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Strain Ageing Behavior of Cold Worked Zircaloy-4 with Varying Oxygen Content

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Abstract

The strain ageing behavior of cold-worked Zircaloy-4 in vacuum was studied as a function of deformation temperature and oxygen content from 1143 ppm to 3500 ppm O. Strain ageing occured in the temperature range between 200 and 450°C for the 0 to 10% cold-worked Zircaloy-4, decreasing with increasing amount of cold work. This suppression of strain ageing by cold work is considered to be due to the trapping of oxygen atoms by cold work-produced defects.

It has been found that the maximum strain ageing stress in cold-worked Zircaloy-4 is proportional to the square root of oxygen content.

요 약

냉간가공한 질칼로이-4의 가공시효(strain ageing) 현상이 진공속에서 변형온도 및 1143 ppm—3500 ppm의 산소 함량의 변수로써 조사되었다. 가공시효 현상이 0—10% 냉간가공한 질칼로이-4의 경우 200—450°C의 온도구간에서 조사되었으며, 이때 가공시효 현상은 냉간가공량이 증가할수록 감소하는 현상을 보였다. 이 냉간가공에 따른 가공시효의 감소는 냉간가공시 발생한 결함에 의해 산소 원자들이 trapping 되는 결과로 기인된 것으로 고려된다.

냉간가공된 질칼로이-4의 최대 가공시효 응력은 함유된 산소의 량의 평방근에 비례한다는 사실이 밝혀졌다.

1. Introduction

The strain ageing behavior of zirconium alloys has been studied by several workers[1-5] especially on the effect of neutron irradiation as well as heat treatment. Little is known, however, about the role of interstitial oxygen atoms in the strain ageing behavior of cold-worked zirconium alloys. The strain ageing in both annealed and quenched ziroconium alloys was found in the temperature range 150 to 500°C and this is known to affect the creep rate to decrease between 250 and 350°C. Veevers[3] observed that at 300°C the strain ageing in cold-worked Zircaloy-2 decreases with increasing amount of cold work. The suppression by cold work has not been identifed but was suggested that it could be explained if the number of available oxygen atoms was not sufficient to pin a significant number of the dislocations introduced by the cold work. Strain ageing occured in annealed and quenched Zircaloy

Table 1. Chemical analysis 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

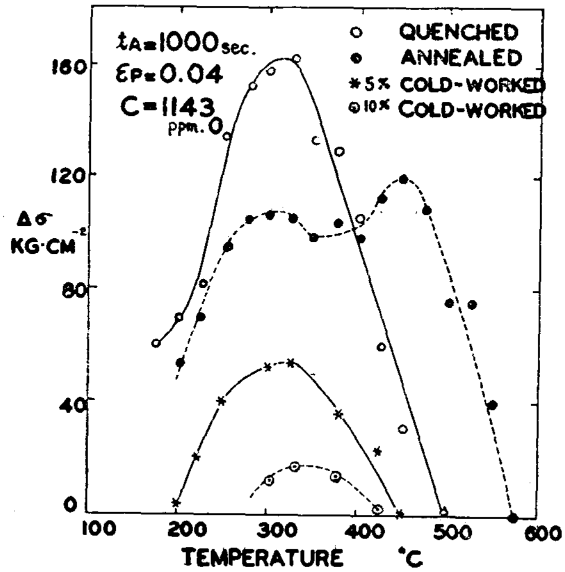


Fig. 1. $\Delta\sigma$ **Versus Ageing Temperature for 5% and 10% Cold-worked Zircaloy-4 Compared with Annealed at 750°C and Quenched from 750°C Zircaloy-4.**

has been attributed to the segregation of interstitial oxygen atom pairs to cell walls during ageing, thus stabilizing the dislocation substructure. The effect of oxygen content[6] on strain ageing has been found that strain ageing stress at 300°C in zirconium alloys is proportional to the square root of oxygen content.

This paper describes the strain ageing study in cold worked Zircaloy-4 with varying oxygen content.

