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EFFECT OF PRINT-OUT SILVER ON INTERNAL FRICTION OF SILVER CHLORIDE SINGLE CRYSTAL

By

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Abstract

Effect of print-out silver on the internal friction was investigated in AgCl single crystals. Strain-independent decrement δ_I and strain-dependent decrement δ_H are affected in a quite different way. Particularly for the latter case, δ_H measured under excitation driving voltage is much influenced upon ultraviolet radiation, compared to that in the non-excited state. The possible explanations to the results are here presented.

Introduction

One of the unique ways to study the mechanical properties of AgCl is to observe the dislocations in the crystal in one way or another, since the mechanical behavior of crystals largely depends on that of dislocations. In order to make dislocations inside a crystal visible, we have to decorate them by precipitating foreign substances on the dislocations, or to print out silver specks on the dislocations. Dislocations provide excellent sites where either foreign atoms or photoelectrons may be trapped. The former method was developed mainly by MITCHELL and his group since 1957[1], the latter by HEDGE and MITCHELL[2] and by CASTLE[3], and CHILDS and SLIFKIN[4] who used the same principle initiated by HAYNES and SHOCKLEY[5]. The process by which silver atoms deposit on the dislocation (and slip bands and grain boundaries) has been discussed by SEITZ in 1951[6]. The method of printing out silver photoelectrically on the dislocations seems to have several advantages over the chemical method: for example, the arrangement of dislocations in question is not disturbed by the decoration procedures themselves, and also the decoration can be obtained throughout the thickness even in a thick sample.

MILLER[7] measured the strain-stress curve for two samples, one of which was exposed to light to form internal print-out silver, the other not exposed. The print-out silver in the interior of AgCl raises the initial yield stress by 60%. This is consistent with the work by SHASKOL'SKAYA and VEKILOV[8], in which the stress-strain relation was measured on thin wire of polycrystalline AgCl, exposed and not exposed. Photolytic silver evidently locks movable dislocations, causing the crystal to be mechanically

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harder. Thus one may reason that internal friction in AgCl, measure of dislocation damping, could be affected by an exposure to light. A. FUKAI and L. SLIFKIN[9] conducted for the first time the measurement of internal friction of AgCl by the method of composite oscillator to find the strain-aging phenomena. Results obtained are qualitatively consistent with works by KABLER, MILLER and SLIFKIN[10].

Experimental Procedures

Method of Measurement

Measurements of internal friction have been carried out by means of the method of the composite oscillator, initiated by MARX[11]. This method utilizes the mechanical vibration obtained piezoelectrically in quartz properly cut with regard to crystallographic orientation, so that the coupling between longitudinal and shear modes may be minimized along the desired direction. It is customary to use two quartz rods of the same cut and dimensions, cemented end to end. One crystal, called the driver, produces longitudinal mechanical vibration in an axial direction in response to an oscillatory electric signal applied to two side faces. The other crystal, called the gauge crystal, picks up an electric signal developed perpendicular to the direction of the mechanical oscillation which is transferred from the driver crystal through the joint between them. The lengths of the driver and gauge crystals must be matched to the frequency to be used within 0.5%, so that the joint of the vibrating components coincides with the stress node of the normal mode of vibrational strain. The glued joint thus gives no contribution to the decrement, a measure of the energy loss, of the vibrating system. The two opposite sides of each component are silver-plated in proper portion of total length. The cross section of each is usually square for the technical convenience. The two component quartz rods, assembled by gluing end to end, are vertically supported by thin wires at horizontal notches located at the centers of the silver-plated sides. The supporting wires are also used as input and output lead wires. The notched portion contacting the supporting wire corresponds to the location of maximum strain amplitude and hence of zero displacement. When assembled into a single unit, silver-plated opposite sides of one component crystal are axially rotated 90° relative to those of the other in order to avoid electrostatic coupling between them. The driver and gauge crystals, when assembled, give rise to a background damping present even when a specimen is not mounted at either end of this unit.

Marx derived a relation between the voltage on the gauge crystal V_g and the strain amplitude ε_g and also a relation between decrement of the total system and V_d/V_g, where V_d is the voltage applied to the driver crystal[11]:

$$\varepsilon_g=\left[4.54\times 10^{-8}\frac{1}{w_g}\frac{C_g+C_m}{C_g}\right]V_g, \tag{1}$$

$$\delta_t=\left[9.85\times 10^{9}\frac{C_g}{C_g+C_m}\frac{w_g}{2}\frac{b_g}{l_g}\frac{1}{m_t f_t^2}\right]\frac{V_d}{V_g}, \tag{2}$$

for the fundamental frequency. The meaning of quantities in these formulas are as follows:

b_g, w_g, l_g: the breadth of electrode face, width of nonsilver-plated face, and the length of gauge crystal, respectively

C_g, C_m : capacitance of equivalent circuit of gauge crystal, and that of measuring circuit, respectively

m_t : mass of oscillating system

δ_t, f_t : decrement of the total system, resonant frequency, respectively

In deriving the formulas, it is assumed that driving crystal and gauge crystal are silver-plated on the two opposite sides along the full length for the driver and only in the middle one-third for the gauge. The quantity within the bracket is considered constant for a given apparatus, except in the region where f_t changes due to decrement in high strain-amplitude region of an added specimen. So the strain amplitude in the gauge crystal is proportional to output voltage V_g. The decrement δ_t for the total system, specimen plus two quartz crystals, is simply proportional to the ratio of driving voltage to picked-up voltage, V_d/V_g.

