A rate theory of strain relaxation
Krausz, A. S.

Publisher's version / Version de l'éditeur:

Materials Science and Engineering, 4, 4, pp. 193-197, 1969-06-01

National Research Council of Canada
Conseil National de Recherches du Canada

A RATE THEORY OF STRAIN RELAXATION

by

A. S. KRAUSZ

Reprinted from
MATERIALS SCIENCE AND ENGINEERING
Vol. 4, No. 4, July 1969
pp. 193–197

Research Paper No. 401
of the
Division of Building Research

OTTAWA
June 1969

Price 10 cents

NRC 10772

UNE THEORIE DE LA VITESSE D'ELASTICITE DIFFEREE

SOMMAIRE

L'étude de la mobilité des dislocations indique que la forme symétrique de la barrière d'énergie et l'expression hyperbolique correspondante, sur lesquelles on se base pour l'analyse des phénomènes d'élasticité différée, ne s'accordent pas avec les résultats obtenus par la mesure de la rapidité de montée des dislocations. Dans la présente étude l'auteur établit une expression de l'élasticité différée en complet accord avec les mesures de la vitesse de montée des dislocations. Trois formes typiques de barrières d'énergie sont analysées en détail. Il remarque qu'une de ces barrières rend compte de l'élasticité différée d'allure logarithmique que l'on observe le plus souvent au début, lors de la phase de forte contrainte. Pour ce qui est des deux autres barrières considerées, on montre que les déformations s'approchent asymptotiquement d'une valeur limite. L'analyse indique également que les contraintes internes ne peuvent pas être entièrement annulées lorsque la barrière d'énergie est asymétrique.

A Rate Theory of Strain Relaxation

A. S. KRAUSZ

Snow and Ice Section, Division of Building Research, National Research Council of Canada, Ottawa (Canada)

(Received January 27, 1969)

SUMMARY

Dislocation mobility studies indicate that the symmetrical form of the energy barrier and the corresponding sinh expression, usually assumed in the analysis of strain relaxation, cannot be reconciled with the results obtained in dislocation velocity measurements. In the present study an expression for strain relaxation is derived from the transition state theory for the asymmetrical forms of the energy barrier. The expression obtained is in full agreement with the dislocation velocity measurements. Three typical energy barrier shapes are analyzed in detail. One of the barriers is identified to be associated with logarithmic strain relaxation often observed during the initial, high stress period. For two of the barriers considered, the strain is shown to approach asymptotically to a limiting value. The analysis indicates that internal stress cannot be relieved completely when the energy barrier is asymmetrical.

RÉSUMÉ

Les études de mobilité des dislocations montrent que la forme symétrique des barrières d'énergie, que l'on considère en général dans l'analyse de la relaxation plastique, et l'expression en sinus hyperbolique que l'on en déduit, ne permettent pas de rendre compte des résultats de mesure de la vitesse des dislocations. Dans la présente étude, une expression pour la relaxation plastique est obtenue dans le cas de barrières d'énergie non symétriques, à l'aide de la théorie des états transitoires. L'expression obtenue est en accord total avec les mesures de vitesse des dislocations. Trois formes typiques de barrière d'énergie sont analysées en détail. L'une d'elles est identifiée comme étant celle qui donne lieu à la relaxation logarithmique que l'on observe souvent au cours de la première phase où la contrainte est élevée. Pour deux des barrières considérées, la déformation tend asymptotiquement vers une valeur limite. L'analyse montre de plus que pour une barrière dissymétrique la contrainte interne ne peut pas s'éliminer totalement.

ZUSAMMENFASSUNG

Aus Untersuchungen der Versetzungsbeweglichkeit geht hervor, daß die symmetrische Form der Energiebarriere und der entsprechende sinh-Ausdruck, wie er bei der Analyse des Dehnungsrelaxations üblicherweise angenommen wird, mit den Messungen der Versetzungsgeschwindigkeit nicht in Einklang gebracht werden können. In der vorliegenden Arbeit wird aus der Theorie des Übergangsstadiums für die asymmetrischen Formen der Energiebarriere ein Ausdruck für die Dehnungsrelaxation abgeleitet. Der gefundene Zusammenhang ist in voller Übereinstimmung mit Messungen der Versetzungsgeschwindigkeiten. Drei typische Formen der Energiebarriere werden ausführlich analysiert. Eine der Barrieren hängt mit der logarithmischen Dehnungsrelaxation zusammen, wie sie oft während einer Anfangsperiode bei hohen Spannungen beobachtet wird. Es wird gezeigt, daß sich die Dehnung bei zwei der untersuchten Barrieren asymptotisch einem Grenzwert nähert. Die Analyse ergibt, daß innere Spannungen nicht vollständig abgebaut werden können, wenn die Energiebarriere asymmetrisch ist.

