

《Original》

## The Effect of Ageing Time and Temperature on the Strain Ageing Behaviour of Quenched Zircaloy-4

Karp Soon Rheem and Won Koo Park

Korea Nuclear Fuel Development Institute

Chong Chul Yook

Department of Nuclear Engineering, Hanyang University

(Received August 7, 1977)

### Abstract

The strain ageing behaviour of quenched Zircaloy-4 has been studied as a function of ageing time and temperature in the temperature range 523 to 588 K for a short-ageing time of 1 to 52 seconds. At the test conditions, the strain ageing stress increased with ageing time and temperature at a strain rate of  $5.55 \times 10^{-4} \text{ sec}^{-1}$ . Applying stress on the quenched Zircaloy-4, the strain ageing effect indicated following two stages: an initial stage having an activation energy of 0.39 eV considered to be due to Snoek type ordering of interstitial oxygen atoms in the stress field of a dislocation and a second stage having an activation energy of 0.60 eV, due to mainly long-range diffusion of oxygen atoms.

### 요 약

소입된 질칼로이-4의 가공시효(strain ageing) 현상에 미치는 시효시간 및 온도의 효과를 523-588 K 온도 구간에서 1~52초의 짧은 시효시간에 조사하였다. 이 실험 조건하에서, 가공시효응력은  $5.55 \times 10^{-4} \text{ sec}^{-1}$ 의 신연속도(strain rate) 경우 시효시간 및 시효온도가 증가할수록 증가하였다. 소입된 질칼로이-4의 응력부하 하의 가공시효 현상이 두 단계로 나타나는 것이 확인되었는데 첫단계는 0.39eV의 활성화 에너지값의 구간으로 이는 전위(dislocation) 주위의 응력상태로 인한 침입형 산소원자들의 Snoek타입의 배열(ordering)로 인한 것으로 고려되었으며 두번째 단계는 0.6eV 활성화에너지 값을 갖는 구간으로 이는 주로 산소원자들의 장범위확산에 기인하는 것으로 해석되었다.

### 1. Introduction

Strain ageing phenomena in  $\alpha$ -zirconium

and its alloys have been the subject of a number of investigations<sup>1-9)</sup>. Particularly, over the temperature 473-700K, anomalous creep and mechanical behaviour in Zr and

its alloys have been attributed to some form of strain ageing produced by dislocation-interstitial interaction<sup>10-12)</sup> such as oxygen atoms. A study of this interaction in zirconium alloys is very important since these alloys are widely used in nuclear reactors.

However, only few experiments have been performed to study the interaction mechanism of dislocation and interstitial with relation to the time-dependent strain ageing behaviour in zirconium alloys and little is known about the dislocation-interstitial interaction in the early stage of strain ageing in zirconium and its alloys.

De Paula E Silva et al<sup>2)</sup> proposed that strain ageing effect in zirconium is due to the diffusion of interstitial oxygen atoms by one jump length in the c-direction and suggested Snoek type stress ordering of atoms in the strain fields of dislocations.

Veevers and Snowden<sup>3)</sup> suggested that the rapid increased amount of strain ageing after ~40 sec in Quenched Zircaloy-2 at 300°C is due to a Snoek type ordering of interstitial (i-i) atom pairs and or interstitial-substitutional (i-s) atom pairs.

Rosinger and Craig<sup>13)</sup> found that such a Snoek type ordering phenomena in the strain ageing test of quenched Ferrovac E iron is observed in the early stage of strain ageing with a relationship of (ageing time)<sup>2/3</sup> as proposed by Cottrell and Bilby<sup>14)</sup>. However, Veevers and Rotsey<sup>5)</sup> found that strain ageing behaviour of annealed Zircaloy-2 in ageing time range 50 to 2×10<sup>3</sup> sec does not follow the classical (ageing time)<sup>2/3</sup>. Kelly and Smith<sup>7)</sup> and Rheem and Park<sup>8)</sup> also observed in annealed Zr-O alloy and annealed Zircaloy-4, respectively, that strain ageing behaviour follows a (ageing time)<sup>1/3</sup> relationship in ageing time up to 1000sec.