The experimental procedure to measure the decrement is as follows. Suppose we apply an input voltage V_d with the frequency close to expected resonant frequency. Then all we need to know is output voltage V_g for the system at resonance; that is, the maximum V_g that could be obtained for the constant V_d by tuning the frequency to the exact resonant frequency f_t.

For a given set-up with the specimen mounted, one has to know the constants in the bracket in the preceding formulas. This will be discussed shortly. When δ_t is obtained, the decrement of the sample δ_s is calculated by

$$\delta_s = \frac{\delta_t m_t - \delta_q m_q}{m_s}, \tag{3}$$

where

$$m_t = m_s + m_q. \tag{4}$$

m_q and δ_q are the mass and decrement of driver-gauge component, respectively. The strain amplitude in the specimen ε_s is related to that in gauge crystal ε_g as

$$\varepsilon_s = \frac{c_g}{c_s}\varepsilon_g = \frac{l_g}{l_s}\varepsilon_g, \tag{5}$$

where c_g and c_s are the axial velocities of sound in quartz and specimen, respectively. Equation (5) shows the strain amplitude of the specimen is inversely proportional to the ratio of the length of gauge crystal to that of specimen. With the help of equation (3) and (5), δ_s and ε_s can be obtained, provided the decrement of the background is known.

Specimen

Silver chloride crystals were purchased from the Harshaw Chemical Company in the shape of discs, 3″ diameter and 1/4″ thick. Slight etching by dilute hypo solution revealed that each disc usually consisted of two or three large subgrains. When cutting specimens from the original blank, these grain boundaries were avoided as far as possible, although it does not seem to affect any contribution to the decrement at the intermediate frequency as employed in this work. As the first procedure of preparation of specimen, the samples were cut out of the blank in oversized dimensions, $2'' \times 3/8'' \times 3/8''$, using a custom-made stainless milling blade. Kerosene was used as a lubricant in cutting the blank in order to prevent overheating. Each sample was then gently polished on silicon carbide polishing papers down to the final size, $3/16'' \times 3/16'' \times 2''$, using distilled water as a lubricant. Then the crystals were etched on a selvyt cloth saturated with a dilute solution of KCN, to obtain smooth surfaces. All specimen thus prepared were annealed on quartz powder at approximately 430°C for a day to remove mechanical strain induced in the crystals during the preparation procedures.

Matching the length of the specimen to the resonant frequency of the driver-gauge composite was carried out by gradually polishing down the length on SiC polishing papers, until the resonant frequency of the total system was equal to that of the composite oscillator, within the allowable limit of 1.5%. In mounting the specimen, ordinary machine grease was used as a glue.

Calibration of specimen decrement was performed by measuring the half width of the resonance curve. The resonance curve was measured twice whenever the sample was changed. In one case the decrement calibrated by this half-width method was compared with one obtained by the method of free damping, in which the free damping of the strain amplitude after cutting off the driving voltage was photographed on an oscilloscope. These two coincide within 5%, comparable to the error due to the mounting.

Apparatus

Quartz crystals, ordered from the Valpey Crystal Company, Holliston, Massachusetts, were $-18.5°$ X cut α-quartz. The length, matched to the desired frequency of 35kc/s, was 2.88″, the cross section being $3/16'' \times 3/16''$. Each was notched on two facing sides in a wedge shape, $0.02-0.025''$ deep, on which the thin silver layers were coated along the full length for the driver and over a center one-third for the gauge crystal. These two crystals were cemented with beeswax. This composite unit was then supported vertically at the notches of each component by #5 steel wire of 0.014″ diameter, which was also used for electrical leads for measuring V_d and V_g. The driving voltage was provided by a General Radio Beat Frequency Audio Oscillator Model 1304B, for which the output frequency can be varied by small amounts, about 1 c/s. This frequency was monitored by a Hewlett Packard Electronic Counter Model 521C. Input and output voltages were all measured by Hewlett Packard Vacuum Tube Voltmeters Model 400H.

