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EFFECT OF VACANCY CLUSTERS ON YIELDING AND STRAIN HARDENING OF COPPER

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J. Galligan and J. Washburn

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Abstract

Clustering of excess vacancies in copper single crystal specimens was followed by resistivity, x-ray small angle scattering, and stress-strain curve observations.

No change in yield stress or strain hardening rate was associated with excess vacancies when they existed primarily as single vacancies, divacancies or perhaps slightly larger aggregates. An increase in the critical resolved shear stress at the yield that was independent of the orientation of the tensile axis accompanied the growth of vacancy clusters in the size range 10 Å to 30 Å. Larger clusters also were associated with orientation dependent changes in the strain hardening characteristics.

EFFECT OF VACANCY CLUSTERS ON YIELDING AND STRAIN HARDENING OF COPPER

by

J. Calligan* and J. Washburn**

INTRODUCTION

Quenching of copper crystals from near the melting temperature can result in retention of a vacancy concentration of 10^{-5} to 10^{-4}. On aging at a temperature high enough for vacancy migration, these excess vacancies tend to cluster. The defects finally formed involve very large numbers of vacancies (of the order of 10^4) in the form of prismatic dislocation loops or stacking fault tetrahedra. (Smallman et al. 1959, Cotterill 1962) These have also been studied in detail for several other FCC metals by transmission electron microscopy. (Hirsch et al. 1958, Silcox and Hirsch 1959, Mader et al. 1961, Cotterill 1961, Cotterill et al. 1962) Large prismatic loops or tetrahedra result in a moderate hardening of the crystal. (Maddin and Cottrell 1955, Tanner and Maddin 1959, Kimura et al. 1959, Meshii and Kauffman 1959)

Irradiation experiments show that hardening can also be produced by much smaller clusters that cannot be clearly identified by transmission electron microscopy as loops or tetrahedra. (Blewitt et al. 1957, Makin 1957, and Makin and Blewitt 1962) These have been called "black spot" defects. They may be stacking fault tetrahedra or loops with dimensions less than 50 Å. It has been suggested by de Jong and Koehler (1963) that vacancy clusters as small as six vacancies can collapse to form a stacking fault tetrahedron

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and that these can grow by absorbing individual or divacancies at their edges. Because small clusters within the size range 10 Å to 50 Å can be formed in very great density in a crystal by heavy particle irradiation, the hardening that can be achieved can be very much greater than that possible by quenching and aging.

It also seems likely that small clusters of vacancies and interstitials are formed by moving screw dislocations. These may play a much more important role in strain hardening than is usually assumed. The flow stress might not be dependent only on the dislocation substructures that are observed, but also on the density of invisible clusters of point defects. (Hashburn 1960) Therefore, further investigation of the effects of small vacancy clusters on mechanical properties should be important not only to a better understanding of quench hardening and radiation hardening but perhaps also to the theory of strain hardening.

The disappearance of single excess vacancies and divacancies can be followed during aging of a quenched crystal by electrical resistivity measurements. If it is assumed that they disappear at clusters or voids, then some information concerning the growth of clusters is obtained.

The growth of the clusters themselves in the size range 10 Å to 100 Å can be followed by small angle x-ray scattering, provided that double Bragg scattering can be avoided. X-ray small angle scattering measurements on quenched copper crystals aged at 80°C have revealed the formation of clusters having oblate spheroidal shapes. (Chik et al. 1962)

In the present experiments the relation between hardening and cluster size was studied by comparing small angle x-ray scattering measurements with stress-strain curves after different amounts of aging at 20°C of quenched copper crystals. A series of test temperatures and two different initial orientations of the single crystal specimens were employed.

EXPERIMENTAL PROCEDURE

Pure (99,999%) copper obtained from American Smelting and Refining Company was used for all the experiments. The copper employed for the resistivity and mechanical measurements was drawn into wire .04 cm in diameter by Sigmund Cohn Co., Mount Vernon, New York.

For small angle scattering measurements single crystal sheets 1 x 1 x .02 cm were grown by recrystallization. After cold rolling a copper bar to about 95% reduction in thickness, it was heated in an evacuated mullite tube (pressure $< 10^{-5}$mm Hg) for 30 minutes at 600°C followed by four days at 1030°C.

Wire crystals for mechanical testing and electrical resistivity measurements having either a [111] axis or an axis near [123] were grown from the melt, ten at a time in a graphite mold. The wires were surrounded by fine graphite powder that was clamped between two graphite slabs, one of which was grooved. The ends of the wires were clamped in contact with a seed crystal having the desired orientation. Specimen diameter was .015 cm.

