [25–28], at temperatures above about 673 K. The creep behavior above this temperature seems to be controlled by mechanisms involving jog–drag, controlled by diffusion.

Several diffusion-controlled dislocation models [29–31] have been proposed in the literature to explain the internal friction peaks on the HTIF of metals and alloys. These models, however, cannot be used to make a quantitative analysis of peak P_1 until a systematic study, including the influence of the strain amplitude, the grain-boundary configuration, the impurity content, etc., on the HTIF of zirconium has been performed.

The internal friction versus strain amplitude curves for Zr and Zircaloy-4 reported by Fernandez and Povolo [13], for example, show an abrupt change for temperatures above about 673 K. This might be an indication of a transition from glide-controlled to diffusion-controlled dislocation movements.

As shown in fig. 6, two peaks have been observed, at least at low frequencies, on the HTIF of Zircaloy-4. According to table 3, the lowest-temperature peak, P_1', tends to give a higher activation enthalpy and a lower relaxation time than peak P_1 in the pure metal, even if the characteristics are similar, within experimental error. Furthermore, peak P_1' in the alloy is located at a higher temperature.

It was not possible to measure the characteristics of peak P_2', occurring at higher temperatures (fig. 6), due to the fact that this peak is masked by the high-temperature background at intermediate frequencies and it was only resolved at low frequencies. It might be possible also that this peak was not observed at intermediate frequencies due to a different condition of the specimen used (for example, the grain size). It must be pointed out that also different measuring techniques were used: free decay at low frequencies and constant amplitude at intermediate frequencies. A comparison should be made between peaks P_1' and P_2' obtained in Zircaloy-4, and the internal friction peaks reported by Mishra and Asundi [1,2] for several substitutional and interstitial solutes in zirconium. The main alloying elements present in Zircaloy-4 are Sn, Fe and Cr, table 2. Mishra and Asundi reported several peaks due to substitutional Sn or Fe and interstitial O or N complexes in Zr, as shown in table 4. The authors have not studied the influence of Cr but its atomic volume is similar to Fe, so that internal friction peaks located in the same positions as for Fe-interstitial complexes should be expected. A comparison of tables 3 and 4 shows that peak P_1'(T_p = 876 K, $f_p = 0.63\ \text{s}^{-1}$) could be assumed to be produced by Zr–Sn–O complexes (T_p = 900 K, $f_p < 1\text{s}^{-1}$).

The activation enthalpies and the peak heights are quite similar and the Zircaloy-4 used contains 1.1 at% Sn and 0.6 at% O. The problem is that the peak due to Zr–Sn–O complexes is a Debye type peak, as shown by the coincidence between the activation enthalpies measured through a change in frequency and from the peak width, table 4. Peak P_1', on the contrary, is much wider than a Debye peak, with a relaxation time much lower than what would be expected for atomic jumps.

We believe that P_1' is related to P_1 present in pure Zr and controlled by similar mechanisms. It is clear that without a precise knowledge of the process or processes controlling peak P_1 in the pure metal it is difficult to give firm conclusions about P_1'.

In general, one or two grain-boundary relaxation

Table 4
Internal friction peaks due to substitutional–interstitial complexes in zirconium, reported by Mishra and Asundi [6,7], for an initial oscillation frequency of 1.3 s^{-1}. (a) Activation enthalpy obtained from a change in the oscillation frequency and (b) from the peak width.

Complex	Concentration (at%)	T_p (K)	Q_p^{-1}	ΔH(kJ mol^{-1}) (a)	(b)
Zr–Sn–O	1(0)	900	4×10^{-3}	351	339
Zr–Sn–O–O–O	0.22(0)	918			
Zr–Sn–N	0.4(0)	688	4.4×10^{-3}	192	163
Zr–Sn–N–N–N	0.4(0)	815			259
Zr–Fe–O	0.032 and 0.8 (Fe)	623	2.7×10^{-3}	167	
Zr–Fe–O–O–O	0.032 and 0.8 (Fe)	698			192

All the Zn–Sn alloys contained 0.5 at% Sn and 0.09 at% N. The Zr–Fe alloys contained 0.3 at% 0.

peaks are observed in substitutional solid solutions, depending on the concentration of the second component [32]. In the base metal the normal grain-boundary peak, called PM, is observed; in the alloy a second peak, at higher temperatures, is present, which increases with concentration. This is named SS. As SS increases PM decreases, disappearing at high concentrations. Mosher and Raj [33], have observed three internal friction peaks in normal and oxidized Cu–Ge and Cu–Si alloys. One was the normal PM peak, the second one the SS peak and the third one, occurring at the higher temperature, was attributed to the influence of GeO_2 and SiO_2 particles at grain boundaries. All peaks were interpreted as due to grain-boundary sliding with elastic accomodation.

