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Strain Ageing in Zircaloy-4

Karp Soon Rheem and Won Koo Park

Korea Atomic Energy Research Institute, Seoul, Korea

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Abstract

The strain ageing behaviour of Zircaloy-4 has been studied in the temperature range 175°C to 575°C for both quenched and annealed specimens. The strain ageing in quenched Zircaloy-4 was found in the temperature range 175°C to 500°C and its peak occured at 325°C while the strain ageing in annealed specimens occured in the temperature range 175-575°C, showing two peaks, one at 325°C and a higher one at 450°C.

The peak at 325°C in both quenched and annealed specimens is considered to be due to the segregation of interstitial oxygen atoms to cell walls during ageing. The peak at 450°C in annealed specimens is considered to be due to the interaction of dislocations with Fe atoms.

It has been found that strain ageing stress at ~300°C in zirconium alloys is proportional to the square root of oxygen content.

요 약

질칼로이-4의 가공시효(strain ageing) 현상을 175—575°C의 온도구간에서 소입된 시편과 소둔된 시편에 대해 각각 조사하였다.

소입된 질칼로이-4의 가공시효가 175—500°C 구간에서 나타났으며, 325°C에서 극대값의 가공시효가 조사되었다. 반면 소둔된 시편의 경우엔 175—575°C 구간에 걸쳐 가공시효가 나타났으며, 이 온도구간 사이에 325°C 및 450°C의 두 지점에서 극대값이 나타나는 것을 확인했다.

소입된 경우와 소둔된 경우에 모두 325°C에서 보인 가공시효의 극대값은 시효동안에 전위조직 속으로 침입형 산소원자들의 응집에 의한 결과로 고려되며 450°C에서 보이는 극대값은 철원자와 전위간의 작용에 기인된 것으로 해석된다. 질코늄 합금의 300°C 근처에서 보이는 가공시효값은 첨가된 산소량의 평방근에 비례한다는 것이 확인됐다.

1. Introduction

Zirconium and its alloys exhibit strain ageing in the temperature range 150 to 500°C[1], and this is known to affect the creep behavior of the materials[2]. Strain ageing in annealed zirconium alloys shows two peaks, one at 300°C and one at 450°C. It was suggested[3] that the peak at 300°C is caused by segregation of interstials oxygen atom pairs to dislocation cell walls during ageing, thus stabilizing the dislocation structure. The peak at 450°C in Zircaloy-2 has not been identified but was suggested to be likely due, in part, to oxygen-dislocation locking and/or a contribution from other elements such as carbon[4] and iron[5]. Strain ageing in quenched Zircaioy-2 shows only one peak at 300°C. The suppression of strain ageing peak in quenched Zircaloy-4 at 450°C where annealed Zircaloy-2 shows a peak response was regarded to be due to trapping of Fe atoms by quenched-in defects.

This paper describes both quenched and annealed results of strain ageing tests for Zircaloy-4 which nearly doubles the contents of oxygen and iron of Zircaloy-2.

2. Meterials and specimens

The Zircaloy-4 was supplied by SANDVIK, Sweden, in the form of 1.5 cm diameter rods and the chemical analysis is shown in Table 1.

Tensile specimens with 3.175 mm diameter along the gage length of 25.40 mm were machined from the rods.

After machining, specimens were cleaned in acetone and then heat-treated in vacuum of 4×10^{-5} torr for one hour at 750°C. Following heat treatment, one group of specimens were quenched in water at 20°C and one group of specimens were furnace-cooled to room temperature. Before testing all the specimens were chemically polished in a solution of 45 parts HNO_3, 5 parts HF and 50 parts H_2O.

Table 1. Composition of Zircaloy-4.

