研究論文

262. *Effect of Impurities on γ -irradiation Hardening of Sodium Chloride Crystals*

NaCl 結晶の γ 線照射硬化に及ぼす不純物の影響

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The radiation hardening effect in sodium chloride single crystals, a large increase in the yield stress in compression by γ -irradiation and its thermal recovery were investigated. The effects of Ag and Ca ions, which are respectively monovalent and divalent impurity, on the thermal healing of the radiation induced hardening and optical absorption were studied. It was found that the thermal stability in radiation hardening was not affected by Ca ions but was influenced by Ag ions and that the thermal recovery of the hardening lags behind the vanishing of color centers.

I. INTRODUCTION

Radiation hardening is an important subject not only in solid state physics but also in the field of engineering, since the phenomenon occurs in engineering materials damaged by irradiation in so complicated a manner that fundamental studies are required. Hardening is introduced into crystals by other methods as well as irradiation⁽¹⁾, for instance, by quenching⁽²⁾, cold work⁽³⁾, additive coloration⁽⁴⁾, addition of impurity and so on. Impurities always play an important rôle in every case when the detailed mechanism of hardening is needed to investigate.

It has been well known that the mechanical strength of the single ionic crystal is very much influenced by the addition of multivalent impurities⁽⁵⁾⁽⁶⁾. Theoretically, Bassani and Thomson⁽⁷⁾ have dealt with the topic on the interaction between dislocation core and point defects. They showed that in NaCl a positive ion vacancy is attracted into a part of core of a (110) dislocation where the lattice is compressed, with a binding or association energy of about 0.4 eV relative to normal lattice positions but that

other impurities have smaller association energies. On the basis of these energies they suggested that the vacancies and the divalent ion-vacancy complexes might be the agent determining the critical shear stress in annealed NaCl, since at lower temperature, *e.g.*, room temperature the divalent impurities tend to form complexes with the positive ion vacancies. On the other hand, according to Eshelby *et al.*⁽⁸⁾, dislocations in an ionic crystal are electrically charged in thermal equilibrium, and are surrounded by Debye-Hückel cloud of vacancies, provided that the energies required to form positive and negative ion vacancies are unequal. They emphasized the rôle of the charge cloud around the dislocation and obtained a yield stress by a purely electrostatic calculation. This charge state is modified by the concentration of divalent ion. As briefly reviewed above, impurity can importantly affect the mechanical properties of the crystals, and moreover comparatively little is known about how irradiation changes the pre-irradiated situation surrounding the dislocation. It is, therefore,

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of value to determine the rôle allotted to impurities in irradiation hardening.

The object of the present work is to investigate the impurity effect on γ -irradiation hardening by examining the thermal stability of yield stress and the optical absorption bands of irradiated sodium chloride crystals.

II. EXPERIMENTAL

1. The preparation of specimens

Experiments were performed on four kinds of specimens of different impurity content. The specimens which are represented by A, P and C were obtained from single crystals grown by Kylopoulos technique. Silver and calcium ions were introduced as chlorides into melted sodium chloride. Those represented by H were purchased from the Harshaw Chem. Co. The concentration of impurities was determined by a spectroscopic analysis*. The specimens were cleaved from a large melt-grown single crystal of sodium chloride. After cleavage, all specimens were annealed in air at 600°C for 10 hr and cooled to room temperature at the rate of 12°C/hr. The dimensions of the specimen used were 4 × 4 × 10 mm throughout the present experiment.

2. The measurement of strain

Strain-stress curves were determined in compression using a 'soft' machine designed so as to give axial loading and to record the strain of the specimen electrically. Stress rate

Fig. 1 Electric micrometer for strain measurement. As the load is applied to a specimen, its strain produces a capacity variation in a tank circuit of Pierce circuit. The variation of resonance frequency of the tank circuit then yields anode current change. A stress-strain curve is obtained automatically by recording the current change against time.

was about 26 g/mm²/sec throughout the experiment. Fig. 1 shows the condenser cell and the mount of the crystal. The small compressive strain which directly caused the corresponding capacity difference, could be detected by the variation in current in the Pierce circuit. An automatic recorder associated with the electronic circuit gives the diagram of strain against stress, as shown in Fig. 2.

Fig. 2 Stress-strain curves for sodium chloride crystals with different impurity content (Measurements were carried out at room temperature.)

Each specimen, with both end surfaces lubricated by saturated brine solution in order to have as uniform distribution of stress as possible, was sandwiched between two thick Telex glass plates. All measurements were made at room temperature in air.

