

RECOVERY AND RECRYSTALLIZATION OF ZIRCALOY-4

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ABSTRACT

We have determined the kinetic parameters of the recovery and recrystallization processes in cold-worked samples of zircaloy-4 (deformation degree 50%) using dynamic DTA techniques. Both phenomena have been individualized and their activation energies, found from the thermograms obtained, are $E_{\text{recovery}} = 2.7 \pm 0.3$ eV, $E_{\text{recrystallization}} = 3.1 \pm 0.4$ eV. The enthalpy changes have been also calculated by integration of the peaks: $\Delta H_{\text{recovery}} = 38 \pm 3$ J g⁻¹, $\Delta H_{\text{recrystallization}} = 188 \pm 10$ J g⁻¹.

INTRODUCTION

Different authors have studied the recovery and recrystallization of cold-worked zircaloy-4 with experiments on hardness and traction [1] and measurements of the electrical resistivity [2], always under isothermal conditions between 670 and 970 K. This is the working temperature range of this alloy, which is used for the metallic coating of heating elements and structural materials for the nuclear industry because of its small capture cross-section to thermal neutrons.

The separation of the two processes gives the activation energies of the physical mechanisms thought to explain them: fall and disappearance of all dislocations during recovery, and growth and coalescence of the subgrains during recrystallization [1–3].

In this paper we propose an analysis of the kinetics of recovery and recrystallization in cold-worked zircaloy-4 with a dynamic temperature study by means of DTA.

Although, in order to calculate the kinetic parameters, dynamic techniques are more difficult and less precise than isothermal ones, they have the advantage of making possible:

(a) the use of the same sample throughout the whole temperature range studied;

(b) the calculation of the total energy liberated in the recovery and recrystallization processes, which may later be correlated with the system's structural parameters such as the deformation degree, microstructure, grain size, and other parameters which affected the material during the cold-temperature work.

EXPERIMENTAL

The zircaloy-4 used was laminated in a direction parallel to direction $[10\bar{1}0]$ until plates of 1.2 mm thickness were obtained, with a deformation degree of 50% and an average grain size of $15\ \mu\text{m}$ [3]. The weight composition of the additional elements to zirconium is: Sn (1.38%), Fe (0.20%), Cr (0.10%), O (1445 ppm), C (110 ppm) and others (Si, Ta, Ni, etc. < 100 ppm).

The zircaloy-4 plates were mechanized, with care not to add further deformation to the material, and discs of 6 mm diameter and a thickness of 1.2 mm were formed. These discs, suitable for use as samples for our DTA system, had an approximate mass of 200 mg and were decocated in a 65% $\text{H}_2\text{O}/30\% \text{HNO}_3/5\% \text{HF}$ solution.

Our furnace has a weak thermal coupling between alveoli. The thermocouples are Pt-Pt/10% Rh and 0.5 mm in diameter, and have three connections in series in each alveolus. The differential output signal was amplified between 2×10^4 and 8×10^4 times. The typical heating rate was $\beta = 5\ \text{K min}^{-1}$.

A dynamic N_2 atmosphere was used in order to avoid oxidation and diffusion of O_2 into the sample. These effects are significant because of the high diffusion coefficient of O_2 in zirconium [4-7]. The diffusion of N_2 is not important below 1070 K [7], well above our working temperature.

The calibration of the experimental system was done between 670 and 1170 K with the substances recommended by ICTA (Ag_2SO_4 , SiO_2 , K_2SO_4 , K_2CrO_4 and BaCO_3) and supplied by NBS [8]. Refractory cement and previously recrystallized zircaloy-4 were the reference materials. Both are theoretically inert in the 570-1090 K range. It is important that a martensitic transition (HCP \rightarrow BCC) occurs in zircaloy-4 at about 1120 K [9].

An HP3478 A digital voltmeter and an Apple II computer to which it is connected comprise our data acquisition system, with which we registered the thermograms or differential output signals in numerical form and later processed the information.

RESULTS

Recovery and recrystallization occur in a temperature range of about 400 K. They are not seen as typical DTA peaks like first-order transitions; their

output signal is so weak that it is difficult to identify it from the baseline. In this paper we have found a solution, which is to consider as net signal the difference between the recording of a first and a consecutive second heating when the sample is already recrystallized and therefore inert. If a third heating is carried out the resulting thermogram is equal to that of the second. Observations made with optical microscopy show that the material is completely recrystallized when previously heated above ~ 1090 K.