Alloying element (wt %)			Impurity (ppm)			
Sn	Fe	Cr	O	N	H	C
1.37	0.22	0.09	1143	35	12	124

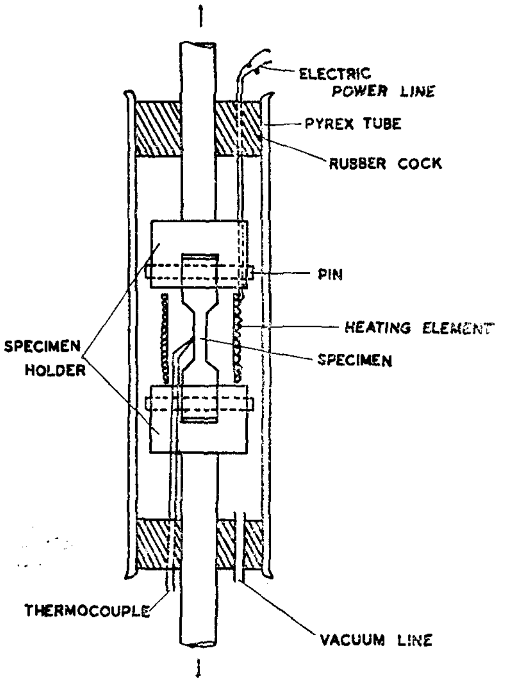

Fig. 1. Schematic drawing of specimen heating apparatus

3. Experimental details

Tests were carried out with the universal tester, Autograph IS-5000, Shimadgu, at a cross head speed of 2.5×10^{-3}cm/sec and a strain rate of 9.8×10^{-4} sec^{-1}.

For the elevated temperature tests the specimen were heated in vacuum capsule (Fig. 1) at a pressure of 10^{-4} torr. Temperatures were controlled to ±2°C over the gage length of the specimen.

Strain ageing tests were carried out in the temperature range 175 to 575°C for ageing times between 0 to 1000 sec at 4% strain.

Pre-straining, ageing and testing were done at the same temperature of a soak about half an hour before testing. The strain ageing parameter was taken as $\Delta\sigma$ at ageing time of 1000 sec in Fig. 2.

Thin foils for transmission electron microscopy were prepared from 0.5mm thick

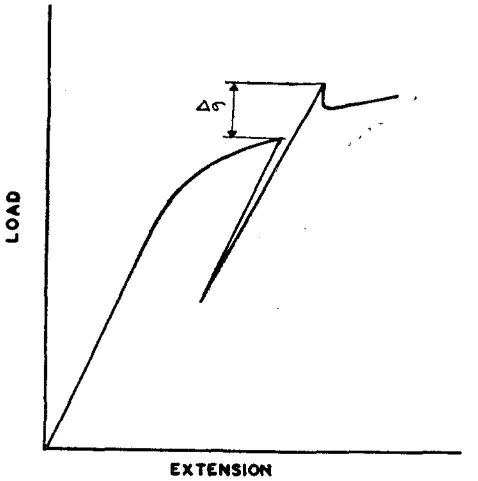

Fig. 2. Schematic drawing of load/extension curve showing strain ageing parameter

discs cut from the gage length of the tensile specimens. An electrolytic jet technique was used to achive a depression in both faces of the disc, which were thinned to perforation in a perchloric/alcohol electrolyte at −70°C. The thin foils were examined with the electron microscope, JEOL type, operating at 100 kV.

4. Results

Effect of temperature

The results of strain ageing tests in the range 175 to 575°C on quenched and annealed Zircaloy-4 are shown in Fig. 3 where other results on quenched and annealed Zircaloy-2 are shown as a reference. The value of $\Delta\sigma$ in quenched Zircaloy-4 increases rapidly with the ageing temperature to a maximum value in the range from 175 to 325°C. Above 325°C $\Delta\sigma$ decreases with increasing temperature from 325 to 500°C.