For the purpose of obtaining the print-out silver within the specimen, the apparatus built by CHILDS[12)] has been used with slight modification of the electrodes. The basic principle of this method (hereafter called the HAYNES-SHOCKLEY method, or simply

H–S method) is the following: The electrons photoelectrically produced at the surface of the crystal are made to drift freely into the interior of specimen by an externally applied pulsed electrostatic field. This field decays with relaxation time dependent on the polarization field developed at the surfaces of the crystal. Since the lifetime of photoelectrons in silver chloride at room temperature is of the order of 1 to 10 microseconds, the experimental set-up must be such that the electric field inside the crystal is maintained at an appreciable level during this time which, fortunately, is much less than the polarization decay time. The repetition rate of the electric field is 1,000 sec^{-1}, with a peak voltage of about 2,000 volts. The duration of the light pulse, synchronized with the voltage pulse, is 10 microseconds. This flash produces approximately 10^9 photoelectrons per cm^2 at the surface. In this work, the sample was exposed to the light while mounted on the composite oscillator, thus enabling one to avoid the interruption and handling strains due to the mounting. The decrement of the total system was observed to decrease by 5% due to the mounting of the electrodes of the H–S apparatus which barely touch the surface.

Presentation of Data

The present experiments were concerned with the effect of deposition of print-out silver on the dislocations. It was found that both the strain-independent decrement and strain-dependent decrement were influenced but in different ways, as will be seen