A typical recording using recrystallized zircaloy-4 as reference appears in Fig. 1. Proof that the sample is completely recrystallized at $T > 1090$ K is that the same results are obtained if refractory cement is used instead of zircaloy-4. Two overlapping peaks, that we have related to recovery and recrystallization, can be seen in Fig. 1. In order to study these peaks individually, we have isolated them by interpolation and point subtraction (Fig. 2).

In an isothermal regime, mechanisms of diffusion-controlled transformations may be described by an empirical equation of the Johnson-Mehl-Avrami type [9]

$$\alpha = 1 - \exp(-kt)^n$$

For example, Derep et al. [1] used it to describe the mechanisms of recovery and recrystallization of zircaloy-4 under isothermal treatment.

Under dynamic temperature conditions with a heating rate β we can make the substitution $t = (T - T_0)/\beta$ in the first equation, thus giving

$$\alpha = 1 - \exp[-k(T - T_0)/\beta]^n$$

If the heating rate constant is taken from the Arrhenius equation

$$k = k_0 \exp(-E/k_B T)$$

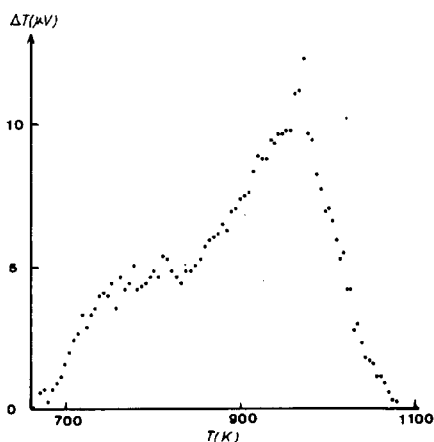


Fig. 1. Net signal obtained by DTA after the baseline correction ($\beta = 5 \text{ K min}^{-1}$).

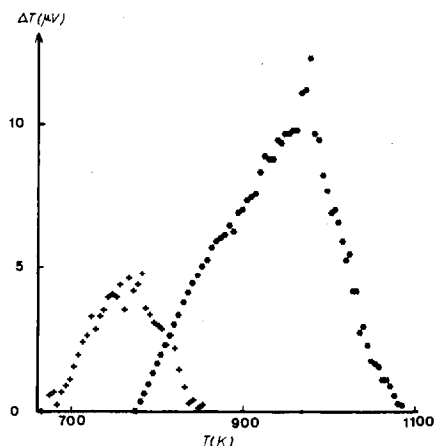


Fig. 2. Individualization of the thermograms corresponding to recovery (+) and recrystallization (*).

the following expression results

$$\frac{1}{n} \ln \left[\frac{-\ln(1-\alpha)}{(T-T_0)^n} \right] = \ln(k_0/\beta) - \frac{E}{k_B T} \quad (1)$$

where k_0 is the frequency factor, k_B is Boltzmann's constant, E is the activation energy and T_0 a fixed temperature value that we have taken as the initial temperature of recovery and recrystallization.

The procedure has been to use this last equation for different α intervals, varying the parameter n . The selection of E among all the possible values is dependent on k_0 , which is related to the atomic frequency of vibration [10], which ranges between 10^{11} and 10^{16} s^{-1} for solid-state processes [11,12].

Other well-known kinetic methods (Coats and Redfern, Šesták, etc.) lead to a restriction of α to the range $0 < \alpha < 0.2$ in order to obtain coherent values for k_0 [8] when applied to these two processes.

TABLE 1

Kinetic parameters determined for recovery

n	E (eV/atom)	k_0 (s^{-1})	r^a
0.40	3.0	3.8×10^{16}	-0.9993
0.42	2.9	2.9×10^{15}	-0.9993
0.44	2.7	2.8×10^{14}	-0.9993
0.46	2.6	3.3×10^{13}	-0.9994
0.48	2.4	4.6×10^{12}	-0.9994
0.50	2.3	7.6×10^{11}	-0.9994

^a r = linear regression coefficient.

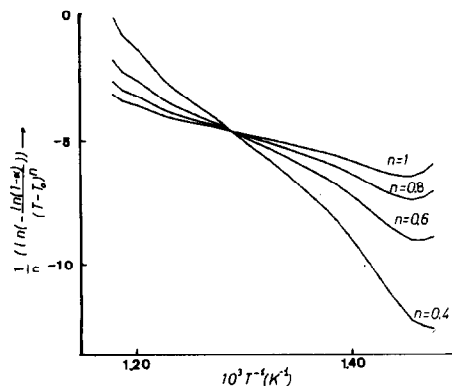


Fig. 3. Diagram of $\frac{\ln\{-\ln(1-\alpha)/(T-T_0)^n\}}{n}$ vs. $1/T$ applied to recovery, for different values of n .