(a) Small Angle Scattering Measurements

After chemical polishing, crystals were selected that did not give Bragg reflections when placed relative to the beam in the same orientation to be used for small angle scattering measurements. These selected crystals were heated by induction to 1070°C in a helium atmosphere at a distance of only one centimeter above a quenching bath. They were quenched into an aqueous solution of calcium chloride at -20°C. The length of travel within the bath was made long so that liquid flow past the crystal helped to remove gas bubbles. The cooling rate was in excess of 10^{4}°C/sec. After quenching, the specimens were immediately cooled to -196°C.

The scattered intensity in the range $\frac{1}{2}$ to 3° from the primary beam was measured with the geometry shown in Fig. 1. During the measurement the specimen temperature was maintained at -196°C. A helium path was provided for the X-ray beam resulting in measured intensities of 10^6-10^7 cps.

Changes in scattering due to clustering were followed by allowing the crystal to warm to room temperature for short intervals of time followed by recooling to -196°C for the next scattering measurement.

(b) Electrical Resistivity

For resistivity measurements, copper potential leads .002 cm in diameter were attached to the wire crystals by sintering in a vacuum at 900°C.

Wire specimens were heated for quenching by passing a current through the wire while it was inclosed in an evacuated chamber. The walls of the chamber were maintained at -196°C. Quenching was accomplished by cutting off the heating current and simultaneously introducing helium gas into the chamber. Electrical contacts and mechanical support for the wire was provided by allowing its ends to pass through holes somewhat larger than the diameter of the wire. The space around the wire was tightly packed with powdered graphite. This provided electrical contact and at the same time allowed lengthwise expansion and contraction without development of high enough stresses to cause serious plastic deformation.

Resistivities were measured at -196°C while the specimen was immersed in a stirred liquid nitrogen bath. A current of 100 ma ± .001 ma was passed through the specimen and the potential measured using a Rubicon thermofree potentiometer.

Changes in resistivity during aging were followed by allowing the specimen to warm to room temperature for an interval of time before recooling to -196°C for the next resistivity measurement.

(c) Stress-Strain Curves

The same quenching procedure as that described for electrical resistivity measurements was employed for all the mechanical tests. Prior to quenching, each crystal was cut into two parts. One half was then tested in the annealed condition and the other was tested after the desired quenching and aging treatment.

During the test the specimen was surrounded by helium gas. Its temperature was determined by the temperature of the grips and walls of a surrounding chamber which was immersed in liquid nitrogen or some other low temperature bath.

It was not possible to measure mechanical properties in the as-quenched condition because several minutes at room temperature were required for mounting of the specimen in the grips, closing the chamber and cooling to the test temperature.

The strain rate used for all tests was 10^{-4}/sec. Some play was provided at the lower grip to avoid prestraining the specimen during cooling to the test temperature. The load extension curve was recorded on a speedomax recorder.

RESULTS

Disappearance of the excess resistivity introduced by quenching, growth of x-ray scattering centers, and increase in yield stress were almost complete within the first 100 minutes of aging at room temperature, as shown in Fig. 3.

Values of R_o plotted in Fig. 2 are the radius of gyration of the scattering centers obtained by measuring the slope of a plot of ln I vs ϵ^2:

$$\ln I = \frac{-\epsilon^2 R_o^2}{3} + \text{const.}$$

where I is the scattered intensity at a small angle ϵ from the direction of the incident x-ray beam. These plots were straight lines which indicated a sharp distribution of sizes for the scattering centers. (Guinier and Fournet 1955) It was concluded that double Bragg scattering did not contribute significantly to the results for the following reasons: 1.The scattered intensity within the angular range measured was essentially zero immediately after quenching. Mechanical damage to the crystal that might increase the dislocation density and therefore cause some Bragg reflections to appear would be expected to occur during quenching. 2.The scattered intensity at a given value of ϵ for a fully aged specimen increased with increasing temperature of the specimen, whereas the intensity of double Bragg scattering should decrease with increasing temperature. 3. The experimentally observed intensities varied with ϵ in almost exactly the way predicted theoretically for scattering from spherical centers. (Rayleigh 1919) 4. Aging at room temperature even for a period of two years did not produce prismatic dislocation loops large enough to be detected by transmission electron microscopy.