INTRODUCTION

It is often observed that after a specimen is fully unloaded a thermally activated reverse plastic deformation (strain relaxation) takes place. The experimental results are usually analyzed with the Arrhenius equation in which it is assumed that the apparent activation enthalpy ΔH is a function of the effective stress τ_{eff} and the strain γ

$$\Delta H = \Delta H^{\neq} - V\tau_{eff} = \Delta H^{\neq} - V(\tau^{\circ}_{eff} - M\gamma)$$

where $\Delta H^{\neq}$ is the activation enthalpy, V is the activation volume, τ°_{eff} is the effective stress at the beginning of strain relaxation, M is the relaxation modulus[1]. Thus, the Arrhenius equation of strain relaxation is

$$\dot{\gamma} = A\left\{\exp\frac{V(\tau^{\circ}_{eff} - M\gamma)}{kT} - \exp\left[\frac{V(\tau^{\circ}_{eff} - M\gamma)}{kT}\right]\right.$$

$$= 2A \sinh\frac{V(\tau^{\circ}_{eff} - M\gamma)}{kT} \qquad (1)$$

where T is the temperature and the other symbols have their usual meaning. Equation (1) represents a process with a symmetrical energy barrier and recognizes a finite probability for the backward movement of the dislocations against the effective stress.

A description in the form of eqn. (1) is convenient mathematically and was found to represent strain relaxation quite well over a limited range of stress. At high stress the solution of eqn. (1) reduces to a logarithmic function of time t,

$$\gamma = C_1 \ln(C_2 t + C_3),$$

as was first shown by Kuhlmann[2]. For some experiments[3], the sinh expression appeared to be a good representation over the full range of strain.

Two serious objections have to be raised, however, concerning the validity of eqn. (1). First, this equation is not always a satisfactory description of the strain relaxation in the low stress range[4]; secondly, the expression sinh $V\tau_{eff}/kT$ is contradicted by dislocation velocity measurements. The latter is the more serious objection and cannot be overlooked even when an apparent agreement is obtained with experiment.

It is the purpose of this paper to report a theory of strain relaxation which is in agreement with strain relaxation observations and with dislocation velocity measurements over the whole stress range. The proposed theory is developed from fundamental physical concepts utilizing chemical rate theory.

RATE THEORY

In a previous study[5], a description was developed for the stress dependence of the dislocation velocity from the transition state theories of Eyring[6] and Vineyard[7], subject to the additional condition

$$\Delta H = \Delta H^{\neq} - V\tau_{eff}$$

where $\Delta H^{\neq}$ and V are independent of the stress. The expression derived is convenient mathematically and is also physically reasonable as there are several mechanisms for which the apparent activation enthalpy is a linear function of the stress.

The expression obtained for the dislocation velocity, v, was

$$v = A_f \exp\frac{V_f\tau_{eff}}{kT} - A_b \exp\left(-\frac{V_b\tau_{eff}}{kT}\right) \qquad (2)$$

where the pre-exponential factors A_f and A_b are independent of the stress and were defined in terms of statistical mechanical or thermodynamic quantities without making use of any empirical parameter. The subscripts f and b indicate that the quantity is associated with the forward and backward movement of the activated complexes respectively.

It has been shown[5] that eqn. (2) described fully the dislocation velocity results obtained in Ge, Si, InSb, GaSb, LiF, NaCl, Fe–3% Si, Ni and W. Subsequent investigations, as yet unpublished, proved that the same expression describes the experimental results obtained by several investigators with Zn, Cu and Nb. The analysis indicated that for all of these crystals the energy barrier was asymmetrical.

Long before dislocation velocity measurements were made, Eyring[8,9] suggested from purely rate theory considerations that solid state processes, including annealing, might be associated with asymmetrical potential energy surfaces. Although his model was not used in subsequent investigations of strain relaxation, it is now clear that asymmetrical energy barriers have to be considered when the activation enthalpy is linearly stress dependent.