Unfortunately, in above experiments, strain ageing behaviour in early stage of ageing less than 50 sec was not checked in detail since the strain-ageing response is not distinct in annealed zirconium especially within 50 sec of ageing time.

Evidence in literature<sup>15-16)</sup> indicates that quenching of specimens retains interstitials in solution with the result that bigger yield points are usually observed on strain ageing, which may help the observation of early stage of strain ageing to study the dislocation-interstitial interaction with relation to Snoek type ordering in zirconium alloys.

The strain ageing behaviour in quenched Zircaloy-4 was studied in the present investigation as a function of ageing time and temperature in an attempt to clarify the mechanism.

## 2. Materials and Specimens

The Zircaloy-4 was supplied by SANDVIK, Sweden in tubing of usual PWR size, 10.7 mm in outer diameter, 0.65mm wall thickness and the chemical analysis is shown in Table 1, in which the oxygen content is 1143 ppm by weight. The as-received material in tube was cold-rolled into sheet of 0.62mm thickness at room temperature. After cold rolling, sheets were machined to the size of 2.5mm width along the gage length of 45mm of tensile specimens. After machining specimens were cleaned in acetone and then heat-treated in vacuum of 4×10<sup>-5</sup> torr

Table 1. Composition of Zircaloy-4

Alloying element (wt%)		Main impurity (ppm)				
Sn	Fe	Cr	O	N	H	C
1.37	0.22	0.09	1143	36	12	124

for one hour at 800°C. Following heat-treatment, specimens were quenched in water at 23°C. Before testing all the specimens were chemically polished in a solution of 45 parts HNO<sub>3</sub>, 5 parts HF and 50 parts H<sub>2</sub>O.

### 3. Experimental procedure

The testing procedures were similar to those employed in the previous experiment<sup>9</sup>. The nominal strain rate used was  $5.55 \times 10^{-4}$  sec<sup>-1</sup>.

Interrupted tensile tests were carried out in the temperature range 523 to 588K for ageing times between 1 to 52 sec. Testing consisted of pre-straining the specimen to constant strain of 4%, stopping the cross-head down, ageing for a desired ageing times and restraining the specimen.

The ageing temperature and ageing stress were kept constant while the cross head was stopped. The strain ageing stress  $\Delta\sigma$  and the fractional increase in flow stress  $\Delta\sigma/\bar{\sigma}$  were taken as the strain ageing parameters, where  $\Delta\sigma$  is difference between yield

stress ( $\sigma_y$ ) after ageing and flow stress ( $\sigma_f$ ) before ageing, and  $\bar{\sigma}$  is an average of the sum of two stresses,  $\sigma_y$  &  $\sigma_f$  obtained after and before ageing. The permanent hardening, was also checked in long-time ageing curves.

### 4. Result

Fig.1 shows a typical strain ageing curve of interrupted tensile test. Pre-strain, ageing and restrain yield the ageing stress  $\Delta\sigma$ , the difference between yield stress( $\sigma_y$ ) after ageing for time  $t$  and the flow stress ( $\sigma_f$ ) before ageing and fractional increase in flow stress,  $\Delta\sigma/\bar{\sigma}$  (where  $\bar{\sigma} = (\sigma_y + \sigma_f)/2$ ). There are two-types of strain ageing curves: for short time ageing test, the stress level after ageing ( $\sigma_a$ ) was almost same as the flow stress before ageing ( $\sigma_f$ ). For longer ageing times, permanent hardening,  $\Delta H$ , difference between two stresses ( $\sigma_a'$  &  $\sigma_a$ ) was found.

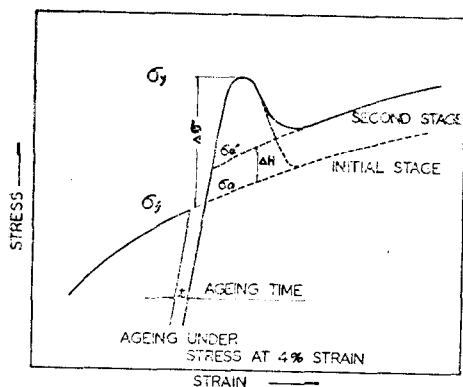


Fig. 1. Schematic Diagram Showing The Way the Parameters  $\Delta\sigma$ ,  $\sigma_f$ ,  $\sigma_y$ ,  $\sigma_a$  &  $\Delta H$  Were Measured on the Stress Strain Curves With Initial Stage and Second Stage of Ageing Curves.