In Figure 2 the difference in yield stress between the unquenched and the quenched and aged part of each crystal is plotted as a function of aging time. Both single slip (open circles) and multiple slip (dark circles) orientations are included. The yield stress rises rapidly during the first 100 minutes of aging, then decreases slowly for longer aging times. The decrease in quench hardening for long aging times at 25°C was particularly noticeable for the multiple glide orientation.

Quenching and aging not only increased the yield stress, but also affected the flow stress even after large plastic strains. Whereas the change in yield stress for a given aging time was similar for single slip and multiple slip orientations, the effect on strain hardening rate was not. Changes in shape of the stress-strain curve due to quenching and aging are illustrated in Figs. 3 and 4. For the single slip orientation the initial rate of hardening following the yield was always higher for the quenched and aged part of the crystal. However, for the <111> orientation the hardening rate was unchanged for aging time less than about 300 minutes, but for longer times became less for the quenched and aged part of the specimen. At plastic strains above about 10% the quenched specimens shown in Fig. 4 deformed at lower stresses than the originally annealed part of the same crystal.

The temperature dependence of the yield stress was measured down to 4.2°K for two aging times--10 minutes and 600 minutes. Figure 5 shows that the hardening was relatively insensitive to temperature of testing even for the shortest aging time.

DISCUSSION

Uniformly distributed excess vacancies, divacancies, and perhaps slightly larger clusters that exist immediately after quenching cause no hardening in FCC metals. This has been shown by these experiments and by previous investigations for copper (Kimura et al. 1959) and gold. (Meshii and Kauffman 1959) When specimen dimensions are small enough to make quenching strain negligible, then the yield stress of annealed and as-quenched crystals is the same except perhaps very close to 0°K. This result is not unexpected because escape of dislocations from defects having atomic dimensions is associated with a small activation energy.

More surprising is the observation that the entire stress-strain curve appears to be unaffected by the presence initially of a high supersaturation of vacancies. For both multiple glide and single slip orientations of single crystal wires there was no change in the rate of strain hardening due to the presence of vacancies. This was true in spite of the fact that the supersaturation was probably reduced during deformation by the absorption of vacancies at moving dislocation lines. (Wintenberger 1960, and Strudel et al. unpublished)

Lack of any change in the yield stress suggests that the dislocation multiplication process that begins to operate at the yield was unaffected by the climb of moving dislocations accompanying absorption of individual vacancies. The fact that the hardening rate was also unchanged implies that this climb of the moving dislocations also did not affect the amount of damage left behind in the slip plane when a dislocation moved across it.

When quenched crystals were aged so as to allow some growth of larger vacancy clusters, both an increase in the yield stress and changes in the hardening rate were observed. However, a quantitative theory of the changes is made difficult by the complexity of the substructures that develop.

Near other sinks such as external surfaces, dislocations, and subgrain boundaries, all of which are present during quenching, there are volumes of crystal that do not contain vacancy clusters. The excess vacancies that were present within a critical distance from dislocation lines or interfaces can reach these sinks during aging. The percentage of the total volume occupied by loop-free or cluster-free regions can be greatly increased if multiplication of dislocations is caused by quenching stresses. This percentage is also increased by an increase in the aging temperature. Surrounding defect-free volumes there are regions within which the critical supersaturation for nucleation of clusters has just been exceeded. The largest vacancy clusters or dislocation loops are formed here. At still greater distances from sinks the density of clusters reaches its maximum and cluster size its minimum. Typical colonies of loops in a quenched and aged aluminum crystal are shown in Fig. 6. (Vinçotte 1962)

Another major difficulty in the way of a quantitative description of the effects of clustered vacancies on the stress-strain curve is a lack of a complete theory of yielding and strain hardening even for a crystal that is initially in the annealed state. It is not yet possible to predict for any given defect substructure how the number of moving dislocations and their average velocity should change with increasing stress and strain.

Theories of quench hardening and irradiation hardening have been applied only to the yield. The flow stress at the smallest easily measured plastic strain is usually the stress necessary to form the first slip bands. Dislocations must move over long enough distances for multiplication processes to become operative. At first, the regions where plastic strain is

taking place are relatively isolated. Therefore, the flow stress can be related rather directly to the stress necessary to move a dislocation over long distances through the initial substructure. By assuming that dislocations must cut through a uniformly distributed field of vacancy clusters or prismatic loops, Seeger (1958) and Friedel (1963) have developed theories that are consistent with the observed magnitude of the hardening.