2. Materials and specimens

The Zircaloy-4 was supplied by SANDVIK

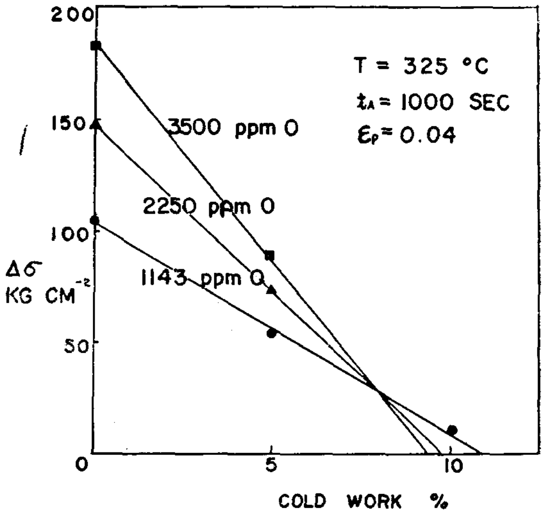


Fig. 2. $\Delta\sigma$ **Versus cold work for Zircaloy-4.**

Sweden in tubing of usual PWR size, 10.7 mm in outer diameter, 0.6mm wall thickness and the chemical analysis is shown in Table 1, in which the initial oxygen content is 1143 ppm by weight. The as-received material in tube was cold-rolled into sheet of 0.56mm thickness at room temperature. After cold rolling sheets were annealed for 3 h at 650°C in a vacuum of 10^{-4} torr.

Variations in oxygen concentration from 1143 ppm to 2250 and 3500 ppm were achieved by oxidation at 600°C for different lengths of time[7] followed by homogenization[8] at 820°C for one week. The oxygen content were confirmed by the measurement of strain ageing peaks in annealed specimens[6, 9]. After annealing specimens were cold-rolled to the required degree of cold-worked thickness ×2mm width were machined from the cold-rolled sheet. Before testing specimens were chemically polished in a solution of 45 parts HNO_3, 5 parts HF and 50 parts H_2O.

3. Experimental details

The experimental procedures were almost

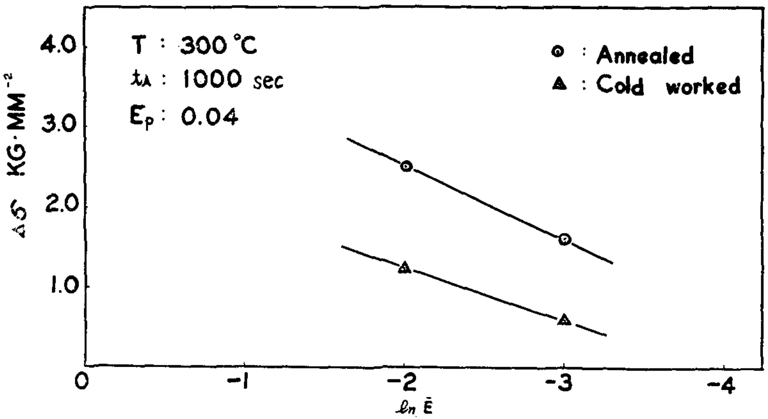


Fig. 3. $\Delta\sigma$ **Versus Strain Rate for Zircaloy-4.**

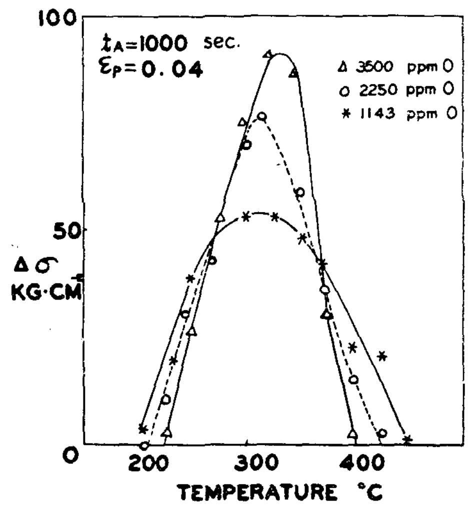


Fig. 4. $\Delta\sigma$ **Versus Temperature for 5% cold-worked Zircaloy-4.**

the same as those in a previous paper[6]. The nominal strain rates of 9.8×10^{-4} and 9.8×10^{-3} sec^{-1} were used. The ageing stress difference between the yield stress after ageing and the flow stress before ageing $\Delta\sigma$ was taken as the strain ageing parameter.

