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MICROCALORIMETRIC INVESTIGATION OF THE RECRYSTALLIZATION BEHAVIOUR OF POLYCRYSTALLINE COPPER DEFORMED AT ROOM-TEMPERATURE

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The recrystallization of 5 N copper samples which had been deformed at room-temperature by torsion to an average shear of $\bar{\gamma} = 1.75$ by rolling to 65% r.c.s. was investigated by means of a commercial heatflow calorimeter.

During recrystallization, which was also studied by hardness tests and optical microscopy, a stored energy release of the order of 0.145 cal/g was observed. Some problems inherent in the use of microsamples are discussed. By kinetic analysis, based on variation of the linear heating rate, a value of 21.9 kcal mole^{-1} was determined for the apparent activation energy of the recrystallization process in torsion samples.

The main scope of this investigation was to demonstrate the feasibility of a commercial microcalorimeter (DSC 900 Du Pont) for quantitative studies of the recrystallization process in metals.

Copper was chosen as the sample material since a great number of experiments have been performed on this metal recently [1–5], and a direct comparison with results obtained by other working groups on the same sample material was possible. The results of this comparison form the subject of a separate publication [6].

It was the aim of the present study to determine on differently prepared specimens the amount of stored energy released during recrystallization, and the dependence of this on grain size, purity, etc. Further, it was to look into the question of whether any contribution from recovery and/or annealing of point defects, as well as the change of specific heat due to plastic deformation, could be detected by the instrument under consideration. Finally, an attempt was made to determine the apparent activation energy of the recrystallization process.

Experimental

Sample material

The experiments were performed on two differently pretreated sample materials:*

1. Torsion samples 13.5 mm in diameter and 150 mm in length were prepared at room-temperature from high-purity (99.999%) Degussa copper. To minimize

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the effect of the radial inhomogeneous deformation obtained by torsion, hollow cylinders 10 mm in (external) diameter and with a wall thickness of 0.5 mm had to be machined from the deformed rod material. To avoid recovery or recrystallization and for lubrification purposes, the specimens were kept under alcohol at −90° during machining. The sample tubes then had an almost homogeneous deformation, corresponding to an average shear of $\bar{\gamma}_s = 1.75$.

2. Elmore copper (purity 99.997%) was cast into a square-shaped ingot and subsequently deformed at room-temperature by too-and-fro-rolling to 65% r.c.s. Due to the preparation technique, this material showed a rather coarse grain and also a great scatter of the Vickers hardness values ($H_v^{2kp} = 103-128$).

Further details of the sample preparation are given elsewhere [3, 7, 8].

Method of measurement

The release of stored energy during recrystallization of the deformed Cu samples was determined by means of a Du Pont Differential Scanning Calorimeter (DSC 900), which in principle is a heat flow calorimeter and has been described in detail elsewhere [9].

As reference specimen (dummy) a completely recrystallized sample of the batch material was used. Specimens and dummy had very closely the same dimensions (⌀ = 5 mm, $d = 0.5$ mm) and weight (ca. 100 mg) and were placed inside open aluminium pans in the calorimeter cell. The runs were performed under very pure nitrogen or helium, flowing through the apparatus at 0.1 l/min.

The amount of stored energy was determined from two linear heating experiments run at between 5° and 40°/min; each was continued to about 50° above the completion of the recrystallization peak. Extreme care was taken to perform the second run after slow cooling under conditions identical to the first one.

The released energy can then be obtained from integration between the two curves:

$$Q = \int_{T_0}^{T_e} (C_p^{c.w.} - C_p^{recry})\mathrm{d}T = \frac{1}{H}\int_{T_0}^{T_e} \frac{\Delta T_I(T) - \Delta T_{II}(T)}{R_d(T)}\,\mathrm{d}T \qquad (1a)$$

or

$$Q = \int_{t_0}^{t_e} \frac{\Delta T_I(t) - \Delta T_{II}(t)}{R_d(t)}\,\mathrm{d}t \qquad (1b)$$

if the recording is made by a constant time base recorder. $c_p^{c.w.}$ and c_p^{recry} stand for the specific heat in the deformed and recrystallized state, respectively.