Friedel's theory for uniformly distributed small dislocation loops gives the hardening as:

$$\Delta\tau \simeq \frac{Gbd^{\frac{2}{3}}}{5}$$

where G is the elastic shear modulus, b is the Burgers vector, d is the diameter of the loops and N is the number of loops per unit volume. When d is larger than a few interatomic distances, the energy necessary to pull the dislocation away from a loop is large. Therefore, the hardening should be insensitive to testing temperature, as was observed (Fig. 5).

If N is assumed to be constant as the clusters grow in size, then the hardening increases directly with d. The small angle scattering and yield strength changes during the first hour of room temperature aging were within the experimental uncertainty, consistent with this prediction (Fig. 2).

Changes in hardening rate following the yield cannot be related so directly to a simple model. As shown by these experiments, the initial hardening rate can be either greater, unchanged or less when compared to a crystal that does not contain vacancy clusters. Many other factors in addition to initial orientation of the tensile axis are probably also important (for example, the cross section of the tensile specimen).

We would like to suggest that destruction of the clusters or loops by moving dislocations (Vandervoort and Washburn 1960, Greenfield and Wilsdorf 1961, Greenfield 1962, and Saada and Washburn 1962) is the basic

cause for changes in hardening rate. This instability of the initial substructure leads to continued growth of the first few slip bands that form, rather than continuous nucleation of new bands during increasing strain. Less uniform distribution of shear strain is generally observed in both irradiated and quenched materials. (Seeger 1958, Cottrell 1958, Tanner and Maddin 1959, Greenfield and Wilsdorf 1961, and Eyre 1962) In thin wire single crystals, such as those used in these experiments, the growth of fewer slip bands might be expected to decrease the initial hardening rate for the multiple glide orientation because there would be fewer intersections between slip bands on the three active slip planes. For the easy glide orientation, however, growth of a few isolated slip bands might be associated with a greater hardening rate because of the local lattice rotation and associated bending moments that are produced. Secondary slip systems may operate locally during the growth of these wide bands almost from the start of plastic extension. This explanation, although obviously too simple, is consistent with the observation that the difference between the initial hardening rates for multiple slip and single slip orientations was much less for quenched and aged specimens than it was for annealed sections of the same crystals.

CONCLUSIONS

1. Excess vacancies in the form of single vacancies, divacancies and, perhaps, slightly larger clusters cause no increase in yield stress over that of an annealed copper crystal.

2. Unclustered excess vacancies cause no change in the shape of the stress-strain curve for either single slip or multiple slip orientations of the tensile axis.

3. The critical resolved shear stress for yielding increases rapidly during the first 100 minutes of aging at 25°C. This increase in yield is independent of the orientation of tensile axis.

4. To a first approximation the increase in yield stress is directly proportional to the size of the clusters as measured by X-ray small angle scattering during the first 100 minutes of aging.

5. The first effect of aging is to raise the stress level of the entire stress-strain curve without changing its shape. Longer aging times produce both a change in yield stress and a change in strain hardening rate following the yield.

6. Long aging times cause an increase in initial hardening rate for easy glide oriented specimens. Often the easy glide stage is completely absen absent. The same treatment results in a decrease in hardening rate for the <111> multiple slip orientation.

7. No clusters large enough to be resolved as dislocation loops or tetrahedra are formed in copper during aging at 25°C even for an aging time of 10^6 minutes.

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References

Blewitt, T. H., Coltman, R. R., Holmes, D. K., and Noggle, T. S., 1957, Creep and Recovery of Metals, ASM, Cleveland.

Chik, K., Seeger, A., and Ruhle, M., 1962, Proc. 5th Int. Congress Electron Microscopy (New York: Academic Press) p. J-11.

Cotterill, R. M. J., 1961, Phil. Mag., 6, 1351.

Cotterill, R. M. J., 1962, Ph.D. Thesis, Cambridge University.

Cotterill, R. M. J., and Segall, R. L., 1962, Proc. 5th Int. Congress Electron Microscopy (New York: Academic Press) p. J-13.

Cottrell, A. H., 1958, Inst. Met. Rep. and Mon., Ser. No. 23.

de Jong, M., and Koehler, J. S., 1963, Phys. Rev., 129, 49.

Eyre, B. L., 1962, Phil. Mag., 7, 1609.

Friedel, J., 1963, Electron Microscopy and Strength of Crystals, (New York: John Wiley and Sons, Inc.) p. 605.

Greenfield, I. G., and Wilsdorf, H. G. F., 1961, J. Appl. Phys., 32, 827.

Greenfield, I. G., 1962, Proc. 5th Int. Congress Electron Microscopy, (New York: Academic Press) p. F-4.