In comparison with Zircaloy-2, the quenched Zircaloy-4 shows higher strain ageing stress than quenched Zircaloy-2 and the ageing peak of quenched Zircaloy-4 is twice that of annealed Zircaloy-2 at the same temperature. In annealed Zircaloy-4 it also shows higher strain ageing stress and shows

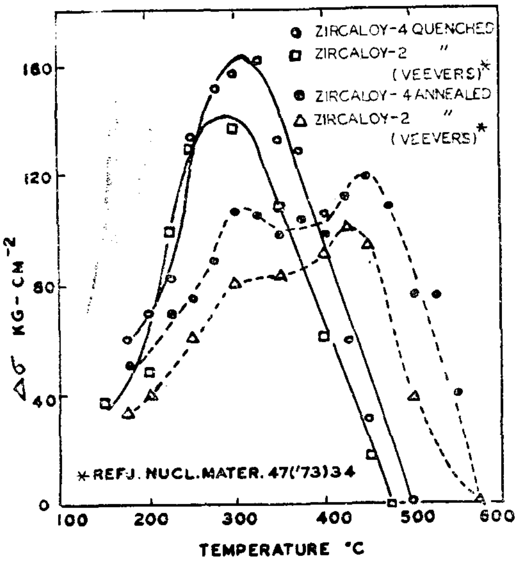

Fig. 3. $\Delta\sigma$ versus temperature for zircaloy-4 annealed at 750°C and quenched from 750°C compared with zircaloy-2 curves

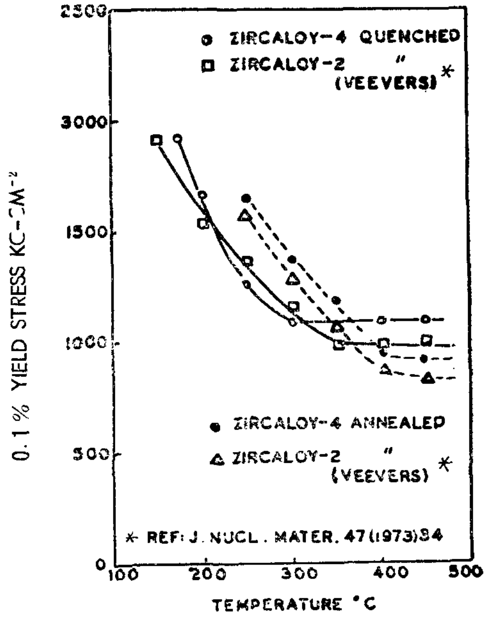

Fig. 4. 0.1% yield stress versus temperature for zircaloy-4 quenched from 750°C

apparent two peaks one at 325°C and one at 450°C while the value of $\Delta\sigma$ in annealed Zircaloy-2 shows a plateau between 300 and 350°C and then one peak at 425°C.

The temperature dependence of the 0.1% yield stress for Zircaloy-4 in Fig. 4 shows similar athermal region between 400 and 450°C as in Zircaloy-2.

Effect of ageing time

Strain ageing response on specimens aged for times between 0 and 1000 sec at 325°C shows that $\Delta\sigma$ in quenched materials increases very sharply with ageing times from 0 to 50 sec, after 50 sec it is approximately constant.