4. Results

Effect of temperature

The results of strain ageing tests in the 175 to 575°C on 5% cold-worked Zircaloy-4 are shown in Fig. 1 where other curves for quenched and annealed specimens are compared with it as reference. The value of 5% cold-worked Zircaloy-4 increases with increase of ageing temperature reaching a maximum peak at 320°C. Above 320°C. $\Delta\sigma$ decrease with increasing temperature.

Effect of cold work

Strain ageing stress on the specimens with 1143 ppm 0 was investigated in the temperature range 200 to 450°C as a function of cold work 0 to 10% (Fig. 1) The strain ageing stress are suppressed by cold work and the temperature of the maximum increases with amount of cold work. $\Delta\sigma$ at 300°C with degree of cold work of 0, 5 and 10% is shown in Fig. 2 where the strain ageing decreases linearly with increasing cold work. Fig. 2 shows that the more the amount of oxygen content the faster the suppression of $\Delta\sigma$ occurs.

Effect of strain rate

The effect of strain rate on $\Delta\sigma$ at 300°C was obtained for annealed and 5% cold-worked Zircaloy-4 of 1143 ppm 0 as shown

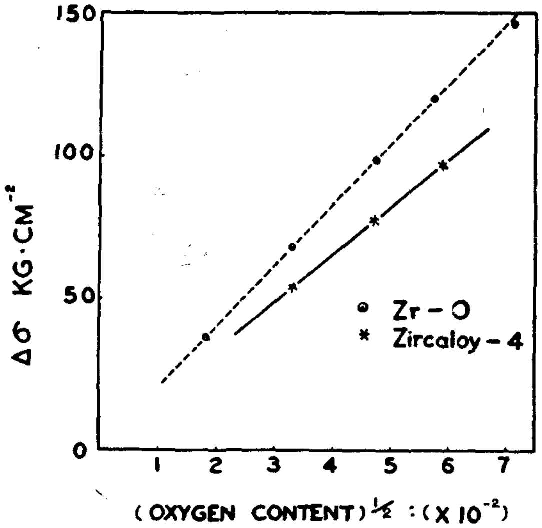


Fig. 5. $\Delta\sigma$ **Versus (oxygen content)½ for 5% cold-worked zircaloy-4 compared with annealed Zr-O Alloy.**

in Fig. 3 where the increase in $\Delta\sigma$ for annealed specimen is more sensitive than for cold-worked one.

Effect of oxygen content

Strain ageing in 5% cold-worked samples was measured in the temperature range 200 to 450°C as a function of oxygen contents (Fig. 4). The magnitude of maximum strain ageing shows its peak value which is propoitonal to square root of oxygen interstitial content (Fig. 5). The temperature of the maximum $\Delta\sigma$ increases with the oxygen content.

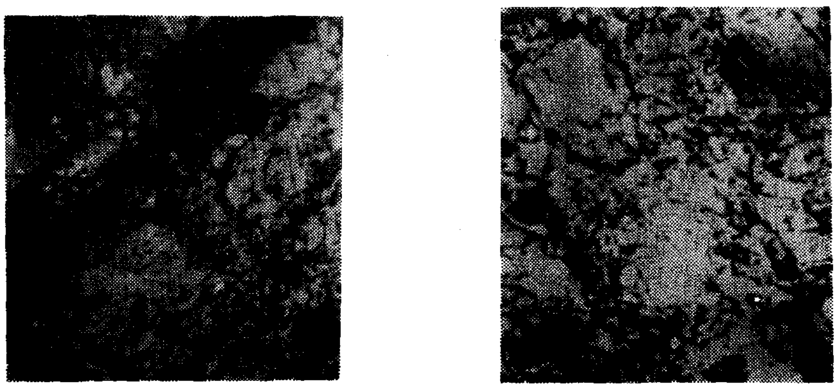
Electron microscopy

Transmission electron microscope observations were made on thin foil prepared from 5 and 10% cold-worked Zircaloy-4 which had been deformed again, aged and tested at 300°C. A little tangled cell structure was revealed out in 5% cold-work specimen. The 10% cold-worked specimen revealed no cell walls (Fig. 6).

5. Discussion

It is of interest that yield stress is increased by cold work but strain ageing is suppressed by it.