ΔT is the recorded actual temperature difference between sample and dummy, H is the linear heating rate and R_d is the temperature-dependent calibration constant of the apparatus. This constant was frequently checked throughout the experiments, both by measurements of metals of well-known specific heat and by means of the fusion enthalpies of Sn and Bi [9].

The Vickers (macro) hardness was measured by means of a DIA-Wolper tester on 0.5 mm thick samples at a load of 1 kp. About ten indentations were made for each point.

To observe the grain boundaries, micrographs were taken on ground and electropolished samples which had been etched in 10% ammonium persulphate solution.

Results and discussion

Relation between release of stored energy and hardness and the proceeding of recrystallization

In order to establish the direct relation between the stored energy released during linear heating experiments and the proceeding of the recrystallization process, a series of torsion samples were heated at 25°/min in the calorimeter to temperatures between 200 and 500°. After fast cooling, the Vickers hardness was measured and micrographs of the samples were taken.

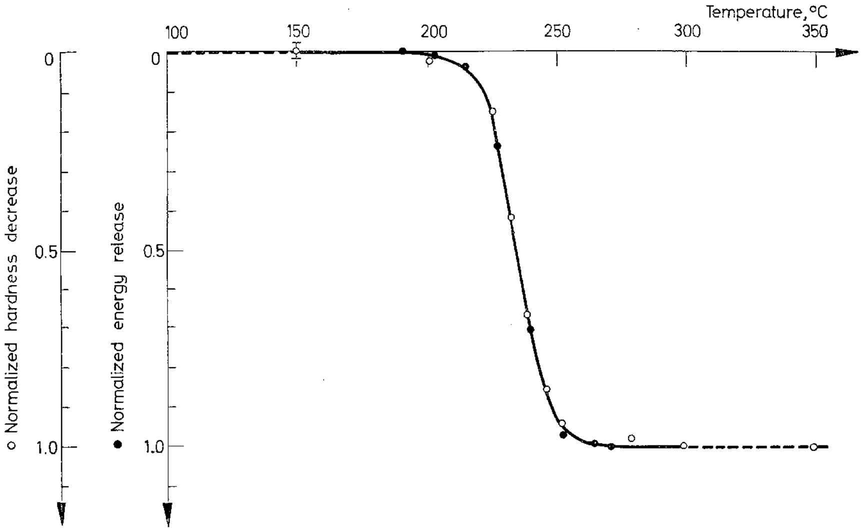
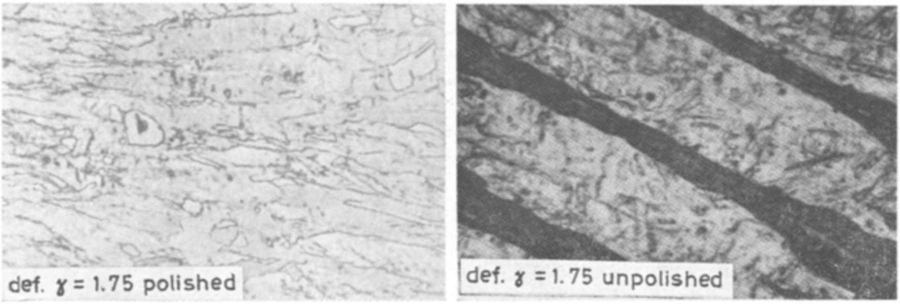


Fig. 1. Normalized variation of the Vickers hardness of torsion-deformed Cu samples upon heating at 25°/min in the calorimeter to the indicated temperatures. A typical normalized energy release curve is included