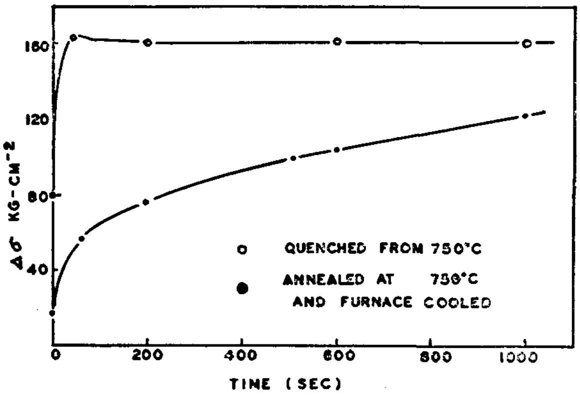

Fig. 5. $\Delta\sigma$ versus ageing time for Zircaloy-4 tested at 325°C

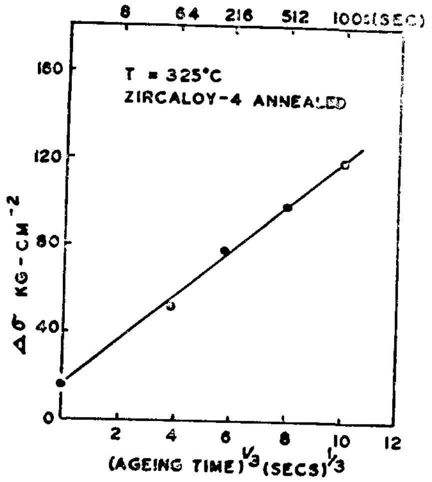

Fig. 6. $\Delta\sigma$ at 325°C versus (ageing time)$^{1/3}$ showing the linear relation during the initial stages of ageing

$\Delta\sigma$ in annealed specimens increases slow with time and shows no evidence of saturation (Fig. 5)

The other observation is that the initial stage of ageing follows a (time)$^{1/3}$ relationship rather than the (time)$^{2/3}$ relationship proposed by Cottrell and Bilby (Fig. 8). Similar behaviour has been observed during strain ageing of Fe-C alloys[6].

Electron microscopy

Transmission electron-microscopy observations were made on thin foils prepared from both annealed and quenched Zircaloy-4, which had been deformed to 4% strain and aged for 1000 sec at 325 and 450°C. Well-defined cell structures were revealed out in annealed specimens tested at both 325 and 450°C as shown in Fig. 7-a and c. At 325°C in quenched Zircaloy-4, the cell boundaries were composed of tangled dislocations and sets of straight dislocation segments could be seen in the cell structure, Fig 7-b. At 450°C in quenched materials, where no strain ageing was found, the cell structure was replaced by random networks of dislocations, Fig. 7-d.

5. Discussion

The observed results on the strain ageing behavior of Zircaloy-4 shows strong temperature dependence. Specimens which were deformed, aged and tested at below 175 and above 500°C did not show any strain ageing response, while specimens deformed, aged and tested in the range 175 to 500°C exihibited strain-ageing. The explanation obviously lies in the difference in dislocation structure produced at the temperatures. In the tem-