Expressing now the dislocation velocity during strain relaxation by eqn. (2), assuming as usual that the effective stress is a linear function of the strain, and introducing the equation proposed by Orowan[10],

$$\dot{\gamma} = b\rho v,$$

the rate equation of strain relaxation is

$$\dot{\gamma} = b\rho \left\{ A_{\rm f} \exp \frac{V_{\rm f}(\tau^{\circ}_{\rm eff} - M\gamma)}{kT} - A_{\rm b} \times \exp \left[- \frac{V_{\rm b}(\tau^{\circ}_{\rm eff} - M\gamma)}{kT} \right] \right\} \quad (3)$$

For mathematical convenience in the following analysis, it will be assumed that the mobile dislocation density ρ does not change during relaxation. Equation (3) can be easily extended, however, to the $\rho \neq$ constant case by approximating the stress dependence of the mobile dislocation density with an exponential expression. A schematic representation of the stress dependence of strain rate according to eqn. (3) is shown in Fig. 1.

ANALYSIS OF THE STRAIN RELAXATION EQUATION

Three types of asymmetrical energy barriers were discussed in the dislocation mobility study[5]. These will also be considered in the present analysis of the strain relaxation equation.

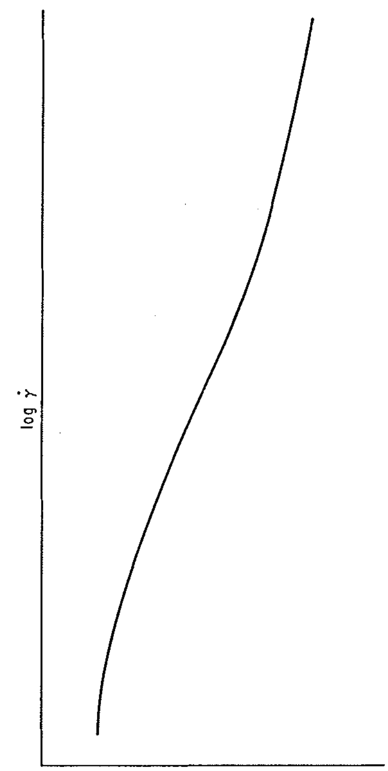

Fig. 1. Schematic diagram of the stress dependence of strain rate γ according to eqn. (3).

Type A barrier

The energy barrier can be characterized as

$$A_{\rm f} \neq A_{\rm b}, \text{ and}$$
$$V_{\rm f} \neq V_{\rm b}.$$

From the dislocation mobility analysis[5] this type of energy barrier is expected to be associated with the deformation process in LiF and NaCl. It should be noted, however, that the identification of the energy barrier shape requires more information than is as yet available and all suggested associations are only tentative.

Type B barrier

This type of energy barrier is represented by the following description

$$A_{\rm f} \neq A_{\rm b}, \text{ and}$$
$$V_{\rm f} = V_{\rm b} = V.$$

For this barrier the relaxation rate given in eqn. (3) is:

$$\dot{\gamma} = b\rho \left\{ A_{\rm f} \exp \frac{V(\tau^{\circ}_{\rm eff} - M\gamma)}{kT} - - A_{\rm b} \exp \left[- \frac{V(\tau^{\circ}_{\rm eff} - M\gamma)}{kT} \right] \right\}$$

The solution of this differential equation is

$$\gamma = \frac{kT}{VM} \ln \tanh (C_1 t + C_2) + C_3 \quad (4)$$

where

$$C_1 = \frac{VM}{kT} (A_{\rm f} A_{\rm b})^{\frac{1}{2}} b\rho$$

$$C_2 = \tfrac{1}{2} \ln \frac{\left(\frac{A_{\rm f}}{A_{\rm b}}\right)^{\frac{1}{2}} \exp \left(\frac{V\tau^{\circ}_{\rm eff}}{kT}\right) + 1}{\left(\frac{A_{\rm f}}{A_{\rm b}}\right)^{\frac{1}{2}} \exp \left(\frac{V\tau^{\circ}_{\rm eff}}{kT}\right) - 1}$$

$$C_3 = \frac{kT}{2VM} \ln \left(\frac{A_{\rm f}}{A_{\rm b}}\right) + \frac{\tau^{\circ}_{\rm eff}}{M}.$$