Guinier, A., and Fournet, G., 1955, Small-Angle Scattering of X-Rays, (New York: John Wiley and Sons, Inc.)

Hirsch, P. B., Silcox, J., Smallman, R. E., and Westmacott, K. H., 1958, Phil. Mag., 3, 897.

Kimura, H., Maddin, R., and Kuhlmann-Wilsdorf, D., 1959, Acta Met., 7, 154.

Köster, W., 1948, Zeit. fur Metallkunde, 39, 1.

Maddin, R., and Cottrell, A. H., 1955, Phil. Mag. 46, 735.

Mader, S., Seeger, A., Simsch, E., 1961, Z. Metallk., 52, 785.

Makin, M. J., 1957, AERE M/R 2080 Harwell Berks.

Makin, M. J., and Blewitt, T. H., 1962, Acta Met., 10, 241.

Meshii, M., and Kauffman, J. W., 1959, Acta Met., 7, 180.

Rayleigh, L., 1919, Phil. Mag., 6, 37.

Saada, G., and Washburn, J., Proceedings at the 1962 Tokyo Symposium on Mechanical Aspects of Lattice Defects, Japanese J. Phys., in press.

Seeger, A. K., 1958, Second Geneva Conference on the Peaceful Use of Atomic Energy, 6, 250.

Silcox, J., and Hirsch, P. B., 1959, Phil. Mag., 4, 72.

Smallman, R. E., and Westmacott, K. H., 1959, J. Appl. Phys., 30, 603.

Smallman, R. E., Westmacott, K. H., and Coiley, J. A., 1959, J. Inst. Met., 88, 127.

Strudel, J., Vincotte, F., and Washburn, J., to be published.

Tanner, L. E., and Maddin, R., 1959, Acta Met., 7, 76.

Vandervoort, R. and Washburn, J., 1960, Phil. Mag., 5, 24.

Vincotte, F., 1962, M.S. Thesis, University of California, Berkeley.

Washburn, J., 1960, Strengthening Mechanisms in Solids, ASM, p. 51.

Wintenberger, M., 1960, Ann. Phys., 5, 1185.

Figure Captions

Fig. 1 Geometry used for small angle scattering measurements.

Fig. 2 Changes in yield stress, excess resistivity, and radius of x-ray scattering centers in copper during aging at 25°C after a rapid quench from 1070°C.

Fig. 3 Stress-strain curves showing effect of vacancy clusters for a single slip orientation of the tensile axis. Dashed curves are for a length of the same single crystal tested without quenching. Test temperature 78°K except as indicated.

Fig. 4 Stress-strain curves showing effect of vacancy clusters for a multiple slip orientation (tensile axis [111]). Dashed curves are for a length of the same single crystal tested without the quenching and aging treatment. All tests at 78°K.

Fig. 5 Temperature dependence of the yield stress for different aging times. Values of shear modulus, G, taken from (Köster 1948).

Fig. 6 Typical distribution of vacancy loops in quenched and aged aluminum (Vincotte 1962).

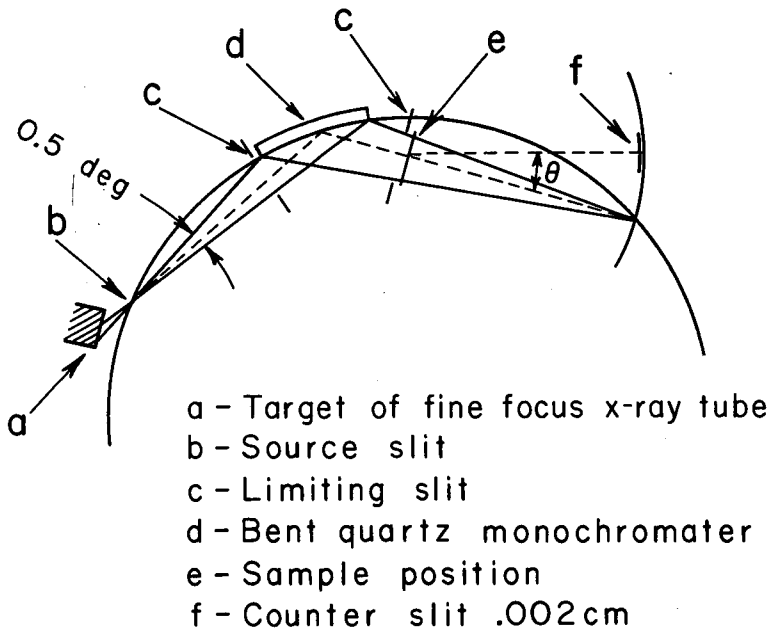

c
d
e
f
c
0.5 deg
b
θ
a
a - Target of fine focus x-ray tube
b - Source slit
c - Limiting slit
d - Bent quartz monochromater
e - Sample position
f - Counter slit .002cm
MU-30153