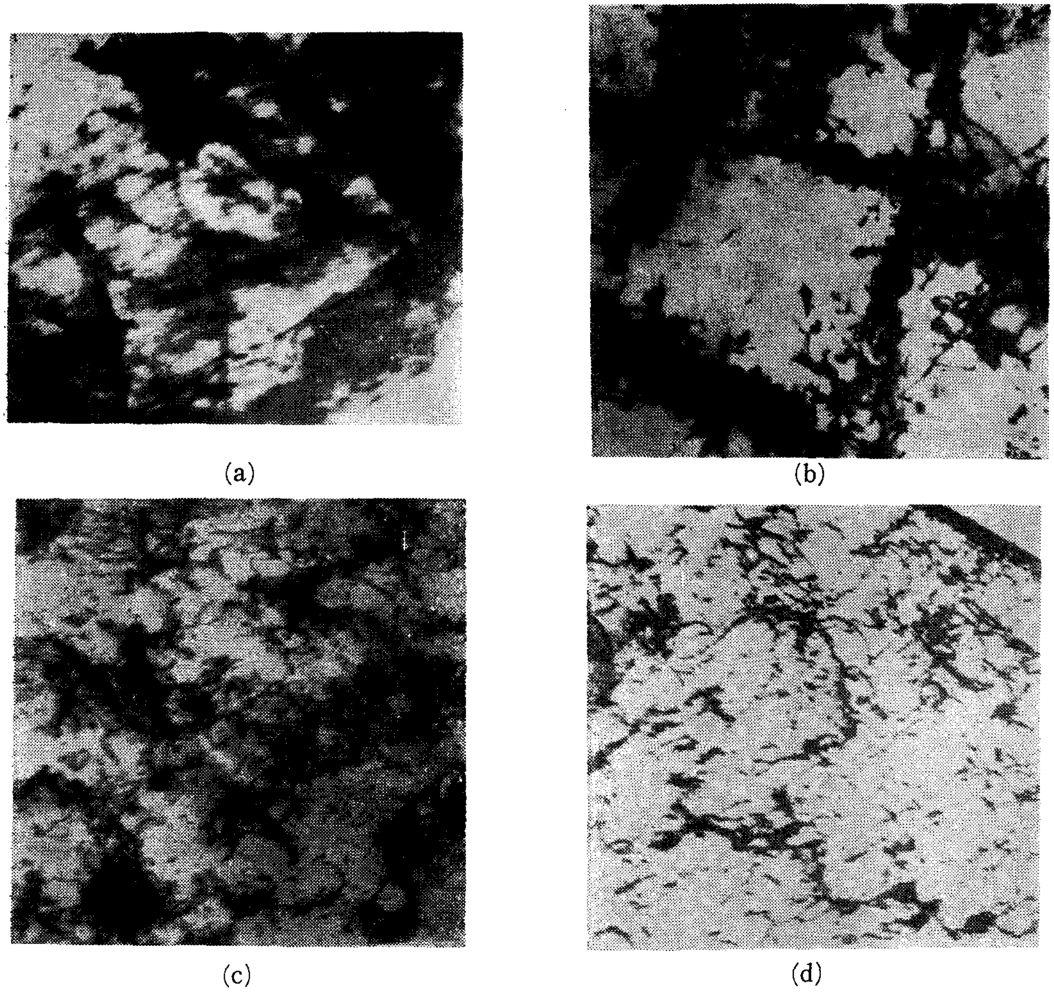
(a) (b) (c) (d)

Fig. 7. Electron micrographs of Zircaloy-4: (×26000)

a) annealed at 750°C and strain aged at 325°C
b) quenched from 750°C and strain aged at 325°C
c) annealed at 750°C and strain aged at 450°C
d) quenched from 750°C and strain aged at 450°C

perature range of absence of strain ageing response the dislocation substructure is regular and uniform, while between 175 and 500°C a dense cell structure is developed. One interesting feature is the presence of twin ageing peaks in annealed Zircaloy-4 whose magnitude is higher than that of Zircaloy-2.

Veevers and Rotsey³⁾ suggested that in anneled Zircaloy-2 one peak at 325°C is due to oxygen and one peak at 450°C is due to something other than oxygen such as Fe, Cr and Ni.

There are some evidence that in the present study the strain ageing at 325°C in annealed Zircaloy-4 is also caused by oxgen.

This evidence is on the basis of the approach to the theoretical analysis of the relationship between strength and interstitial content. Kelly and Smith⁴⁾ and Veevers et al proposed that the strength of Zr-O alloy and Zircaloy-2 are proportional to the interstitial content. In the present study, however, the authors propose that the strain ageing stress at~300°C is proportional to the square root of interstitial oxygen content instead of linear value of interstitial oxygen content. Then the equation of strain ageing stress may be written as follow:

$$\Delta\sigma = \mathrm{Kem} \cdot C^{\frac{1}{2}} \qquad (1)$$

where $\Delta\sigma$= strain ageing stress difference between the yield stress after ageing and the flow stress before ageing, (kg/mm^2) (at strain ageing peak)

Kem= proportional constant, empirical value of K (kg/mm^2)

C= interstitial oxygen content (ppm)

Above Eq. (1) is reasonably supported by a graph (Fig. 8) plotted with some other experimental data[1, 4, 5] and present data. As shown in Fig. 8, the strain ageing stress $\Delta\sigma$ varies linearly with the square root of oxygen content, $C^{\frac{1}{2}}$.