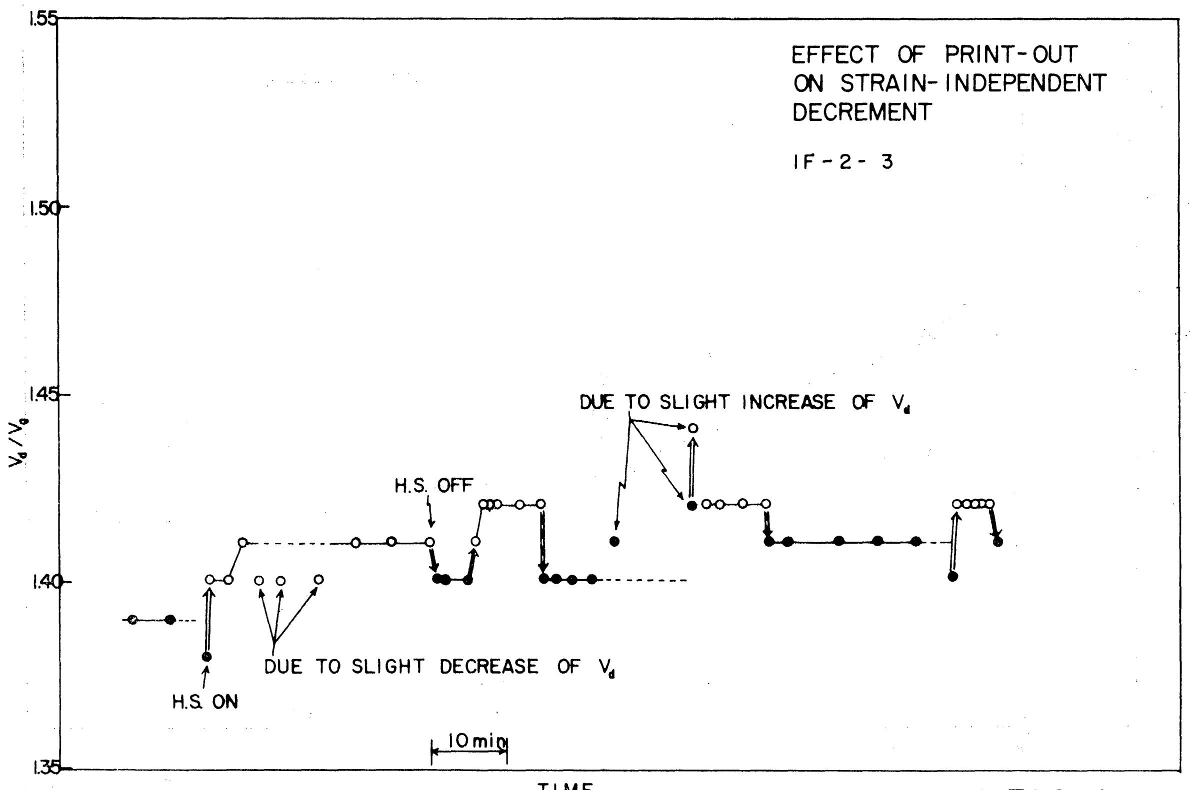

FIG. 1

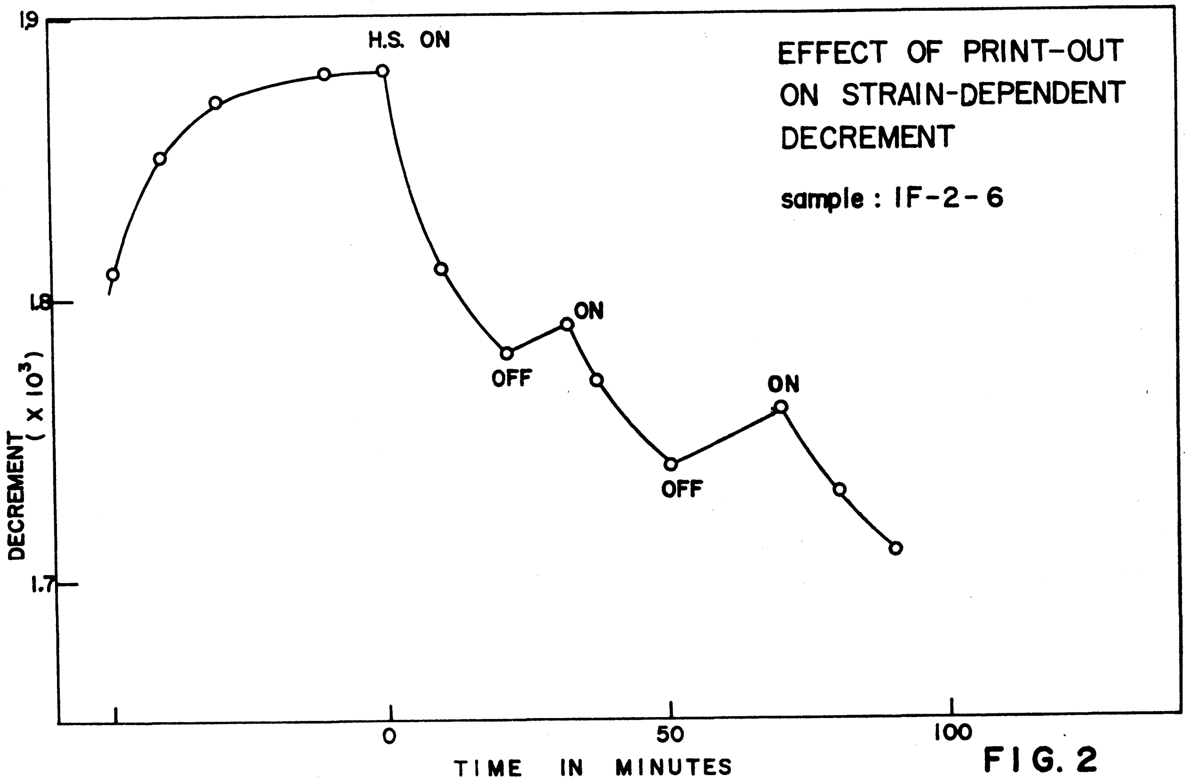
EFFECT OF PRINT-OUT
ON STRAIN-DEPENDENT
DECREMENT
sample : IF-2-6
H.S. ON
ON
OFF
ON
OFF
DECREMENT (x 10³)
1.9
1.8
1.7
0
50
100
TIME IN MINUTES

FIG. 2