Following this line, P_1 might be thought as a PM peak, P_1' as a SS peak and P_2' as produced by some precipitate at the grain boundaries. Menoni et al. [34], have recently observed $Zr(Cr + Fe)_2$ intermetallic precipitates in Zircaloy-4.

The available information in zirconium and zirconium alloys is not enough to draw additional conclusions about P_1, P_1' and P_2' and further work is needed. Furthermore, the different models proposed for grain boundary peaks are still controversial [35] especially when the influence of the strain amplitude is considered [36].

Finally, some comments will be made on the high-temperature background found in the HTIF of zirconium and zirconium alloys. It is generally assumed that the high-temperature background can be described by [37]

$$Q^{-1} = (A/\omega) \exp(-\Delta H_v/kT) \quad (2)$$

or

$$Q^{-1} = (B/T) \exp(-\Delta H_v/kT) \quad (3)$$

or [38]

$$Q^{-1} = (K/\omega^n) \exp(-n\Delta H_v/kT) \quad (4)$$

where A, B, K and $n (0 \leqslant n \leqslant 1)$ are constants for a given specimen, ΔH_v is the activation enthalpy for self-diffusion and ω is the angular frequency of the vibrations. The dependence of the reciprocal frequency implied by eq. (2) is not observed in practice.

Eq. (4) has been used by Ritchie and Sprungmann [12] to determine n and ΔH_v from the high-temperature internal friction data in zirconium, given $n \simeq 0.3$ and $\Delta H_v = (308 \pm 39)$kJ mol^{-1}. Furthermore, they compared the n and ΔH_v obtained in different metals and alloys [39,40] to confirm that eq. (4) applied to the high-temperature background of Zr gives a reasonable value for ΔH_v. According to eq. (4), a plot of $\log(Q^{-1}\omega^n)$ versus T^{-1} should give a straight line of slope $n\Delta H_v/k = \Delta H/k$, where $\Delta H = n\Delta H_v$ is the apparent activation enthalpy. In fact, ω changes only slightly with T so that a plot of $\log Q^{-1}$ versus T^{-1} should give a straight line with the same slope.

We will not discuss in detail the validity of eq. (4) to determine ΔH_v from the experimental high-temperature background, since this will be done in another publication [41], but in zirconium and zirconium alloys it was found that the plots of $\log Q^{-1}$ versus T^{-1} were not linear. Similar results were obtained by plotting $\log(Q^{-1}T)$ versus T^{-1}, as suggested by eq. (3).

Figs. 7 and 8 show $\log Q^{-1}$ versus T^{-1} plots for zirconium and zirconium alloys. To avoid any influence

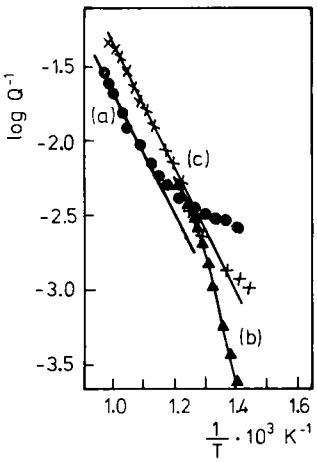

Fig. 7. High-temperature background for zirconium: (a) single crystal, (b) specimen with a bamboo structure, and (c) specimen with large grains. All data measured at low frequencies.

of additional peaks, only data taken either on single crystals or on specimens with large grain sizes, except for curves (a) and (b) of fig. 8, were used.

Curve (a) of fig. 7 was taken from fig. 13 of Ref. [12] and corresponds to a zirconium single crystal measured on cooling. It is clear that the plot is not linear and a straight line drawn through the data points at high temperatures gives $\Delta H = 79$ kJ mol^{-1}. Curve (b) of fig. 7 corresponds to a zirconium specimen with a bamboo structure and was taken from fig. 1 of Ref. [4]; again the log Q^{-1} versus T^{-1} plot is not linear. Considering the approximate linear behavior at low temperatures gives $\Delta H = 166$ kJ mol^{-1}. Curve (c) of fig. 7, for a zirconium specimen with large grains (> 245 μm), was taken from fig. 6 of Ref. [11]. The approximately linear plot gives $\Delta H = 79$ kJ mol^{-1}.

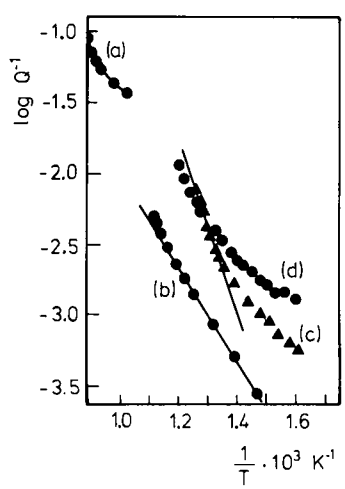

Fig. 8. High-temperature background for zirconium and some zirconium alloys: (a) Zr with 2.4 pct Hf at $f = 1$ s^{-1}, (b) Zircaloy-4 polycrystal at 5×10^4 s^{-1}, (c) Zr–0.18 wt% Cu with large grain sizes at $f = 2$ s^{-1} and (d) zirconium with bamboo structure at $f = 0.8$ s^{-1}.