This reduces to

$$\gamma \cong \frac{kT}{VM} \ln (C_1 t + C_2) + C_3 \quad (5)$$

in the early stages of strain relaxation. Equation (5) is in formal agreement with the expression obtained

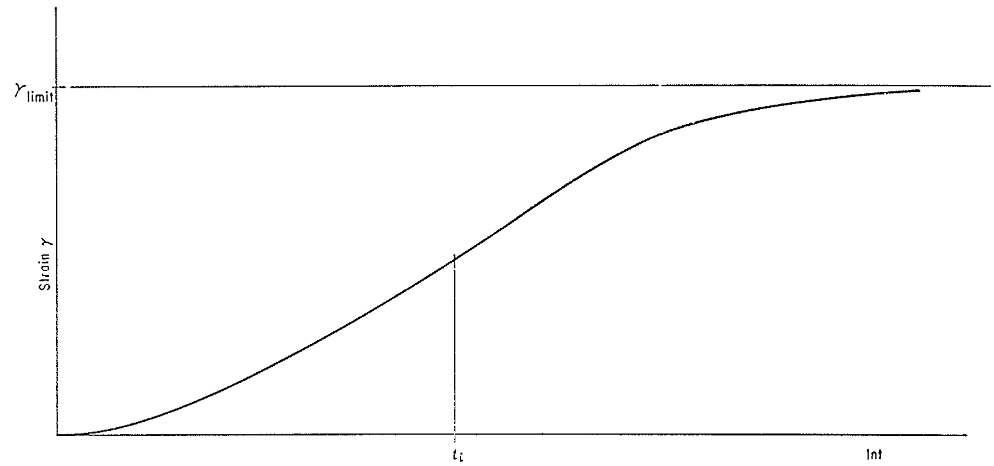

Fig. 2. Schematic diagram of the time dependence of strain.

by Kuhlmann[2] and other investigators, but with a different interpretation of the constants C_1, C_2 and C_3. Equation (4) shows that the often-used logarithmic relation is only an approximation and that at sufficiently long times the strain approaches asymptotically the limit

$$\gamma_{limit} = \frac{\tau^{\circ}_{eff}}{M} - \frac{1}{2}\frac{\Delta H_f^{\neq} - \Delta H_b^{\neq}}{VM}, \tag{6}$$

where $\Delta H_f^{\neq}$ and $\Delta H_b^{\neq}$ = the activation enthalpies in the forward and backward direction respectively.

It follows from eqn. (6) that, because the energy barrier is asymmetrical, the limit strain is less than the total recoverable strain τ°_{eff}/M, and thus the internal stress cannot be relieved completely.

It is customary to represent the relaxed strain as a function of the logarithm of time (Fig. 2). In this representation it follows immediately from eqn. (4) that an inflexion occurs at time t_i given by

$$\tanh\left[2C_1 t_i + 2C_2\right] = 2C_1 t_i .$$

Thus the theory predicts that the inflexion is a function of the temperature T and the initial stress τ°_{eff}. This relation can be tested experimentally.

Type C barrier

The energy barrier is described by the following expressions:

$$A_f \neq A$$
$$V_f \neq 0$$
$$V_b \cong 0 .$$

From the dislocation velocity analysis this type of energy barrier is expected to be associated with the plastic deformation process occurring in Ge and Si.

For this energy barrier the relaxation rate eqn. (3) simplifies to

$$\dot{\gamma} = b\rho A_f \exp\frac{V_f(\tau^{\circ}_{eff} - M\gamma)}{kT} - b\rho A_b .$$

The solution of this differential equation is

$$\gamma = \frac{kT}{V_f M}\ln\left[\frac{A_f}{A_b}\exp\frac{V_f\tau^{\circ}_{eff}}{kT} - \frac{A_f\exp\left(\frac{V_f\tau^{\circ}_{eff}}{kT}\right) - A_b}{A_b}\exp\left(-\frac{b\rho V_f M A_b}{kT}t\right)\right].$$

The recovery strain approaches asymptotically to the limit

$$\gamma_{limit} = \frac{\tau^{\circ}_{eff}}{M} - \frac{(\Delta H_f^{\neq} - \Delta H_b^{\neq})}{V_f M}.$$

When the recovered strain is represented as a function of ln t (Fig. 2), inflexion occurs at time t_i given by

$$\left[1 - \frac{V_f M}{kT}A_b t_i\right]\exp\frac{V_f M A_b t_i}{kT} = 1 - \frac{A_b}{A_f}\exp\left(-\frac{V_f\tau^{\circ}_{eff}}{kT}\right).$$

The inflexion time is again a function of the temperature and the initial stress.