Fig. 1

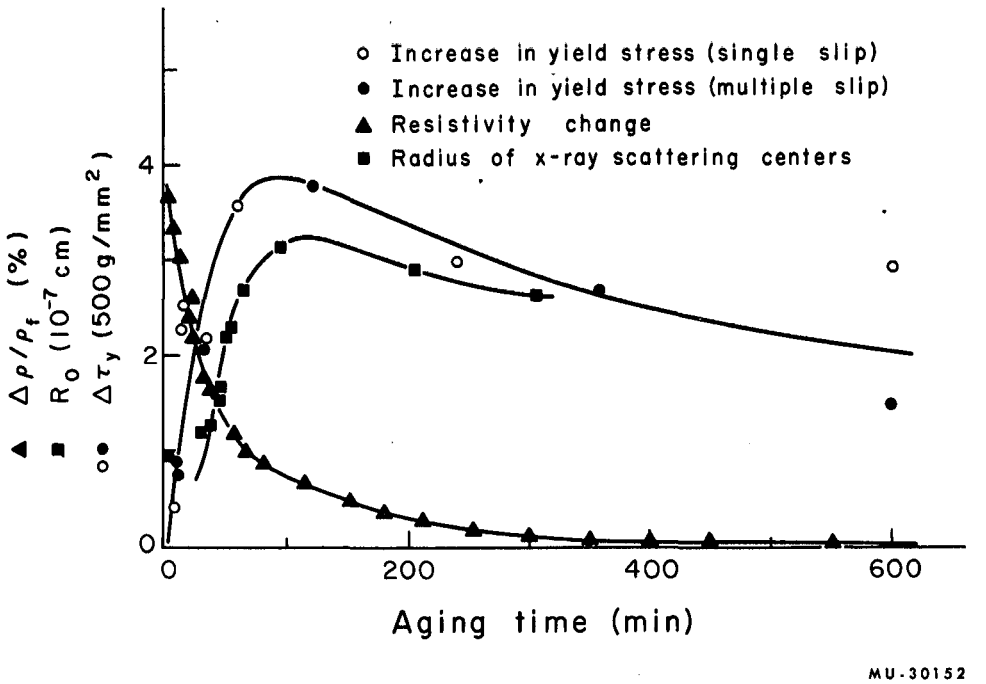

Increase in yield stress (single slip)
Increase in yield stress (multiple slip)
Resistivity change
Radius of x-ray scattering centers
▲ Δρ/ρf (%)
■ Ro (10-7 cm)
○● Δτy (500 g/mm2)
0
2
4
0
200
400
600
Aging time (min)
MU-30152