Curve (a) of fig. 8, for a zirconium specimen containing Hf, was obtained from fig. 1 of Ref. [10]; the plot shows a strong curvature even if the data were obtained at temperatures well above the grain-boundary peak. Curve (b) of fig. 8, corresponding to a Zircaloy-4 specimen measured at a frequency of 5×10^4 s^{-1}, was obtained from fig. 3(a) of Ref. [13]. It is seen that the data points deviate from a straight line at high temperatures. A comparison between figs. 1 and 3(a) of Ref. [13] shows that the deviation from the linear behavior begins where the damping becomes strongly amplitude-dependent. These are the only data reported in the literature where the amplitude dependence of the damping is considered in detail. The straight line (b) of fig. 8 gives $\Delta H = 64$kJ mol^{-1}. Curve (c) of fig. 8 is for a Zr–0.18 wt%Cu alloy with large grains and was obtained from fig. 5 of Ref. [14]. The straight line drawn through the data points at high temperatures give $\Delta H = 130$ kJ mol^{-1}. Finally, curve (d) of fig. 8 is for a zirconium specimen with a bamboo structure and was taken from fig. 4 of Ref. [14]. The plot shows a strong curvature.

Thus, it can be stated that the log Q^{-1} versus T^{-1} plots for the high-temperature background of zirconium and zirconium alloys are generally not linear. In this condition any n or ΔH_v value obtained from the experimental data should be taken with caution, since n does not remain constant even in a small temperature region. A similar situation was encountered with the high-temperature background measured at two frequencies, reported by the Batist [40] in iron–chromium alloys.

Fig. 9 gives the approximate activation enthalpies versus grain size for the high-temperature background of Zr and Zircaloy-4 at various frequencies. The open circles give the values obtained from curves similar to those shown in fig. 3, for Zircaloy-4 at 0.9 s^{-1}. The open triangle is for Zircaloy-4 at 90 s^{-1} and the half-full circle for the same material but at 5×10^4 s^{-1}, i.e. the value obtained from curve (b) of fig. 8.

A smooth decrease of the apparent activation enthalpy with increasing grain size is observed in Zircaloy-4, independently of the oscillation frequency. The situation is completely different for zirconium and no correlation is found between the apparent activation enthalpy and the grain size.

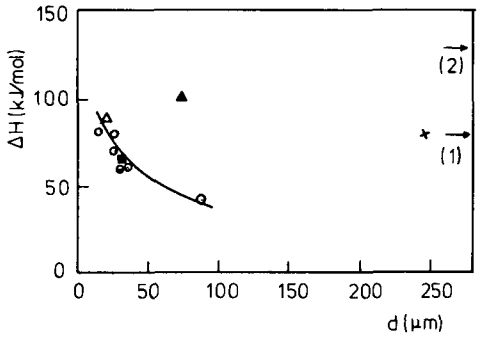

Fig. 9. Apparent activation enthalpies versus grain size for the high-temperature HTIF background of zirconium and Zircaloy-4.

thalpy and the grain size.

The full square of fig. 9 indicates the value obtained in Zr at 0.9 s^{-1} and the full triangle at 90 s^{-1}. The dot indicates the value obtained from curve (c) of fig. 7 and arrow (1) for a zirconium single crystal(curve (a) of fig. 7); arrow (2) represents the value for a Zr–Cu alloy with large grains (curve (c) of fig. 8).

4. Conclusions

The high-temperature damping spectrum of pure zirconium shows two internal friction peaks: one at low temperatures, probably related to thermally activated unpinning of dislocations from interstitial oxygen, and a second one, at higher temperatures, probably associated with diffusion-controlled movement of dislocations at grain boundaries or subgrain boundaries. Both peaks are strongly amplitude- and structure-dependent.

The high-temperature damping spectrum of Zircaloy-4 shows a peak similar to the grain-boundary peak observed in pure zirconium, but located at a higher temperature, and a second peak, probably related to precipitates at grain boundaries.

The high-temperature internal friction background, both of zirconium and Zircaloy-4, is strongly amplitude- and structure-dependent and, in general, does not increases exponentially with the reciprocal of the temperature.

Further studies of the high-temperature internal friction of zirconium and zirconium alloys, with controlled strain amplitudes and specimen structures, are needed.

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