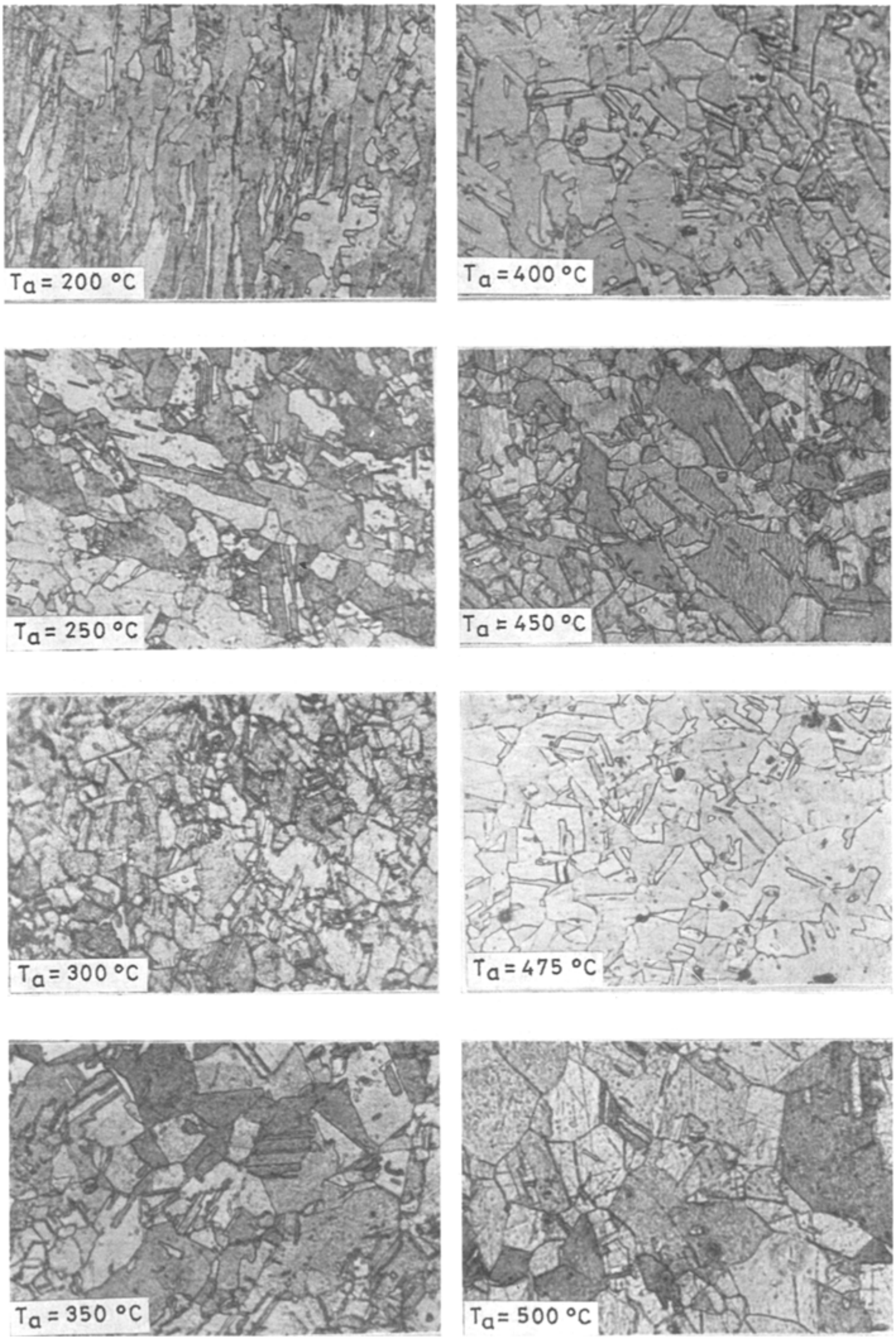


Fig. 2. Micrographs taken on the samples of Fig. 1 which were heated at 25°/min in the calorimeter to the indicated temperatures and fast cooled

In Fig. 1 the variation of hardness under these special heating conditions is shown, as well as a typical stored energy release curve. It can be seen from this plot that in fact the width of the energy release curve agrees fairly well with the decrease in hardness. In addition, the micrographs taken on the respective samples show, as follows from Fig. 2, that the torsion-deformed Cu samples are completely recrystallized after having been heated at 25°/min to temperatures above 300°. It can be concluded from these findings that the release of stored energy as measured by means of the DSC is proportional to the proceeding of the recrystallization process. The first micrograph of Fig. 2. shows quite nicely the slip line pattern induced at the sample's surface by the torsional deformation.

Determination of the stored energy

Torsion sample

A series of calorimeter experiments were run at various heating rates between 5° and 40°/min on torsion samples, with the primary purpose of determining the most appropriate heating rate for quantitative measurements, and to obtain information on the activation energy of the recrystallization process in this material (see above).

A number of such runs are presented in Fig. 3. It is seen that the stored energy is released in a single process at around 230°. An average energy release of 152 mcal/g was calculated from these experiments.