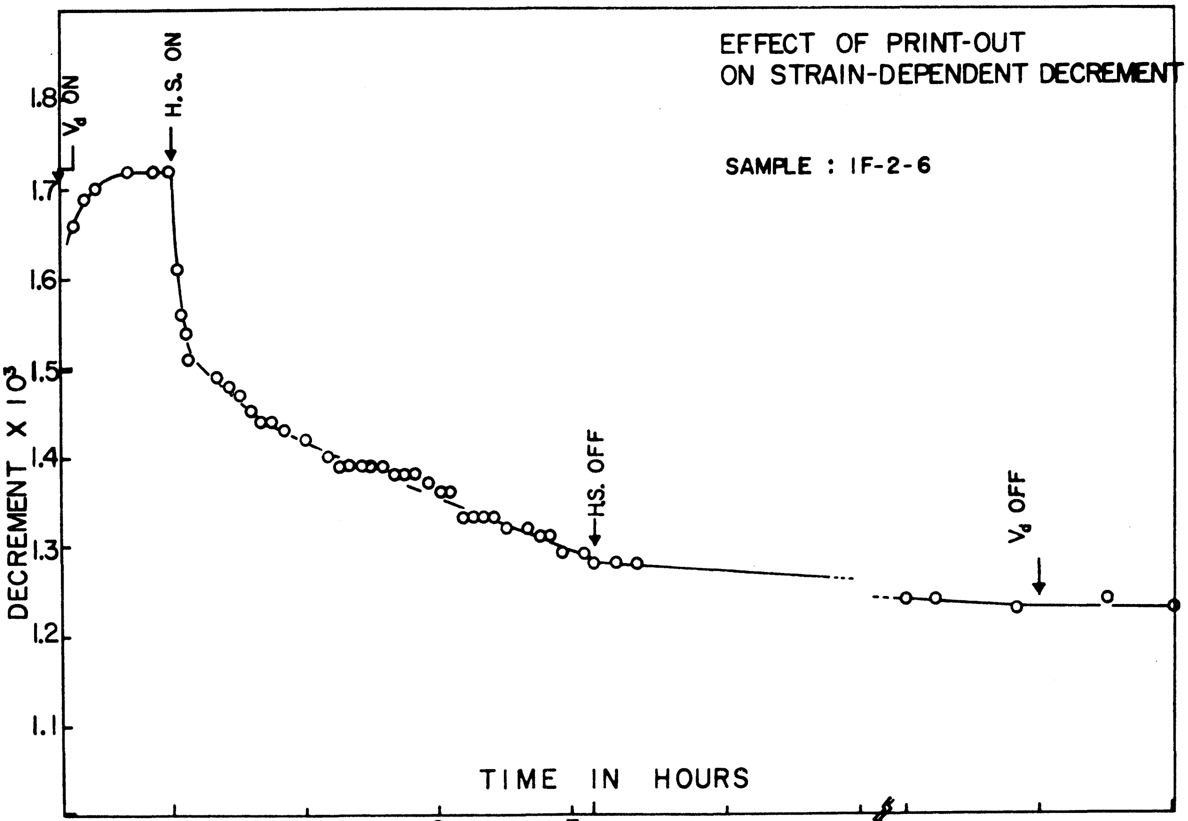
EFFECT OF PRINT-OUT
ON STRAIN-DEPENDENT DECREMENT
SAMPLE : IF-2-6
V_d ON
H.S. ON
H.S. OFF
V_d OFF
DECREMENT X 10³
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
TIME IN HOURS
0
1
2
3
0
1
2
4
5
6