CONCLUSIONS

In a previous study[5] an investigation was carried out to determine if mechanisms with linearly stress dependent activation enthalpy could lead to a rate theory which is capable of explaining the dislocation mobility observations. It was shown that this can be done and that the simplest expression that describes the stress dependence of dislocation velocity is the asymmetrical form of the rate equation.

In the present study the view was taken that the theory of strain relaxation, as well as the theory of any macroscopic test, has to be in full agreement with the dislocation mobility observations. It follows from this that the usual assumption that strain relaxation is controlled by a symmetrical energy barrier and that the corresponding sinh $\alpha\tau$ form of the rate equation is invalid. A satisfactory description has to be asymmetrical.

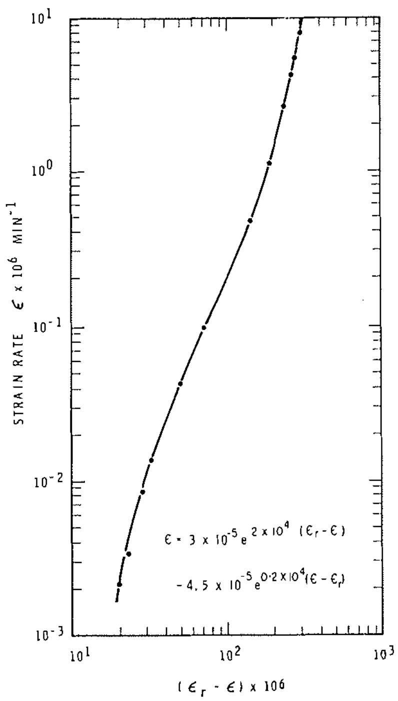

Fig. 3. A typical experimental result obtained in strain relaxation of ice. The points indicate the measured values; the solid line was calculated from the rate equation of the A type barrier where ε is the normal strain and $\varepsilon_r - \varepsilon \propto \frac{\overset{\circ}{\tau}_{eff}}{M} - \gamma$.

The asymmetrical form of the strain relaxation rate equation was analyzed for three types of energy barriers. The dependence of the strain on the temperature and on the initial internal stress was derived for two of these and expressions were obtained which can be tested experimentally. The analysis indicates that the often observed logarithmic relation is only an approximation; logarithmic strain relaxation occurs in the early stage if the activation volume is the same in the forward and backward directions or when $V_b \tau_{eff} \gg kT$. It was also shown that a direct consequence of the asymmetrical barrier shape is that the internal stress cannot be relieved completely. The experiments[4] carried out to check some of the conclusions were in full agreement with the theory (Fig. 3).

The results of this study provide another method for the experimental investigation of dislocation mobility and have a bearing on the stress relaxation as well. This will be discussed in a future paper.

ACKNOWLEDGEMENT

Discussions with L. W. Gold were most helpful and are gratefully acknowledged. This paper is a contribution from the Division of Building Research, National Research Council of Canada and is published with the approval of the Director of the Division.

REFERENCES

1 C. ZENER, *Elasticity and Anelasticity of Metals*, The University of Chicago Press, 1956.
2 D. KUHLMANN, *Z. Physik*, *124* (1947) 468.
3 R. E. REED-HILL AND E. P. DAHLBERG, *Trans. AIME*, *236* (1966) 679.
4 A. S. KRAUSZ, *Scripta Met.*, *2* (1968) 615.
5 A. S. KRAUSZ, *Acta Met.*, *16* (1968) 897.
6 S. GLASSTONE, K. J. LAIDLER AND H. EYRING, *The Theory of Rate Processes*, McGraw-Hill, 1940.
7 G. H. VINEYARD, *J. Phys. Chem. Solids*, *3* (1957) 121.
8 F. WM. CAGLE, JR. AND H. EYRING, *J. Appl. Phys.*, *22* (1951) 22.
9 S. J. HAHN, T. REE AND H. EYRING, Non-crystalline solids, paper presented to *Conf. on Non-Crystalline Solids, New York, 1958*, Wiley, New York, 1960, p. 297.
10 E. OROWAN, *Proc. Phys. Soc.*, *52* (1940) 8.