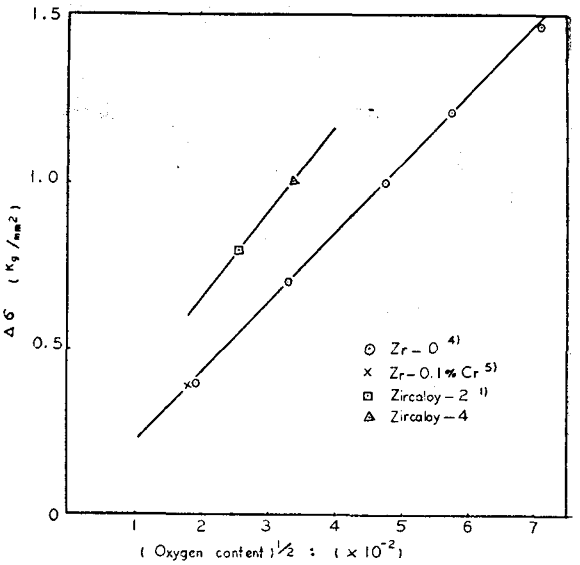

Fig. 8. Relation between strain ageing stress $\Delta\sigma$ and square root of oxygen content, $C^{\frac{1}{2}}$

From the graph, we find two kinds of proportional constants; one Kem=21.176 for Zr-O and Zr-0.1% Cr and another Kem=31.092 (kg/mm^2) for Zircaloy-2 & -4. Then we can get calculated $\Delta\sigma$ in Eq. (1) by using the above Kem values.

The comparison of calculated $\Delta\sigma$ with measured $\Delta\sigma$ is shown in Table 2.

It is interesting that there are only two kinds of Kem for all the zirconium alloys; the binary alloys such as Zr-O and Zr-Cr have one common value of Kem and the quaternary alloys such as Zircaloy-4 and -2 have another common value of Kem regardless of the amounts of oxygen concentration.

Then we shall discuss the reason why the Kem values have such specific values. One

Table 2. Comparison of calculated $\Delta\sigma$ with measured $\Delta\sigma$ in annealed Zirconium alloys (test temperature: 300°C±25)

Specimen (annealed)	Oxygen content: C (ppm)	$C^{1/2}$ (×10^{-2})	Kem (kg/mm^2)	$\Delta\sigma$(kg/mm^2)		Test Temp. (°C)
				Calculated	Measured	
Zircaloy—4	1,143	3.3808	31.092	1.051	1.050	325
Zircaloy—2[1]	660	2.5690	〃	0.798	0.790	300
Zr—O alloys[4]	350	1.8708	21.176	0.396	0.390	300
	1,100	3.3166	〃	0.702	0.700	275
	1,890	4.3470	〃	0.920	0.990	275
	2,230	4.7222	〃	1.000	1.000	300
	3,300	5.7445	〃	1.216	1.210	300
	5,000	7.0710	〃	1.497	1.460	325
Zr+0.1% Cr[5]	330	1.8165	〃	0.384	0.380	300

of the established theories of hardening by interstitials is due to Fleischer[7].

This theory is based on the fact that the interstitials produce an asymmetric or tetragonal distortion in the metal lattice. The stress required to move a dislocation is given by the relationship

$$t=F^{max}/bl \qquad (2)$$

where F^{max} is the maximum retarding force per defect, b is Burgers vector and l is the spacing of defects on the slip plane. For atomic size defects l is given by

$$l=b/(2fC)^{\frac{1}{2}} \qquad (3)$$

where C is the interstitial concentration of defects and f is the fraction of the total defects that have an interaction with a dislocation.