FIG. 3

in Figure 1, Figure 2 and Figure 3. Figure 1 shows the response at low strain amplitude of V_d/V_g (proportional to the total decrement) to photo-electric exposure in the H–S apparatus. A reproducible and instantaneous change was observed; the decrement increases upon turning H–S on and partly decreases with H–S off. The amount of

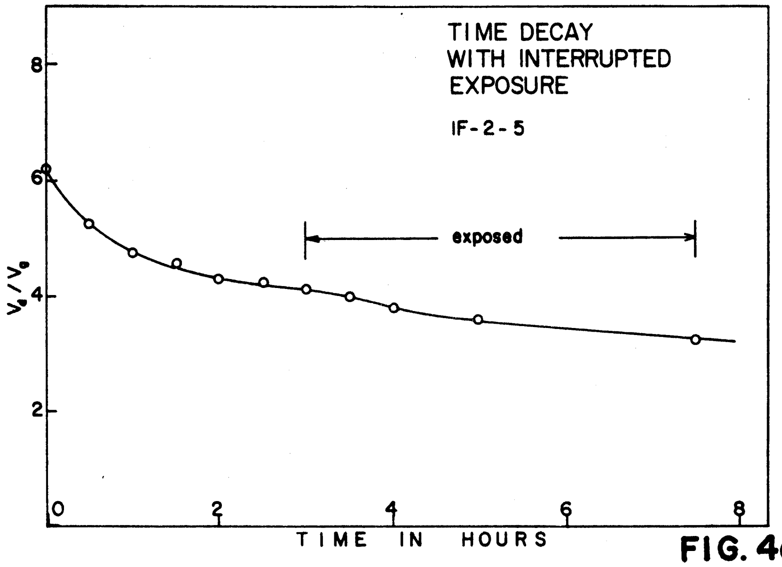

FIG. 4a

ln P VS. ln t PLOT OF FIG. 4a

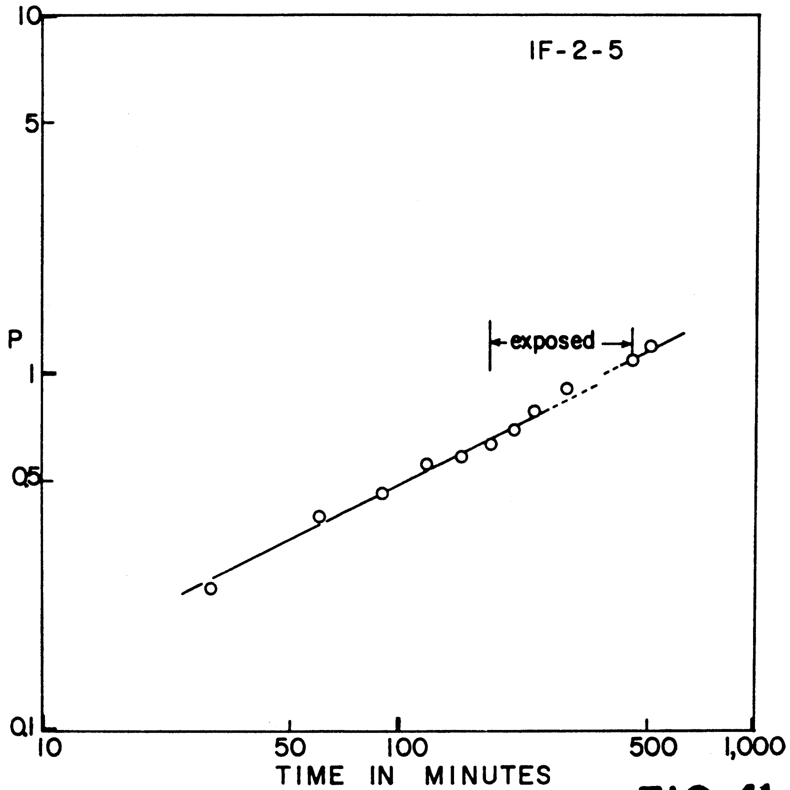

FIG. 4b

change in decrement of specimen was found to be 3%. The strain-dependent decrement, on the other hand, while the crystal is under excitation by the driving voltage, is affected significantly by the H–S exposure, as seen in Figure 2. An immediate increase in decrement is observed whenever the light from the light source in H–S apparatus is shut off. The decrease of decrement due to the excitation voltage after the light is turned on again verifies that the effect observed is directly connected with photolysis caused by the light exposure. Data shown in Figure 3 were obtained in the same sample IF–2–6 as in Figure 2 with the time of H–S exposure extended to three hours. Significant difference here from the previous run is that the decrement does not show any sign of increasing due to the exciting voltage after turning off the lamps. Time decay experiments[9], measurement of decrement after excitation in an elapsed time, have also been carried out on the exposed samples. In Figure 4a, the sample was interruptedly exposed to the light during such a decay process. Note that in such a decay experiment, no driving voltage is applied except momentarily in order to follow the decay process. Figure 4b is a ln P vs. ln t plot of the data shown in Figure 4a, which