On the basis of the foregoing experiments, a heating rate of 25°/min was selected

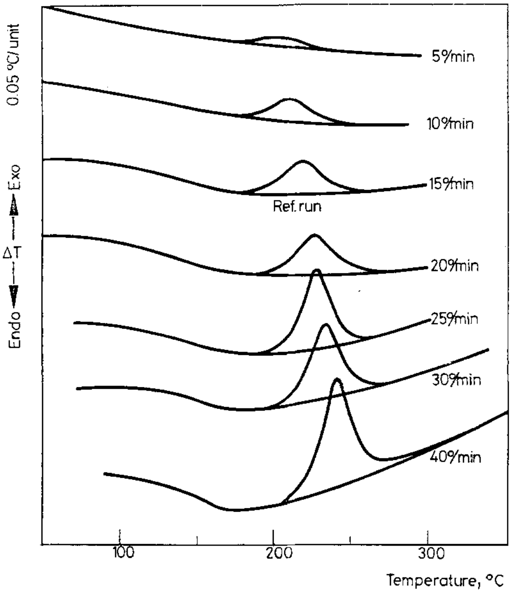


Fig. 3. DTA curves obtained on torsion samples ($\gamma = 1.75$) at various heating rates

to give optimum results with respect to peak area, base line reproducibility, etc., and another series of experiments was run at this rate.

For the stored energy, an average value of 145 mcal/g resulted from a total of ten runs at 25°/min.

The standard deviation in these two sets of experiments amounted to ±15%, which was far greater than to be expected on the basis of the characteristics of the instrument used. A detailed analysis showed that a relation $\ln E = f(1/T_p)$, as found by Broxtermann et al. [3], could be verified, i.e. samples showing a smaller energy release recrystallized at higher temperature (for equal heating rates). As a matter of fact, by testing the torsion sample used it could be proved that there was a longitudinal gradient of the stored energy. Specimens taken from the two ends of the sample tube yielded values of 117 and 155 mcal/g, respectively. It remains an open question, however, as to where this inhomogeneity originated from (preparation or handling operations).

DTA curves obtained on another torsion sample did not exhibit any perceptible dependence on the sample site from which the calorimeter specimens were taken. The average stored energy determined from 14 runs at various heating rates amounted to 142 mcal/g and the standard deviation was 5%, i.e. much smaller. The absolute error due to the manner of calibration was estimated to be about 14 mcal/g, that is 10%.

Rolled sample

In Fig. 4 some representative DTA curves obtained on the rolled sample mateal are shown. The mode of stored energy release can be seen to vary rather strongly

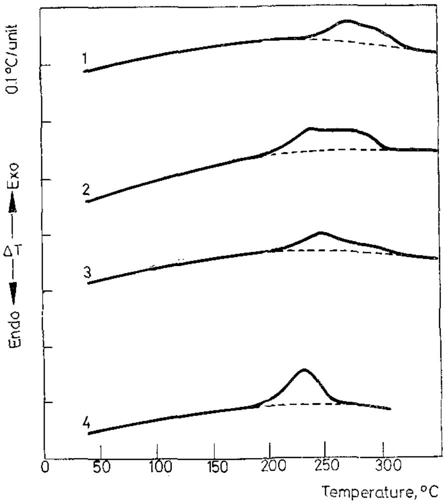


Fig. 4. Some DTA curves obtained on the rolled sample material at 25°/min in a He atmosphere (1)—(3). Curve (4) shows the energy release of the same sample material having been deformed (65%) after recrystallization (2 hr/300°). — —: run 2

from sample to sample with respect to shape, peak temperature and amount of energy. This has to be related to the coarse grain characteristics of the material before deformation (∅ = 4 mm), since the small specimens (ca. 100 mg) used in the present instrument consisted of just a few grains, each of which, depending on its crystal orientation contained a different stored energy, giving rise together to the observed recrystallization spectrum [2].

The average stored energy determined from 15 runs was 115 (±15) mcal/g and agreed fairly well with values obtained by more integral techniques [6].

The above conclusions were confirmed by the fact that when the rolled material was recrystallized by a two-hour annealing at 300°, fine-grain material was obtained; after another 65% deformation by rolling, this showed a well-shaped peak, as can be seen from curve 4 in Fig. 4 which proved to be reproducible.