Fig. 2

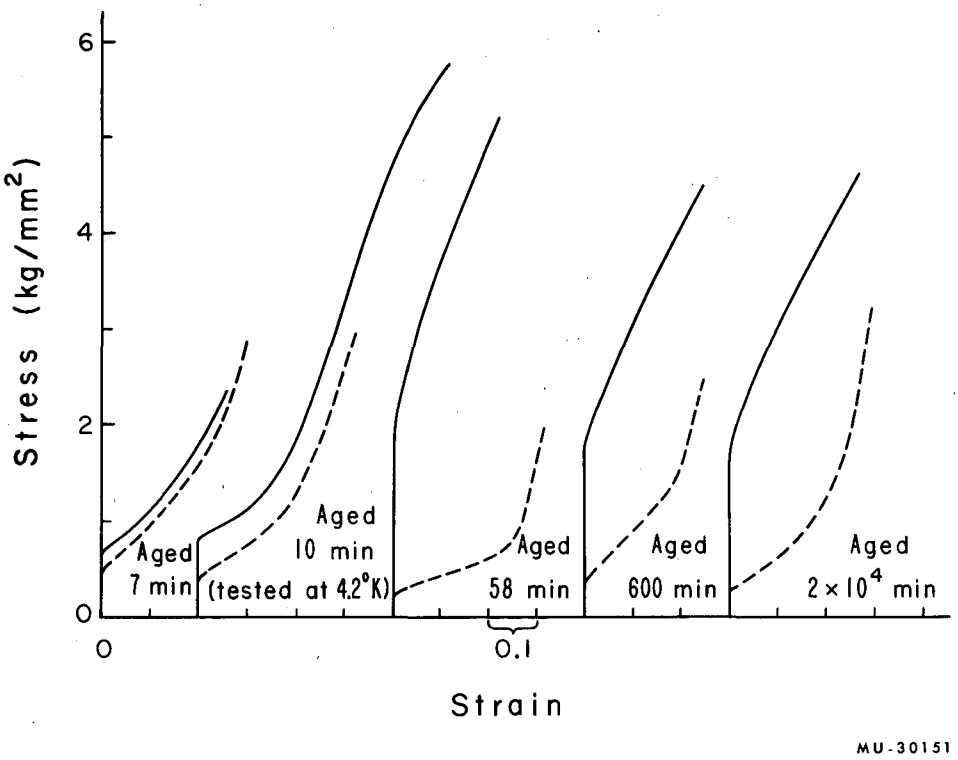

6
4
2
0
Stress (kg/mm²)
Aged
7 min
Aged
10 min
(tested at 4.2°K)
Aged
58 min
Aged
600 min
Aged
2 × 10⁴ min
0
0.1
Strain
MU-30151

Fig. 3

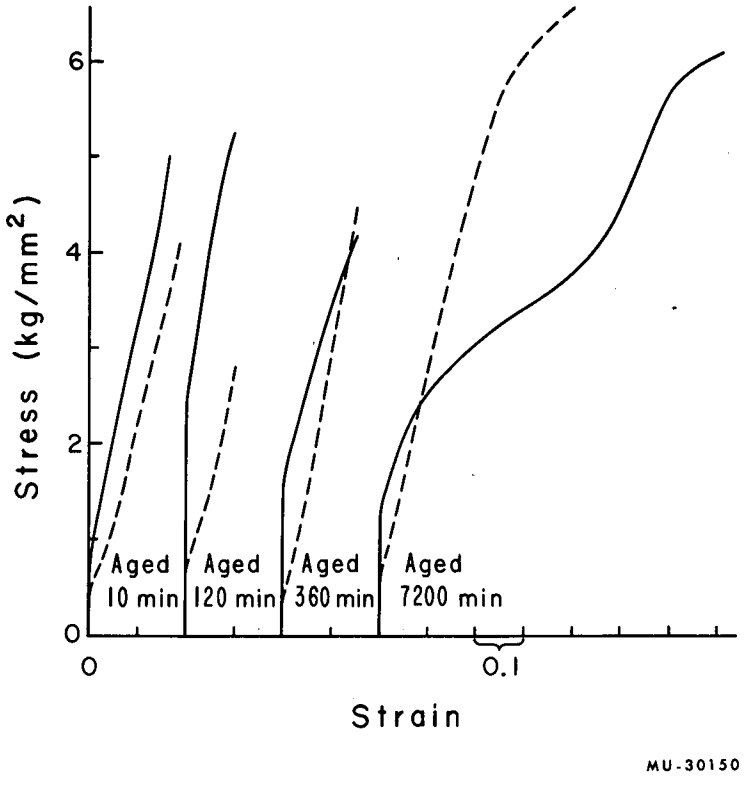
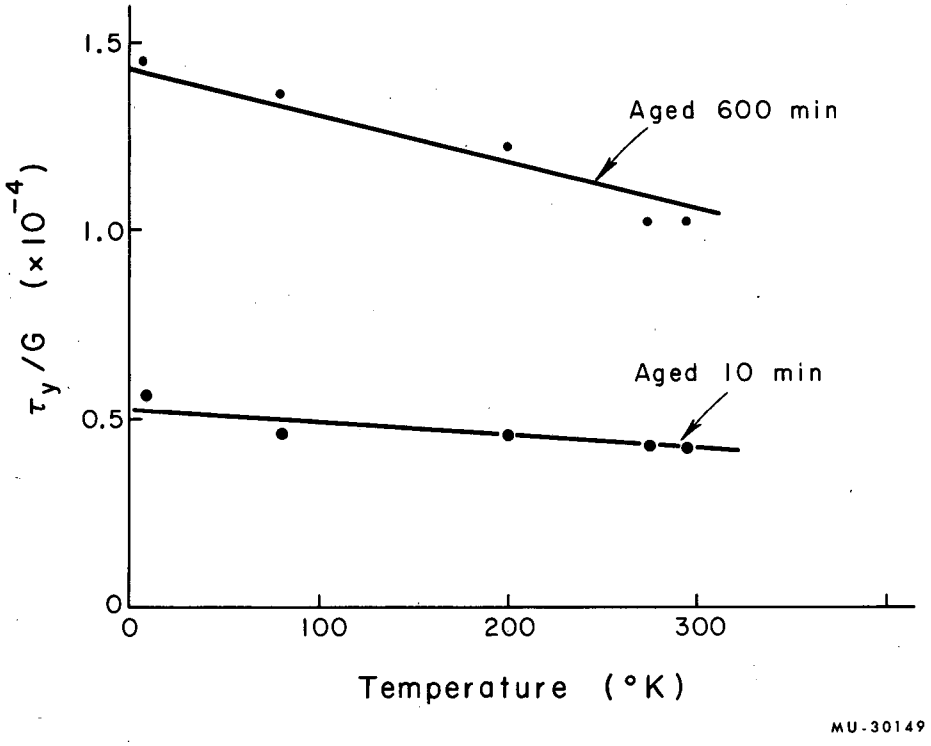