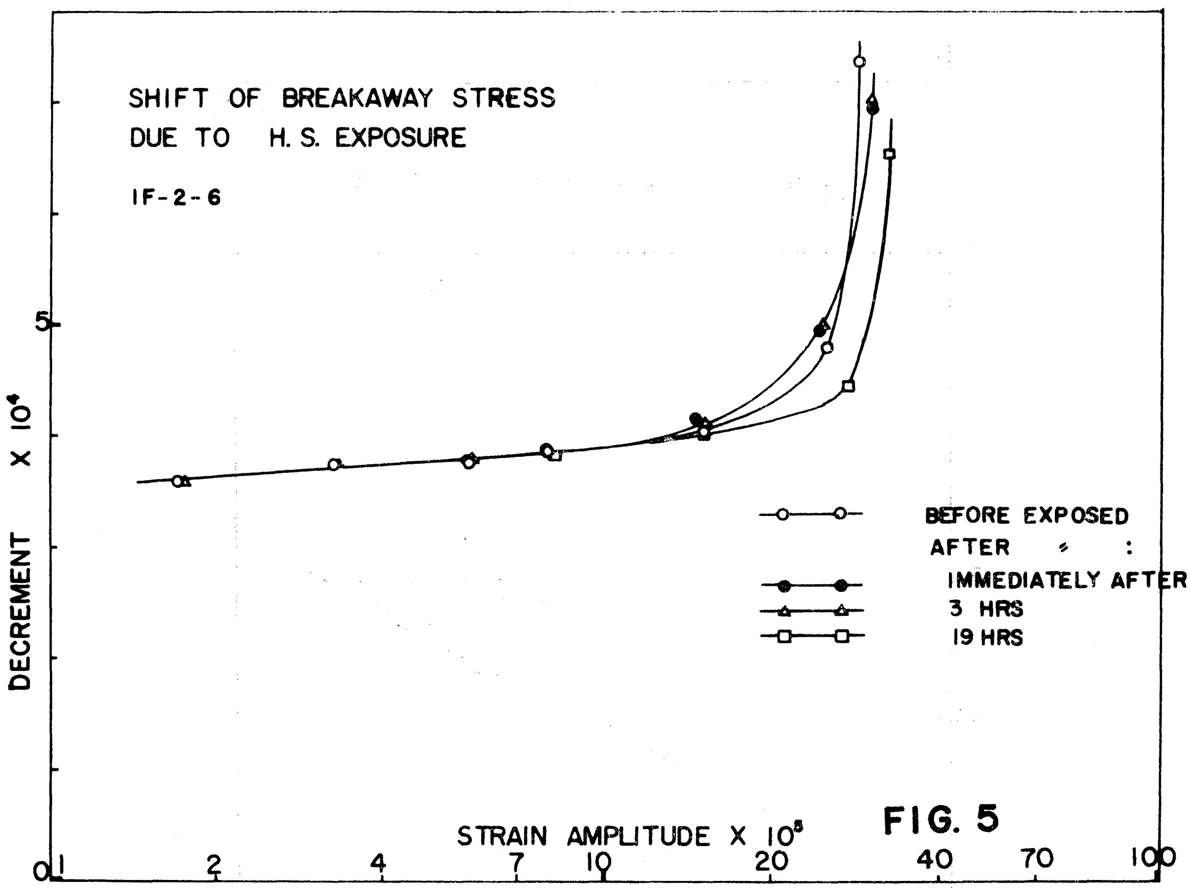

FIG. 5

indicates that the long term decay process remains approximately the same in spite of the interrupted exposure. Here P stands for $\ln(\delta-\delta_0/\delta_1-\delta_0)$, where δ_0 is the decrement at the start of excitation, δ_1 is the decrement at the end of excitation, δ the

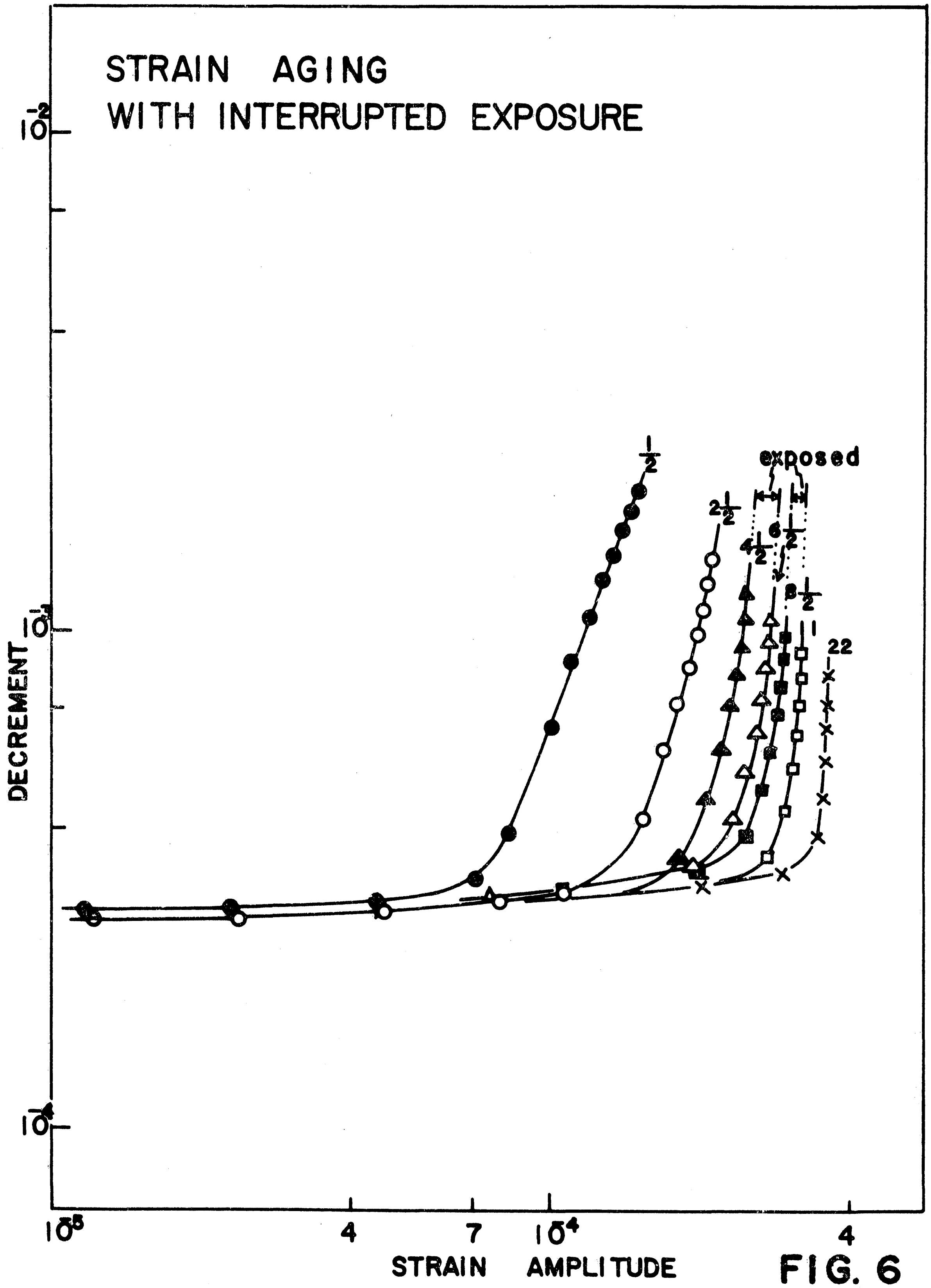
STRAIN AGING
WITH INTERRUPTED EXPOSURE
DECREMENT
10⁻²
10⁻³
10⁻⁴
exposed
22
STRAIN AMPLITUDE
10⁻⁵
4
7
10⁻⁴
4