Here again, no other recovery process besides the recrystallization could be identified from the curves. This implies that the deformation-induced point defects must have annealed out already during the deformation process at RT, and mechanical recovery (as expected for Cu) does not occur.

Determination of the activation energy

Isothermal kinetics of recrystallization have been well established and the results can be expressed fairly accurately by the relationship:

$$x = 1 - \exp\left[-B_0 \exp(-nQ/kT) t^n\right] \tag{2}$$

where x = fraction recrystallized (e.g. energy released)
n = a constant between 3 and 4
t = time
B_0 = constant
k = the Boltzman constant
T = the absolute temperature

The apparent activation energy Q describes the temperature-dependence of the overall process, and can be used to determine the influence of impurities, grain size, deformation degree, etc. on the kinetics of the recrystallization.

Despite the fact that Williams [10] has argued that the course of recrystallization might be quite different for continuous heating conditions as compared to isothermal runs, we have tried to apply Eq. (2) for the determination of Q from linear heating experiments.

By replacing t by $(T - T_0)/H$ (T_0 = starting temperature, H = heating rate), one can obtain an expression for the kinetics of the process during a linear heating experiment:

$$x = 1 - \exp\left[-B_0 \exp(-nQ/kT) \cdot \left[\frac{T - T_0}{H}\right]^n\right] \tag{3}$$

By stepwise integration of the measured rate curves, the release of stored energy during recrystallization can be plotted in a normalized form as shown in Fig. 5.

By comparing the temperatures at which the same of recrystallization, viz. the same energy release, is achieved under linear heating at different rates in different specimens of the same sample a value of 20.7 kcal mole^{-1} was evaluated for the apparent activation energy of the recrystallization process under linear heating conditions. No consistent trend of Q as a function of the percentage of recrystallization was found (Fig. 6).

Since the reaction rate of a process is maximum at the peak temperature, the shift of the latter on variation of the linear heating rate (as observed in Fig. 3) can be directly taken as a measure of the apparent activation energy [8]. From a

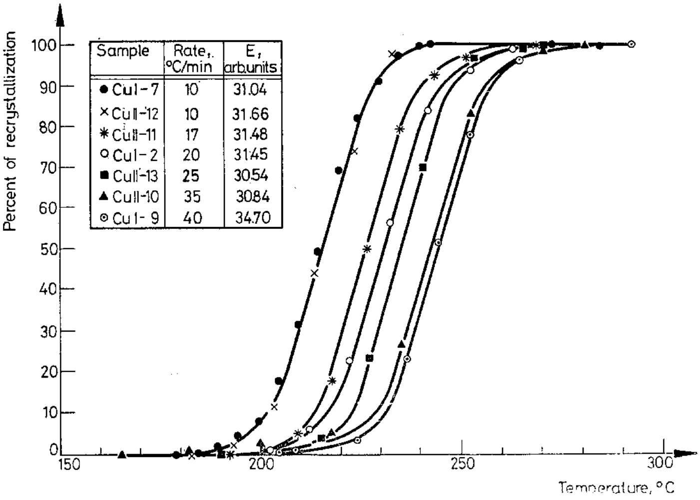


Fig. 5. Normalized release of stored energy during recrystallization of torsion samples at the indicated heating rates

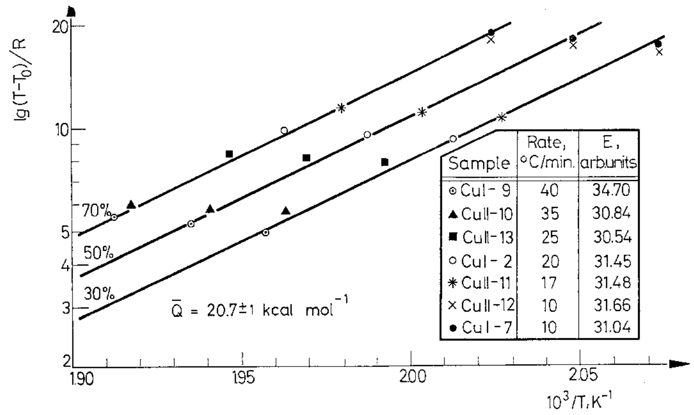


Fig. 6. Determination of the apparent activation energy of recrystallization in Cu from the energy release curves of Fig. 5

set of 10 experiments we obtained an average value of 21.9 ± 1.1 kcal mole^{-1}, in reasonable agreement with that determined from the integrated version. We may add that activation energies of this order have been reported by other authors, on copper of similar purity [11–13].