6
4
2
0
Stress (kg/mm²)
Aged 10 min
Aged 120 min
Aged 360 min
Aged 7200 min
0
0.1
Strain
MU-30150

Fig. 4


1.5
1.0
0.5
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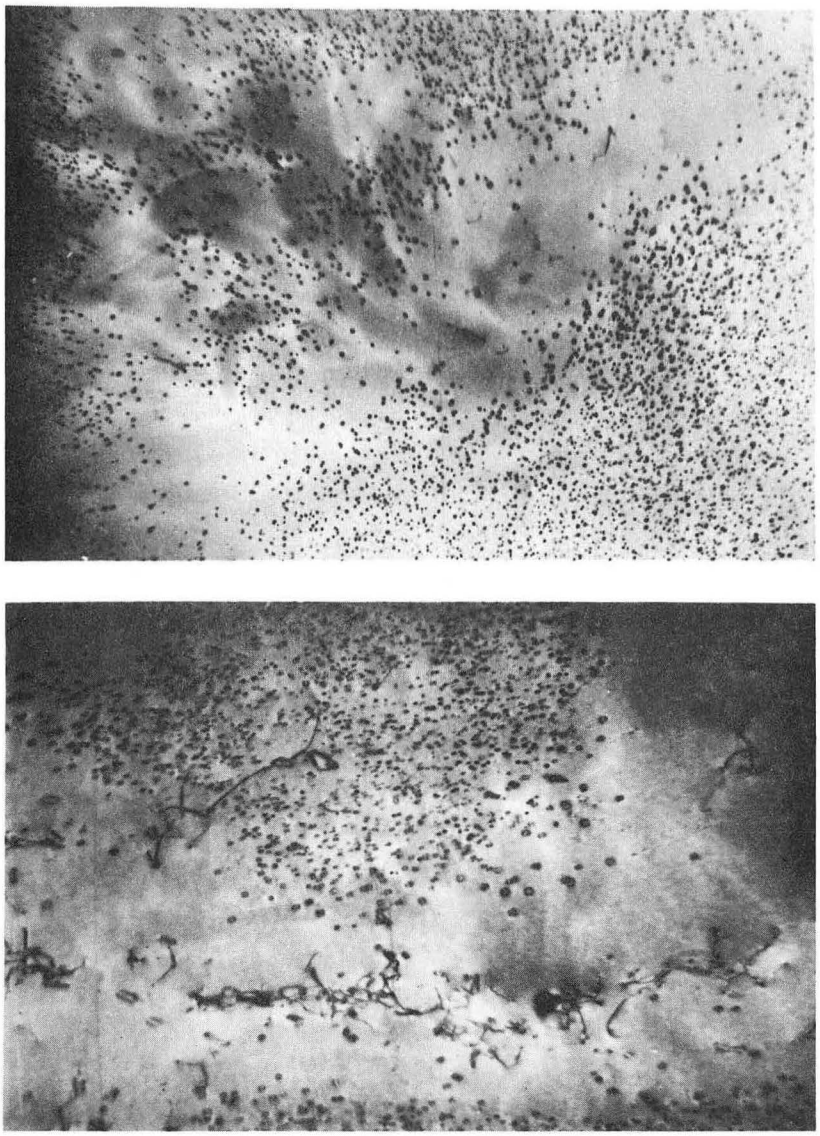
τ_y/G $(\times 10^{-4})$
Aged 600 min
Aged 10 min
0
100
200
300
Temperature (°K)
MU-30149

Fig. 5



ZN-3699

Fig. 6

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