FIG. 6

measured decrement during a decay process. t is the time from a cessation of excitation. These data were taken with momentary pulse of constant driving voltage, not with constant strain. Thus, no quantitative analysis may be done with regards to the rate of time decay. The decay rate has also been checked in a specimen exposed prior to the mounting. The results were found to be almost the same as the unexposed specimen, within the experimental error mentioned previously. This suggests that the decay of the decrement is caused by point defects diffusing to the fresh dislocations introduced in mounting—possibly by handling. Although the effect of exposure on a stationary dislocation (i.e., exposing the specimen under no excitation) seems less pronounced, Figure 5 shows that the breakaway stress (or corresponding breakaway strain) shifts ultimately. This sample was left idle after mounting for two days before exposure, so that no aging is taking place. Observation of the specimen under the microscope showed decoration of dislocations in 1/3 of the total volume of the specimen. The effect of print-out silver on the time change of decrement vs. strain-amplitude relation just after mounting, however, has been checked by using the sample IF-2-6, as shown in Figure 6. The effect observed seems less distinctive, but detectable.

Discussion of Data

Since the strain-dependent and strain-independent decrements have been observed to have different dependences on H-S exposure, it seems appropriate to discuss separately these two types of decrement. This would also be acceptable from the point of view of the current pinning model which treats these two decrements separately[13].

Strain-dependent Decrement

An analysis in terms of GRANATO-LÜCKE model has been attempted on the data on the samples exposed in the H-S apparatus. The data in Figure 5 unfortunately does not have enough points in the strain-dependent region to make a G-L analysis possible. The fact that the shift of the breakaway strain took place after a certain duration of time suggests a gradual increase in the pinning strength. This type of analysis is made, more or less, clear by the data in Figure 6, where the exposure interrupted the aging process. The G-L plot thus obtained shows that the slope increases with time during the exposure just as the case for nonexposed state, however, after cessation of H-S exposure the slopes do not continue to increase but stay almost constant for a time, starting to increase again after several hours. An increase in slope of G-L plot indicates an increase in the concentration of pinning points on the dislocations; L_N, internodal distance along dislocations, also increases. During the period of constant slope, L_N is either constant or perhaps even decreases. Although the increase in L_N during the aging process is not well understood, one might conjecture that after exposure the print-out silver preferentially anchors the dislocation at already occupied sites, thus strengthening the pinning, while some of these pinning points might develop to such a strength that they inhibit the increase of L_N.

The effect of print-out on strain-dependent decrement δ_H depends on the state of the dislocations. Thus, dislocations in motion under a sufficiently large oscillatory stress seem to be effectively anchored by photoelectrically produced silver atoms (print-out silver), while the dislocations in equilibrium or in relatively small oscillatory motion at the time of exposure in the H–S apparatus are less affected. Since the displacement of dislocations in motion at the peak of curve in Figure 3 is probably more than 10 atomic distances, sufficient to leave much of the charge clouds behind, it is conceivable that the oscillating dislocations have more chance to trap Ag^+ or molecular Ag at their jogs or kinks than the stationary ones. According to Seitz[6)], the possible sites for the trapping of Ag^+ are halogen ion vacancies at jogs of edge dislocation (incipient halogen ion vacancies). It is also possible that silver specks of molecular size formed in the immediate neighborhood of the oscillating dislocation quite efficiently pin the fast moving dislocations. The fact that δ_H can no longer be excited after a long exposure, as shown in Figure 3, demonstrates the enhancement of pinning strength due to exposure. No change of δ_I, strain-independent decrement, as a result of exposure was detected, thus supporting the inference reached in the preceding paragraph that pinning due to print-out silver occurs preferentially at sites previously occupied.

Strain-independent Decrement

The small but immediate response of δ_I to ultraviolet radiation in Figure 1 seems to be the same type of phenomena as that reported by Vekilov[14)], except that his data show quite a large amount of change (30%) and a gradual increase in δ_I upon turning radiation on. As proposed by this author, this may be due to the ionization and removal of a small fraction of the print-out silver atoms on the dislocations, thus increasing L_c, distance between minor pinning points.

Summary

The effect of print-out silver on the strain-dependent decrement is significant while the effect on the strain-independent decrement is small but definite. The former is ascribed to the jogged nature of fast moving dislocations that might easily trap Ag^+ or molecular silver in addition to the pinning by print-out silvers produced in the direct neighborhood of dislocations. The latter may be due to the photoionization of silver atoms on the dislocations. Analysis of decrement versus strain amplitude curves taken in the strain-aging sequence with a superimposed interrupted ultraviolet exposure indicates that silver deposits on the dislocations preferentially at sites already occupied, thus strengthening the pinning. This conclusion is corroborated by the experimental fact that the breakaway stress increases upon exposure.

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