The maximum force, F^{max} for defects adjacent to the slip plane is found by Fleischer to be

$$F^{max}=G\Delta\epsilon b^2/\alpha \qquad (4)$$

where G is the shear modulus, $\Delta\epsilon$ is a measure of tetragonality and α is a factor related with geometry between defects and dislocation. The combination of Eqs. (2), (3) and (4) gives

$$t=G\Delta\epsilon(2fC)^{\frac{1}{2}}/\alpha \qquad (5)$$

If t, the stress required just to move the dislocation against the friction due to defects, is assumed to be proportional to the flow stress, we can write:

$$d\Delta\tau/dC^{\frac{1}{2}}\sim G\Delta\epsilon/\alpha \qquad (6)$$

where $\Delta\tau$ is maximum flow stress-increase due to maximum retarding force of dislocation interacting with point defects. Nadeau[8] showed that flow stress-increase by irradiation in LiF is attributed to the tetragonal hardening produced by interstitial defect.

Now, we can apply with Eq. (6) to the present strain ageing study of zirconium alloy. Then the Eq. (6) will be given by

$$d\Delta\tau/dC^{\frac{1}{2}}=\frac{G\cdot\Delta\epsilon}{\alpha/(2f)^{\frac{1}{2}}} \qquad (7)$$

It is believed that there is no interaction between octahedral solutes and $\langle\bar{1}120\rangle$ $\{1\bar{1}00\}$ screw dislocation in α-zirconium of the H. C. P lattice.

Then, Eq. (7) will be changed in term from shear stress with screw dislocations to normal stress with edge dislocations.

Rearrangement of Eq. (7) gives the form of Eq. (1) in term of normal stress as follow:

Table 3. Comparison of calculated K with measured K in annealed zirconium alloys (tested at~300°C)

Specimen (annealed)	$G(10^3\text{kg/mm}^2)$ at 300°C	f	$\alpha/(2f)^{1/2}$	$K(\text{kg/mm}^2)$	
				Calculated	Measured
Zr—O	2.8453	1/2	9.784	21.419	21.176
Zircalloy—2	2.9555	1	6.920	31.442	31.092
Zircalloy—4	2.9199	1	6.920	31.064	31.092

Table 4. Comparison of calculated Kth with measured Kth in quenched Zircaloys (tested at~300°C)

Specimen (quenched)	$G(10^3\text{kg/mm}^2)$ at 300°C	f	$\alpha/(3f)^{1/2}(b/d)^{1/2}$	$K(\text{kg/mm}^2)$	
				Calculated	Measured
Zircaloy—2	2.9555	1	5.260	49.983	47.50
Zircaloy—4	2.9199	1	5.260	49.379	48.00

$$\varDelta\sigma=\frac{2G\cdot\varDelta\epsilon}{(1-\nu)\alpha/(2f)^{\frac{1}{2}}}\cdot C^{\frac{1}{2}} \qquad (8)$$

$$=\mathrm{K}_{th}\cdot C^{\frac{1}{2}}$$

where the theoretial value $\mathrm{K}_{th}=\frac{2G\cdot\varDelta\epsilon}{(1-\nu)\alpha/(2f)}$, $\varDelta\sigma=2\varDelta\tau$, ν is Poison's ratio and $(1-\nu)$ is related to conversion from screw dislocation to edge dislocation. Hence the theoretial value of K is computed as the values in Table 3 when each term of Eq. (8) is taken as; $\alpha=9.784^{7)}$, $\varDelta\epsilon=0.024^{10)}$, $\nu=0.348$ and $G=2.8450$, 2.9555 and 2.9119 $(\times 10^3 \mathrm{kg/mm^2})$ for Zr-O, Zircaloy-2 and Zircaloy-4, respectively[11, 12] and $l=b/(C)^{1/2}$ and $b/(2C)^{1/2}$ for Zr-O and Zircaloys[13].