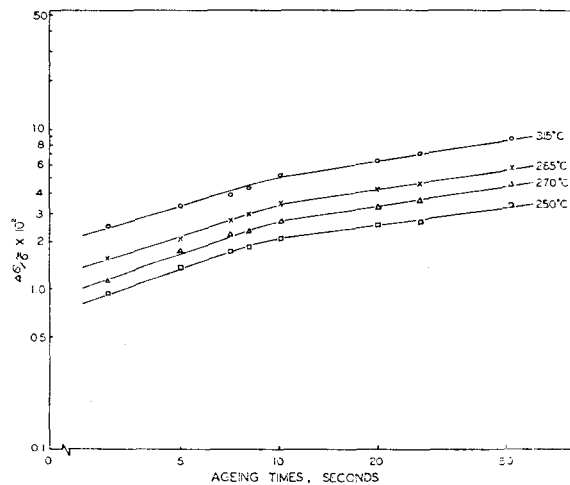


Fig. 2. Log  $\Delta\sigma/\bar{\sigma}$  VS. Log ageing Time

Fig.2 shows a plot of  $\log \Delta\sigma/\bar{\sigma}$  vs.  $\log t$  with test temperature, where  $\Delta\sigma/\bar{\sigma}$  increases with both ageing time and temperature.

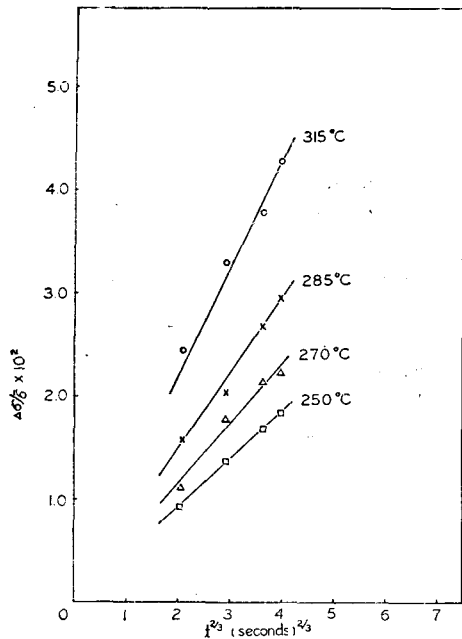


Fig. 3. Strain Ageing Parameter VS.  $t^{2/3}$  For Initial Ageing Stage.

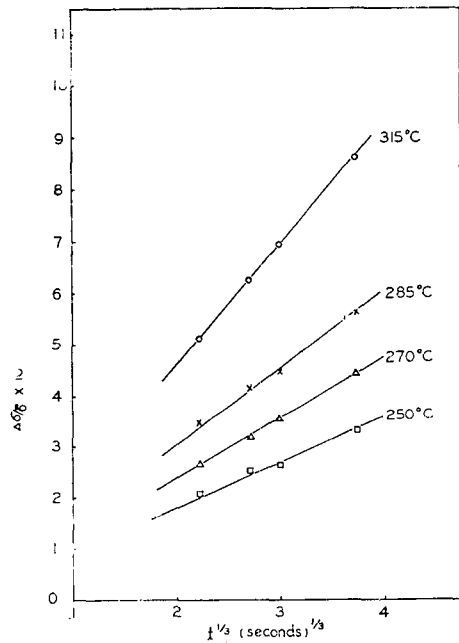


Fig. 4. Strain Ageing Parameter VS.  $t^{1/3}$  For Second Ageing Stage.

The graph also shows two kinds of slope in every curves: one slope for short-time ageing region, another for longer time ageing.