It is well-known that after cold work or neutron irradiation at a temperature below about 100°C, the electrical resistivity of Group Va metals decreases at annealing temperatures of 0.1 to 0.2 of melting point. Tm, whereas hardening is observed in the same temperature range.



(a) (b)

Fig. 6. Electron micrographs (×26,000)
a) 5% cold-worked at 23°C and strain aged at 300°C
b) 10% cold-worked at 23°C and strain aged at 300°C

As observed on Group Va metals, Zircaloy shows the same trend of the increase in strength and the decrease in strain ageing by cold work or neutron irradiation.

The suppression of strain ageing by cold work can be attributed to the trapping of oxygen atoms by cold work-produced defects instead of dislocations. If the oxygen atoms are trapped by defects, there should be a change in the strain ageing response since the strain ageing response strongly depends on the pinning of dislocations by oxygen interstitial atom or atom pairs. No details of the association of oxygen atom with defects have been identified but internal friction resonance study was attempted to find the association mechanism on carbon precipitation in irradiated iron.

Fujita et al[10] suggested that if the defect is the interstitial, an internal friction resonance could be measured and if the defect is a vacancy and oxygen atom is centrally located within vacancy, no such resonance would be observable. However the oxygen atom could rest to the side of such a vacancy and thereby give rise to a resonance. This suggestion can be applied to the case of strain ageing response which is influenced by the interaction of oxygen atoms with vancancies.

To relate the strain ageing in cold-worked Zircaloy to the interaction between defects and dislocation as well as configuration of them, it is necessary to estimate the activation energy for strain ageing in cold-worked and annealed Zircaloy.

Conrad and Frederick's[11] equation for activation volumes for slip is:

$$v=KT\left(\frac{ln\dot{\gamma}_1-ln\dot{\gamma}_2}{\Delta\tau}\right)_T \qquad (1)$$

where v is the activation valume, K is Boltzmann's constant, $\dot{\gamma}_1$ and $\dot{\gamma}_2$ are the two strain rate and $\Delta\tau$ is the increase in shear stresses measured from change of strain rate $\dot{\gamma}_1$ to $\dot{\gamma}_2$.

Assuming that $\Delta\tau$ can be substituted to increase in normal strain ageing stress, Eq(1) is modified to the equation for strain ageing as:

$$v=2KT\left(\frac{ln\dot{\epsilon}_1-ln\dot{\epsilon}_2}{\Delta\sigma_1-\Delta\sigma_1}\right)_T \qquad (2)$$

where $\Delta\sigma_1-\Delta\sigma_2=2\Delta\tau$ and $\dot{\epsilon}$ substitutes for $\dot{\gamma}$. Schoeck[12] has shown that the activation energy for slip is given by

$$\Delta G=\frac{v\left(\frac{\delta\tau}{\delta T}-\frac{\delta\mu}{\delta T}\cdot\frac{\tau}{\mu}\right)}{\frac{1}{T}-\frac{1}{\mu}\cdot\frac{\delta\mu}{\delta T}} \qquad (3)$$

where ΔG is activation free energy for slip, τ is shear flow stress and μ is shear modulus.

Substituting $\Delta\sigma$ for 2τ, Eq(3) becomes for strain ageing process as:

$$\Delta G=\frac{\frac{v}{2}\left(\frac{\delta\Delta\sigma}{\delta T}-\frac{\delta\mu}{\delta T}\cdot\frac{\Delta\sigma}{\mu}\right)}{\frac{1}{T}-\frac{1}{\mu}\frac{\delta\mu}{\delta T}} \qquad (4)$$

where ΔG is activation energy for strain ageing and $\Delta\sigma$ subsitutes for two times the effective shear stress 2τ.

From the data of Fig. 3 we obtained activation volume $v=170b^3$ for cold-worked specimen and $v=116.5b^3$ for annealed Zircaloy-4. With these values we obtained activation energy from Eq(4): $\Delta G=0.43$ ev for strain ageing in 5% cold-worked Zircaloy-4 of 1143 ppm 0 and $\Delta G=0.56$ ev for strain ageing in annealed Zircaloy-4 of 1143 ppm 0. Here each term of Eq(4) is taken as; for cold-worked specimen; $\frac{\delta\Delta\sigma}{\delta T}=4.66\times10^{-3}$kg/mm²/deg from Fig. 1, $\frac{\Delta\sigma}{\mu}=$ 1.73kg/mm², $\frac{\delta\mu}{\delta T}=-7.0\times10^{-5}$/deg[13] and $1/\mu=2.874$, for annealed specimen; $\frac{\delta\Delta\sigma}{\delta T}=8.8\times$