Recovery

We have determined suitable values for k_0 for intermediate values of α ($0.2 < \alpha < 0.8$) and concrete values of n from Avrami's equation. The kinetic parameters corresponding to recovery are shown in Table 1. Figure 3 represents eqn. (1) for distinct values of n .

Recrystallization

In an analogous way to recovery we have obtained adequate values of k_0 for different intervals of α and specific values of n . The results are given in Table 2. Figure 4 represents eqn. (1) for different values of n .

Integration of each of the signals affected by the temperature-dependent calibration factor of the DTA gives the respective output energies. The

TABLE 2

Kinetic parameters determined for recrystallization

n	E (eV/atom)	k_0 (s^{-1})	r	$\Delta\alpha$
0.52	3.5	1.4×10^{16}	-0.9805	0-0.2
0.54	3.3	1.3×10^{15}	-0.9808	0-0.2
0.56	3.2	1.4×10^{14}	-0.9810	0-0.2
0.58	3.0	1.8×10^{13}	-0.9812	0-0.2
0.60	2.8	2.7×10^{12}	-0.9815	0-0.2
0.62	2.7	4.6×10^{11}	-0.9818	0-0.2
0.30	3.7	1.1×10^{16}	-0.9988	0.2-0.8

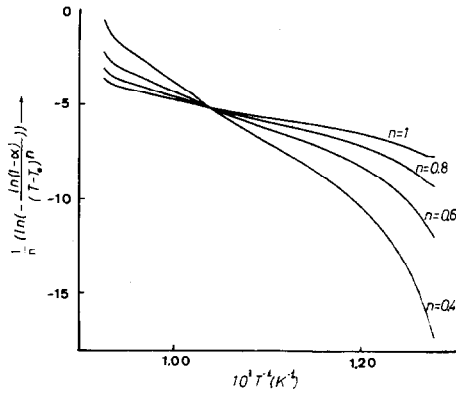


Fig. 4. Diagram of $\frac{\ln\{-\ln(1-\alpha)/(T-T_0)^n\}}{n}$ vs. $1/T$ applied to recrystallization, for different values of n .

TABLE 3

Initial and final temperatures and ΔH of recovery and recrystallization of the studied zircaloy-4

	Recovery	Recrystallization
T_i (K)	670	790
T_f (K)	870	1090
ΔH (J g ⁻¹)	38 ± 3	188 ± 10

values given in Table 3 correspond to cold-worked zircaloy-4 with a 50% deformation degree and a grain size of 15 μm .

DISCUSSION

The activation energy of recovery that we have determined (2.7 ± 0.3 eV/atom for $0.2 < \alpha < 0.8$) is perfectly comparable with the values obtained under isothermal conditions by electrical and mechanical measurements [1-3]. The literature gives values between 2.6 and 2.9 eV/atom for the same deformation degree of the material.

Derep et al. [1] indicate that recrystallization occurs in two steps of different kinetics (steps IIa and IIb) with respective values of 2.8 and 3.5 eV/atom. In the present study we were not able to identify these steps clearly either in the thermogram (Fig. 2) or in the representation of eqn. (1) (Fig. 4).

An average value $E = 3.1 \pm 0.4$ eV is obtained for $\alpha < 0.2$ and $0.52 < n <$

0.62. For $\alpha > 0.2$, higher values of E are found ($E = 3.7$ eV/atom for $0.2 < \alpha < 0.8$ and $n = 0.3$). This last result seems to agree with the existence of the two steps proposed by Derep et al. [1], but it cannot be considered a decisive criterion.

Measurements corresponding to enthalpy changes have still not been developed. It is intended to correlate the enthalpy changes with the system structural parameters in a future paper as it is thought that they may depend on the thermodynamic history of the material, its deformation degree, its microstructure and other factors.

CONCLUSION

The study of the kinetics of recovery and recrystallization in zircaloy-4 is possible under dynamic temperature conditions with DTA. Both processes may be described by the Avrami equation with activation energy values of 2.7 ± 0.3 eV for recovery and 3.1 ± 0.4 eV for primary recrystallization (step IIa according to Derep et al. [1]). Although the activation energy has been found to be higher for $\alpha > 0.2$, step IIb hasn't been clearly identified. The energies liberated for both transformations have been obtained by integration of the net output signals of the DTA. For recovery, $\Delta H = 38 \pm 3$ J g⁻¹ and for recrystallization, $\Delta H = 188 \pm 10$ J g⁻¹.

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