Fig. 3 and 4 show the plot of  $\Delta\sigma/\bar{\sigma}$  vs. short and long ageing times, respectively, where the time exponent is approximately two thirds for short ageing times (initial stage of ageing) and one third for long ageing times (second stage of ageing). In two graphs,  $\Delta\sigma/\bar{\sigma}$  becomes a linear function of the ageing-time exponent.

## 5. Discussion

Veevers and Snowden<sup>3)</sup> found that maximum strain ageing in quenched Zircaloy-2 occurred after  $\sim 40$  sec during which time an oxygen atom would diffuse about one lattice spacing and suggested that the Snoek effect is in accord with the rapid increase in strain ageing with ageing time since it does not depend on bulk diffusion. As the case of Veevers and Snowden, the initial stage of strain ageing in present quenched Zircaloy-4 occurred too quickly to take place long-range diffusion of interstitials. At the test temperature a distinct  $\Delta\sigma$  is observed after only 3 seconds. To explain this rapid strain ageing effect, the rapid Snoek type ordering is postulated for the initial stage of strain ageing under stress since the locking due to Snoek ordering is accomplished merely by atomic arrangement between interstitial atoms and neighbouring lattice sites<sup>17)</sup> in the stress field of dislocation. Besides rapid strain ageing response, another evidence of Snoek type ordering is shown in the initial stage of ageing with a phenomena that there is no difference in stress in stress between  $\sigma_f$  of before-ageing and

$\sigma_a$  of after-ageing. It is known<sup>18)</sup> that if Snoek ordering occurs, the after-ageing stress  $\sigma_a$  is almost at the same stress level of the before-ageing stress  $\sigma_f$ . However, a little difference between  $\sigma_a'$  and  $\sigma_f$  is found in the second stage of ageing probably resulting from the formation of Cottrell atmosphere or precipitates which may cause a permanent hardening.

Finally we can estimate the activation energy for strain ageing from the relationship between ageing time and temperature using Hartley's modification<sup>19)</sup> of Cottrell-Bilby's  $t^{2/3}$  relationship. The equation of Hartley's modification is as follows:

$$\frac{\Delta\sigma}{\sigma} = K_1 + K_2 \left[ \frac{t}{T} \right]^{2/3}$$

where  $K_1$  and  $K_2$  are constants for test condition,  $t$  is the ageing time and  $T$  is the ageing temperature. Hartley also showed that the constant  $K_2$  is proportional to  $D^{2/3}$  where  $D (= D_0 \exp(-Q/RT))$  is the diffusion coefficient of the pinning element. Thus for the initial stage of ageing under stress the slope ( $S_1$ ) of  $\Delta\sigma/\sigma$  vs.  $t^{2/3}$  plot in Fig. 3 is expressed:

$$\text{Slope } (S_1) = \frac{K}{T^{2/3}} D^{2/3}$$

$$\text{or } \log(S_1 T^{2/3}) = \log K + 2/3 \log D_0$$

$$-2/3 \left[ \frac{Q}{2.303RT} \right]$$

The slope of  $\log(S_1 T^{2/3})$  vs.  $1/T$  plot in Fig. 5 gives an activation energy of 0.39 ev for the initial stage of strain ageing.

In the second stage of strain ageing, the  $\Delta\sigma/\sigma$  is proportional to  $t^{1/3}$  in Fig. 4. This  $t^{1/3}$  relationship agrees with the observations of Veevers and Rotsey<sup>5)</sup> in annealed Zircaloy-2, Kelly and Smith<sup>7)</sup> in annealed Zr-O and Rheem and Park<sup>8)</sup> in annealed Zircaloy-4.

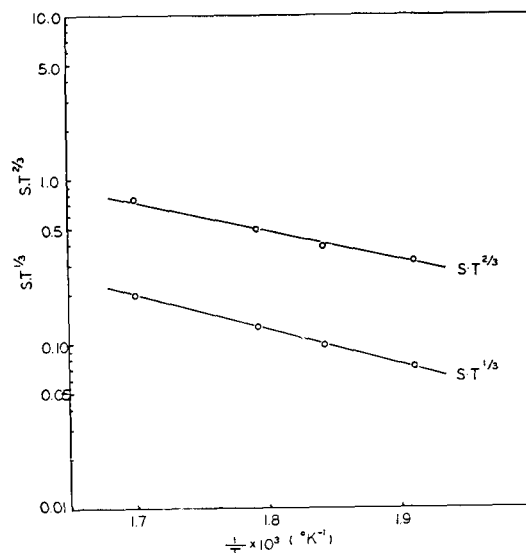


Fig. 5. Determination of Activation Energy For Diffusion of Pinning From Strain Ageing Measurement.