10^{-3}kg/mm^2 from Fig. 1, $\frac{\Delta\sigma}{\mu}=4.59$kg / mm^2 and other values are taken as same ones for cold-worked specimens. The obtained activation energy for strain ageing is low value compared with the limits 0.7 to 1.7 ev estimated by Westlake[14] for dislocations overcoming oxygen barriers in zirconium. Mills and Craig[15], however, find that the free energy of activation for the deformation of polycrystalline zirconium of 0.5 ev at 560°K which is much lower than others. Activation energy in cold-worked state is lower than that in annealed state. It is considered that the low activation energy value obtained may better be explained if the movements of excess vacant lattice sites produced by the cold-work prior to the ageing are taken into account. Now from Fig. 5, we obtain a linear relationship between $\Delta\sigma$ at ~300°C and the square root of oxygen content as follows:

$$\Delta\sigma=K\cdot C^{1/2} \tag{5}$$

where $\Delta\sigma$ is strain ageing stress, K is proportional constant here taken 16.7 kg/mm^2, C is oxygen content. Eq (5) is similar to the equations derived by Rheem and Park[6] for the strain ageing in annealed and quenched zirconium alloys. Now one of possible explanation for K in cold-worked Zircaloy-4 can be deduced from the irradiation hardening theory which was suggested by Crivelli-Visconti and Greenfield[16]. Their equation is written by:

$$\Delta\sigma=\frac{\mu b(d\cdot N)^{1/2}}{W} \tag{6}$$

where $\Delta\sigma$ is an increment in yield stress change before and after irradiation, μ is shear modulus, d is defect diameter, N is defect density, W is arbitrary constant and b is Burgers vector.

Assuming that defect density N equals oxygen content, C, and W is a function of cold work, Eq (6) becomes for strain ageing;

$$\Delta\sigma=\frac{\mu b\ d^{1/2}}{\alpha}\cdot C^{1/2}$$

$$=K\cdot C^{1/2} \tag{7}$$

where $K=\frac{\mu b\ d^{1/2}}{\alpha}$, C is oxygen content and α is cold-work factor. Recently, Loomis and Gerber[17] have shown that the defect density increases with increasing interstitial content in neutron irradiated niobium. Hasson[18] has shown that increase in the room temperature yield stress of neutron-irradiated vanadium is dependent on interstitial content instead of defect density produced by irradiation. Their observations lead to a suggestion that defect density equals interstitial content, assuming that oxygen atom is centrally located within vacancy or vacancy is equally produced at vicinity of oxygen atom. Putting $\mu=2.912\times10^3$ kg/mm^2, $b=3.23\times10^{-8}$cm, $d=$ 50Å, and $\alpha=4.0\times10^{-7}$ Eq (7) gives; $K=16.5$ kg/mm^2. α value can be increased with increasing the degree of cold-workd. d and α which is arbitrarily taken here need further study.

As a result, it is believed that in cold-worked Zircaloy-4 the oxygen atoms will be trapped by the cold work-produced vacancies in manner of which oxygen atom is centrally located within vacancies, resulting in a lack of oxygen atoms to pin the dislocations therefore no strain ageing response occurs in low temperature range. Ageing at high temperature is believed to cause a returning of trapped oxygen from vacancies to solution, then result in appearance of strain ageing response. Now we also conclude that at 300°C the maximum response in strain ageing is proportional to the square root of oxygen content as shown in annealed and quenched zirconium alloys.

6. CONCLUSION

(1) Strain ageing in 0 to 10% cold-worked Zircaloy-4 was found in the temperature range 200 to 450°C.

(2) Strain ageing decreased with increasing amount of cold work. This suppression of strain ageing by cold-work is considered to be due to the trapping of oxygen atoms by cold work-produced defects.

(3) The activation energy for strain ageing in 5% cold-worked Zircaloy-4 was estimated to be $\Delta G=0.43$ ev

(4) Strain ageing response at~300°C is proportional to the square root of oxygen content in cold-worked Zircaloy-4.

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