In contrast to opinions expressed elsewhere [3, 14] we do not believe that it is very meaningful to determine an activation energy for the recrystallization process from the observed dependence of the peak temperature on the stored energy ($\ln E = f(1/T_p)$). The stored energy is, of course, the driving force for the recrystallization, but the kinetics of the process itself are governed by atomic mobilities and diffusion constants, which should not depend on the amount of deformation [11].

Conclusions

It results from the experiments reported here that the stored energy release during recrystallization, as well as the activation energy of the process, can be rather easily determined by means of a commercial microcalorimeter.

Certain sampling problems which are due to the smallness of the calorimeter specimens used can be overcome by statistics, i.e. by performance of a greater number of measurements; this is facilitated by the ease of operation of the instrument. On the other hand, the use of microsamples also permits the detection of inhomogeneities in the sample material with respect to parameters which influence the amount of stored energy.

Note added in proof:

In a recent publication Lucci and Tamanini [15] have pointed out that the temperature calibration of a DSC might influence the determination of the activation energy by the peak shift method considerably. We, therefore, have performed the calibration in the way indicated by the cited authors and corrected appropriately the temperature values used for the evaluation of the activation energy. However, the respective corrections of the recorded temperatures we have found were much smaller than those determined in the work cited [15], and consequently the effect on the reported activation energy (see Fig. 6) was small, too: the temperature correction causes the value to increase from 0.95 eV to 1.05 eV. The reason for the smaller thermal lag observed in our study could be looked for in the thinner samples used by us.

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RÉSUMÉ — On a étudié à l'aide d'un calorimètre à flux de chaleur commercial la recristallisation d'échantillons de cuivre 5 N, préalablement déformés à température ambiante par torsion ($\bar{\gamma}_s = 1{,}75$) ou par laminage (65 %).

Lors de la recristallisation, également suivie par mesures de dureté et examens de structure, on observe un dégagement d'énergie d'environ 0,145 cal/g. Les problèmes qui surgissent lors de l'utilisation de prélèvements micro sont discutés. L'énergie d'activation apparente du processus de recristallisation après l'écrouissage par torsion s'élève à 21.9 kcal mol^{-1}.

ZUSAMMENFASSUNG — Die Rekristallisation von 5 N Kupferproben, die bei Raumtemperatur durch Torsion ($\bar{\gamma}_s = 1{,}75$) bzw. durch Walzen (65 %) verformt worden waren, wurde mit einem kommerziellen Wärmeströmungskalorimeter untersucht. Bei der Rekristallisation, die ebenfalls mit Härtemessungen und Gefügeuntersuchungen verfolgt wurde, wird eine Energiefreigabe von etwa 0.145 cal/g beobachtet. Einige bei der Verwendung von Microproben auftretende Probleme werden diskutiert. Eine Analyse der Kinetik, die auf der Variation der linearen Aufheizgeschwindigkeit basiert, ergab für die scheinbare Aktivierungsenergie des Rekristallisationprozesses in Torsionsproben einen Wert von 21.9 Kcal Mol^{-1}.

Резюме — С помощью промышленного калориметра с тепловым потоком была исследована рекристаллизация 5Н медных образцов, которые были деформированы при комнатной температуре кручением со средним сдвигом $\bar{\gamma}_s = 1.75$ и, соответственно, прокаткой до 65% р. к. с. Во время рекристаллизации, которая также была изучена с помощью испытаний на твердость и оптической микроскопией, установили выделяемую энергию запаса порядка 0.145 кал/г. Обсуждены некоторые проблемы, присущие при исследовании микрообразцов. С помощью кинетического анализа, основанного на изменении линейной скорости нагрева, было определено значение кажущейся энергии активации процесса рекристаллизации торсионных образцов, которое оказалось равным 21.9 ккал мол^{-1}.