With postulation that constant  $K_4$  is proportional to  $D^{1/3}$ , the  $\Delta\sigma/\sigma$  can be related to  $t^{1/3}$

$$\frac{\Delta\sigma}{\sigma} = K_3 + K_4 \left[ \frac{t}{T} \right]^{1/3}$$

where  $K_3$  and  $K_4$  are constant for test conditions.

The slope ( $S_2$ ) of the  $\Delta\sigma/\sigma$  vs.  $t^{1/3}$  plot in Fig. 4 is expressed:

$$\text{Slope } (S_2) = \frac{K^1}{T^{1/3}} D^{1/3}$$

$$\text{or } \log(S_2 T^{1/3}) = \log K^1 + 1/3 \log D_0$$

$$-1/3 \left[ \frac{Q}{2.303RT} \right]$$

Finally, the slope of  $\log(S_2 T^{1/3})$  vs.  $1/T$  plot in Fig. 5 gives an activation energy of 0.60 ev for the second stage of strain ageing.

As the results, a low value of activation energy, 0.39 ev was determined for the initial stage of ageing and a high value of 0.60 ev was determined for the second stage

of strain ageing.

The reason that the low activation energy for initial stage of strain ageing could be attributed to the Snoek type ordering of oxygen on the basis of that the Snoek type pinning is relatively weak compared with Cottrell type pinning.

Rosinger and Craig<sup>13)</sup> also found that the activation energy for Snoek ordering in quenched Ferrovac E iron was much lower than that for long-range diffusion; 0.287 eV for Snoek ordering and 0.76 eV for Cottrell type pinning. Kamber et al<sup>20)</sup> also found this trend in annealed and cold-worked iron.

Atrens<sup>21)</sup> obtained a binding energy of 0.2 eV for pinning of oxygen atoms to dislocation in a damping test of annealed Zr-O alloys between 300 and 700°K and described that the value of binding energy varies 0.14 to 0.5 eV depending upon the dislocation cell structure.

The activation energy of 0.39 eV for initial stage of strain ageing in Zircaloy-4 is within the order of the binding energy for pinning of oxygen interstitials to dislocations. The 0.39 eV for initial stage of strain ageing is close to the value of 0.37 eV obtained by Hammard et al<sup>22)</sup> from a slope of  $\log \Delta\sigma$  vs.  $1/Tq$  plot in quenched Zr.

The activation energy of 0.60 eV for the second stage of strain ageing is much higher than that for the initial stage of ageing. This value is in close agreement with the activation energy for the deformation process for dislocations overcoming oxygen barriers in zirconium alloys which is in the range 0.5 to 0.89 eV. Mills and Craig<sup>23)</sup> found an activation energy of 0.89 eV at 560°K for the deformation process in Zr-O single crystals and reported 0.5 eV at 560°K

for polycrystalline Zr. Westlake<sup>24)</sup> obtained an activation energy of 0.7 eV for dislocation overcoming oxygen barriers. Recently, Swanson et al<sup>25)</sup> obtained an activation energy of 0.6 eV and 0.7 eV for vacancy formation from electrical resistivity measurements on quenched Zr. If Swanson's observation is true, the 0.60 eV for the second stage of strain ageing in present study may be associated with vacancy as well as oxygen. Meshii and Kaufman<sup>26)</sup> suggested that the increase in yield stress in quenched gold was associated with the quenched-in-vacancies. Veevers and Snowden have suggested that the increased amount of strain ageing in quenched Zircaloy-2 is attributed to a Snoek type interaction between glide dislocations and an increased concentration of oxygen-oxygen (i-i) atom pairs or oxygen-substitution (i-s) atom pairs frozen-in by the quenching treatment.