In analysis of data of quenched Zircaloys, it is believed that the effect of quenched in defects on the asymmetrical lattice distortion and defect spacing must be accounted for the enhancement of strain ageing. Now Eq. (8) is modified as;

$$\varDelta\sigma=\frac{2G\cdot\varDelta\epsilon}{(1-\nu)\alpha/(3f)^{\frac{1}{2}}\left(\frac{b}{d}\right)^{\frac{1}{2}}}\cdot C^{\frac{1}{2}} \qquad (9)$$

where $(3f)$ comes from $l=b/(3fC)^{1/2}$ and $\left(\frac{b}{d}\right)$ is the ratio of diameter of vacancy loops and slip distance. The theoretical K_{th} in quenched specimen is calculated as values in Table 4 when each term of Eq. (9) is taken as; $\left(\frac{b}{d}\right)=\left(\frac{2}{\sqrt{3}}\right)^{14)}$, $\varDelta\epsilon=0.029^{10)}$, and other values are taken as same values in annealed specimen.

As shown in above tables, the calculated values from the proposed theoretical equations show an excellent agreement with the measured values of $\varDelta\sigma$ and K's in various experimental data.

Therefore, on the basis of both empirical and theoretical proof, it can be concluded that strain ageing stress~300°C is proportional to the square root of interstitial oxygen concentration instead of linear value of interstitial concentration.

It is believed that the segregation of oxygen to cell walls makes glide dislocation pinned, thus stabilizing the dislocation structure.

As far as the strain ageing at 450°C is concerned, Veevers and Snowden suggested that the peak at 450°C in annealed Zircaloy-2 is attributed to Fe. Recently Veevers has shown that Fe is responsible for the presence of peak at 450°C in the strain ageing tests on zirconium alloyed separately with Sn, Fe, Ni and Cr, the alloying element in Zircaloy-2. In his experiment, only Zr-Fe alloy showed a peak in strain ageing at 450°C whereas Zr-Sn, and Zr-Ni have a peak in the range 275 to 325°C. Zr-Fe also showed a well-defined cell structure in transmission electron microscope observation.

Strain ageing test at 450°C on Zircaloy-4 shows identical behaviour as observed in Zircaloy-2, i.e., strain ageing peak occured at 450°C and well-defined cell structure were observed in transmission electron microscopy. These results may imply that the strain ageing peak at 450°C in annealed Zircaloy-4 is also attributed to Fe atoms as suggested by Veevers. As has been known, the behaviour of the Fe atoms at 450°C becomes active to interact with dislocation, but its interaction mechanism has not been identified yet.

In quenched Zircaloy-4, the increased amount of $\varDelta\sigma$ at 325°C can be explained by the increase of the Snoek type interaction between glide dislocation and the increased amounts of oxygen atoms frozen in during quenching. The explanation for the suppression of $\varDelta\sigma$ in quenched Zircaloy-4 at 450°C implies that rapid recovery in quenched structure above 325°C will lead to a large reduction in dislocation density so that the cell walls will no longer provide effective barriers to deformation even in the presence of oxygen and so $\Delta\sigma$ will reduce and disappear. This agrees with the exhibition of uniform and regular distribution of dislocation.

The suppression of $\Delta\sigma$ at 450°C can be explained in another way that Fe atoms are no longer available to interact with dislocations since Fe atoms are considered to be trapped at quenched-in defects such as vacancy clusters, so that the residual concentration of Fe atoms is insufficient to cause significant interaction with glide dislocations.

6. Conclusion

(1) Strain ageing in quenched Zircaloy-4 was found in the temperature range 175 to 500°C and its peak occured at 325°C while the strain ageing in annealed Zircaloy-4 occured in the temperature range 175-575°C, showing two peaks, one at 325°C and one at 450°C.

(2) The peaks at 325°C in both quenched and annealed specimens are related to oxygen atoms. The peak at 450°C in annealed specimen is considered to be due to a contribution from Fe atoms.

(3) The strain ageing response follows a $(\text{time})^{1/3}$ rather than a $(\text{time})^{2/3}$ relationship.

(4) Strain ageing response at ~300°C is proportional to the square root of oxygen concentration rather than linear value of oxygen concentration.

Acknowledgements

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