3. The isothermal annealing experiment

Isothermal annealing of γ -irradiated specimens was carried out in a tubular electric furnace held at fixed temperatures. Both

* Through the courtesy of Dr. Hiroyuki Mizuno, Matsushita Elect. Corp.

specimens, for yield stress measurement, and those for optical absorption measurement were annealed at once and together in the furnace at each of several temperatures for 30 min, and then air cooled by removing directly from the furnace. Fig. 3 (a), (b) and (c) show the annealing of hardening for P-, C- and A-specimens, respectively. It is clear from Fig. 3 (a), (b) and (c) that the above mentioned heat treatment does not produce much difference in the value of yield stress of unirradiated specimens.

4. The optical absorption measurement

The optical absorption measurements were made at room temperature with the Shimadzu QB-50 spectrophotometer in the range 200 ~ 800 m μ .

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

1. Effects of impurities on γ -irradiation hardening

The prepared specimens of various impurity concentrations, as shown in Table 1, were

γ -irradiated together at one time at room temperature. They were then subjected to compression tests in the dark. The stress strain curves are demonstrated in Fig. 2 to compare the mode of hardening of these crystals in terms of yield stress, where H2, P2, A1 and C2 indicate the unirradiated specimens, while P3, A4 and C3 indicate the 8×10^6 r γ -irradiated specimens. Table 1 shows the typical values of yield stress results of the present experiment. It is seen from the table that the difference between yield stresses before and after irradiation, σ_f and σ_i , increase with increasing Ca content. However, it is of interest that the ratio σ_f/σ_i is about 2 in all the above cases.

This constancy of the ratio suggests that the increase in yield stress may not be related to divalent impurities. The behavior of yield stress can be qualitatively explained by a pinning mechanism. Take the mean separation distance of dislocation pinning points to be l and the energy required to overcome the barrier by the dislocation be U . If we neglect the internal stress term in Seeger's expression⁽⁷⁾⁽⁸⁾, the critical shear stress then is given by

$$\sigma = (U - \beta kT) / lb d \quad (1)$$

Table 1 The yield stresses of sodium chloride crystals before and after γ -irradiation

Crystal	Impurity (m/o)	Yield stress, σ_i , as annealed (g/mm ²)	Yield stress, σ_f after irradiated 8×10^6 r (g/mm ²)	$\sigma_f - \sigma_i$	σ_f/σ_i
H (Harshaw)	$(0.56 \sim 1.70) \times 10^{-3}$ CaCl ₂	41.8 (Average of H1 and H2)	67.7	20.4	1.62
A (Containing Ag and Ca)	$(2.14 \sim 6.40) \times 10^{-3}$ AgCl $(1.70 \sim 2.82) \times 10^{-2}$ CaCl ₂	224 (A1)	542 (Average of A3 and A4)	318	2.42
P (Containing Ca)	$(0.56 \sim 1.7) \times 10^{-2}$ CaCl ₂	200 (Average of P1 and P2)	462 (Average of P3 and P4)	262	2.31
C (Containing Ca)	$(1.12 \sim 1.70) \times 10^{-1}$ CaCl ₂	895 (C2)	1640 (Average of C3 and C4)	745	1.83

where β is a constant, b the dislocation strength, and d denotes the quantity relating to the width of the barrier.

Now if we assume that the hardening is due only to a decrease in loop length of moving dislocation, we can expect

$$l = l_0 / \{1 + C(D)\} \quad (2)$$

where l_0 is the initial loop length at $D=0$, and $C(D)$ means the concentration of pinning against irradiation dose D . Substitution of l in Eq.(1) gives that

$$\sigma_f = \{(U - \beta kT) / l_0 b d\} \{1 + C(D)\}$$

therefore, if $\sigma_0 = (U - \beta kT) / l_0 b d$ is taken, then

$$\sigma_f = \sigma_0 \{1 + C(D)\} \quad (3)$$

The $C(D)$ is an increasing function of the irradiation dose, though its exact form is not known. For the present case, as σ_f/σ_i is about 2, the value of $C(D)$ is independent of the impurity content for 8×10^6 r γ -irradiation. It is meaningful here to compare this result with those of other investigators. Podachewsky found that the yield stress and the fracture strength of single alkali halide crystals were increased by a factor of about 2 after 250 kV X-irradiation⁽¹²⁾. As regards metals, Kunz and Holden⁽¹³⁾⁽¹⁴⁾ found the yield stress of single crystals of iron was nearly doubled by neutron irradiation. On the other hand, Makin and Whapham⁽¹¹⁾ found that the yield stress of lithium fluoride crystals, irradiated by 1 MeV electrons, is raised to 15 times the unirradiated value with the dose of 10^{16} electrons/cm². Consequently the precise 'growth curve', *i.e.* the yield stress as a function of irradiation dose, is required before establishing a general law of radiation hardening, since several mechanisms might

operate as irradiation proceeds. The specimen characteristics should also be considered.