It seems reasonable to suggest that the initial stage of strain ageing in quenched Zircaloy-4 is associated with solely Snoek type ordering and the second stage of ageing associated with mainly Cottrell type oxygen pinning as well as Snoek type ordering.

## 6. Conclusion

1) The strain ageing stress in quenched Zircaloy-4 increased with strain ageing time and ageing temperature in the temperature range 523 to 588°K for a short-ageing time of 1 to 52 seconds.

2) The strain ageing under stress in quenched Zircaloy-4 was observed in two stages of strain ageing time; an initial stage showed a relationship of  $\Delta\sigma/\sigma \propto \left[ \frac{t}{T} \right]^{\frac{2}{3}}$

and the second stage showed a relationship

$$\text{of } \Delta\sigma/\bar{\sigma} \propto \left[ \frac{t}{T} \right]^{\frac{1}{2}}$$

3) The initial stage of ageing is considered to be associated with Snoek type ordering of oxygen to dislocation having an activation energy of 0.39 ev. The second stage of strain ageing is thought to be attributed to mainly a long-range diffusion of oxygen atoms having an activation of 0.60 energy ev.

#### Acknowledgements

The authors extend their thanks to Mr. K. W. Lee for mechanical testing

#### References

- 1) E. de paula E Silva, J. Com-Nogue and G. Beranger, C. R. Acad. Sci. Paris 727 C (1971) 180.
- 2) E. De Paula E Silva, J. Com-Nogue and G. Beranger and P. Lacombe, Scripta Met. 5 (1971) 795.
- 3) K. Veevrs and K. U. Snowden, J. Nucl. Mater 47 (1973) 311.
- 4) K. Veevers W. B. Rotsey and K. U. Snowden, ASTM STP 458 (1969) 194.
- 5) K. Veevers and W. B. Rotsey, J. Nucl. Mater 27 (1968) 108.
- 6) A. G. Bedford, P. G. Fuller and D. R. Miller, J. Nucl. Mater 43 (1972) 164.
- 7) P. M. Kelly and P. D. Smith, J. Nucl. Mater 64 (1973) 23.
- 8) K. S. Rheem and W. K. Park, J. Kor. Nucl. Soc. 8(1976) 19.
- 9) K. S. Rheem and W. K. Park, J. Kor. Nucl. Soc. 8 (1976) 151.
- 10) D. Lee, Met. Trans. 1 (1970) 1607.
- 11) V. Fidleris, Atomic Energy Rev. 13 (1975) 51.
- 12) L. G. Bell, AECL-1305 (196).
- 13) H. E. Rosinger and G. B. Graig, Cand. Met. Quart. 8 (1969) 97.
- 14) A. H. Cottrell and B. A. Bilby, Proc. Phys. Soc. (London) A62 (1949) 49.
- 15) K. S. B. Rose and S. G. Glover. Acta Met. 14 (1965) 1 05.
- 16) A. S. Keh and W. C. Lesile, Meterial Science Research Vol. 1 (plenum press, New York, 1968) P. 208.
- 17) G. Schoeck and A Seeger, Acta Met. 7 (1959) 469.
- 18) Y. Nakada and A. S. Keh, Acta Met. 15 (1967) 879.
- 19) C. S. Hartley, Acta Met. 14 (1966) 1237.
- 20) K. Kamber, D. Keefer and C. Wert, Acta Met. 9 (1961) 403.
- 21) A. Atrens, Scripta Met. 8(1974) 401.
- 22) A. M. Hammard, B. D. Sharma and P. Rodriguez, BARC-562 Bhabha Atomic Research Centre, India (1971).
- 23) D. Mills and G. B. Craig, Trans. TMS-AIME 242 (1968) 1881.
- 24) D. G. Westlake, Acta Met. 12 (1964) 1373.
- 25) M. L. Swanson, G. R. Piercy, G. V. Kidson A. F. Quenneville, AECL-3428, Chalk River, Canada (1969).
- 26) M. Meshii and J. W. Kanffman, Acta Met. 7 (1959) 180.