2. Isothermal annealing of radiation hardening and optical absorption

Simultaneous studies of the recoveries of hardening and optical absorption were performed in order to obtain some correlation between the recovery in yield stress and the number of particular color centers.

The experimental procedures were as follows: both specimens for optical absorption and for yield stress measurements were annealed at once and together at the selected temperatures for 30 min, and were air quenched. Measurements followed. One might argue that this procedure could cause great quenching strain and thus introduce additional hardening into the specimens. The examination of the effect of this treatment on the yield stress proves, however, that this is not the case as shown in Fig. 3.

The influence of annealing on the yield

(a) Recovery curve for P-specimen (b) Recovery curve for C-specimen (c) Recovery curve for A-specimen
Closed squares represent the variation of the yield stress of non-irradiated crystal submitted to the same thermal treatment as the irradiated one.

Fig. 3 Thermal recovery of the hardening

stress of P-, C- and A-specimens at room temperature are shown in Fig. 3 (a), (b) and (c), respectively. The shapes of the annealing curves against annealing temperatures for P- and C-specimens are generally similar, though

they contain different amounts of Ca impurity. On the other hand, the annealing curve for the A-specimen is more wavy than those for P- and C-specimens. This suggests that the irradiation hardening in A-specimen is influ-

Fig. 4 Thermal bleaching of various color centers

enced by many kinds of silver activated color centers which were named A, B, C, D, E and F bands and so forth⁽¹⁰⁾⁽¹¹⁾. As the annealing proceeds some parts of these centers are annealed out, but the remainders appear to convert from one to another, and then they interact with dislocations in various complicated manners. Fig. 4 (a) and (b) show the results of thermal bleaching in optical absorption of P- and C-specimens respectively. Fig. 4 (c) demonstrates the inter color center conversion in the A-specimen with elevated temperature.

Comparison between the annealing curves of yield stress and concentration of color centers, especially F centers, clearly show that the hardening recovery lags behind F center recovery in isothermal annealing. This shows that the annihilation of color centers do not necessarily mean the recovery in yield stress. The complex color centers or vacancy clusters might be another cause of γ -irradiation hardening. The existence of hardening due to F centers seems to be masked by other types of hardening. This might be explained qualitatively either by a mechanism of anchoring dislocation in Frank-Read sources, or jog formation on the dislocation by irradiation induced point defects.

Recent studies on internal friction^{(15)~(17)} however, show that radiation induced pinning agents seem to be formed very close to the dislocation even at very low temperature, and that the rate at which the pinning occurs is unaffected by temperature. This means that the vacancy diffusion is not enough to explain the pinning mechanism. So far, a primary effect of radiation hardening appears to be unrelated to impurity.

The conclusions of above discussion are as follows:

- (1) γ -irradiation hardening in sodium chloride crystals in terms of yield stress seems to be independent of impurity concentration.
- (2) The reason the ratio of yield stress, after γ -irradiation by 8×10^6 r, σ_f , to that as annealed, σ_a , is close to 2 for the present case independently of impurity concentration, might be explained by assuming a pinning model.
- (3) The thermal recovery of hardening lags behind the recovery of F centers which are predominant point defects introduced by irradiation.
- (4) Thermal stability which is expressed by

the shape of thermal recovery of yield stress, is not affected by Ca ions, but is influenced, to some extent, by Ag ions. Many kinds of color centers, which were induced by Ag-dope and irradiation, might be the source of this increased stability.

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研究論文

263. A Study of Plutonium Recycle in a Gas-cooled, Graphite-moderated Reactor, (I)

黒鉛減速ガス冷却炉におけるプルトニウムリサイクルの研究, (I)

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A fuel cycle analysis of plutonium recycle in a gas-cooled, graphite-moderated reactor was performed with using the fuel cycle code which can be used for IBM 704, 709 or 7090 computer. The fuel cycle variables investigated were three initial uranium enrichments (natural, 1.0 or 1.3 a/o), four plutonium recycle ratios (total, 90%, 75% or none) and two methods of fuel management (batch irradiation and bidirectional fuel management).

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