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OF DISORDERED Cu_3Au

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EFFECT OF ORDERING ON THE MECHANICAL PROPERTIES
OF DISORDERED Cu_3Au

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ABSTRACT

The effect of temperature and strain rate on the flow stress of disordered polycrystalline Cu_3Au was investigated in the range 273°K - 663°K . The serrations in the stress-strain curves are associated with dynamic reordering of short-range order. From a series of experiments based on annealing, single activation energy of 36 ± 2 kcal/mole was deduced, which is only slightly less than the sum of $E_f + E_m \sim 39$ kcal/mole for formation and migration of vacancies in Cu_3Au . For short annealing times, and over the lower range of test temperature, deformation is principally controlled by the degree of the short-range order. For higher temperatures and longer annealing time, the yield stress depends principally on cutting of antiphase boundaries.

I. INTRODUCTION

A good understanding of the structural and thermodynamic properties of ordered alloys is now available as a result of emphasis in research on these topics. Although a few preliminary probes had been made in the past on their mechanical properties, it is only recently that a sustained effort has been made to develop a systematic rationalization of the deformation characteristics of ordered alloys. As documented in two recent reviews on this subject^{1,2} substantial progress is now being made in uncovering the interesting and often unique dislocation processes responsible for the plastic behavior of order-disorder alloys. Many issues, however, are yet controversial and numerous facets of the subject remain unexplained.

In a recent investigation, Landon and Dorn³ demonstrated that the deformation of Cu_3Au is controlled by Peierls mechanisms over the low-temperature range extending up to $\sim 100^\circ\text{K}$ for ordered Cu_3Au and up to $\sim 330^\circ\text{K}$ for the disordered state. Above $\sim 370^\circ\text{K}$ originally disordered Cu_3Au exhibited serrated stress-strain curves somewhat similar to those that are attributable to dynamic strain aging⁴ in solid solution alloys. In contrast no such serrated stress-strain curves were obtained under otherwise similar conditions for the ordered alloy. On this basis it appears unlikely that the serrated stress-strain curves in originally disordered alloys are attributable to Cottrell⁵ or Suzuki⁶ mechanisms for dynamic strain aging, since the pertinent factors of solute-atom diffusion and interaction with dislocations should also be operative in ordered Cu_3Au . It appears more probable that the serrated stress-strain curves of the originally disordered Cu_3Au arise as a result of

other causes such as those dependent on ordering reactions that can take place at the intermediate test temperatures.

It was the purpose of this investigation to attempt to identify the processes and mechanisms that might be responsible for the serrated stress-strain curves obtained in originally disordered Cu_3Au . Toward this end two types of tests were planned: (1) A complete survey of the yield strength of originally disordered material for two strain rates as a function of temperature over the pertinent range from $\sim 300^\circ\text{K}$ to slightly less than the Curie temperature of $T_c = 663^\circ\text{K}$. (2) Study of thermal variations in the yield strength with time at a series of temperatures over the range from 523°K to 603°K . As will be demonstrated in the text of this report, the serrations in the stress-strain curves are associated with dynamic reordering of short-range order. Consequently such serrations are not obtained in long-range ordered Cu_3Au . Furthermore, the plastic behavior of originally disordered Cu_3Au was observed to be athermal over the complete range of conditions that were investigated, a fact which is in complete harmony with the proposed mechanism of dynamic reordering of short-range order.

II. EXPERIMENTAL TECHNIQUE

In the course of this investigation two heats of Cu_3Au were prepared from high purity Cu and Au (99.998 wt%). The heats were cast into a graphite mold, forged to 0.75 in. in diameter and finally cold swaged to 1/8 in. in diameter rods. Tensile test specimens of 0.085 in. diameter having an 0.68 in. long gage section were then machined from the rods. The final analyses shown in Table I, which were obtained from selected specimens following testing, reveal that the composition of two heats were almost identical and in close agreement with the stoichiometric composition.

All specimens were given the same disordering heat treatment. This treatment was selected to provide a compromise between the quenching-in of vacancies and short-range order. Whereas very high quenching temperatures are expected to reduce the quenched-in short-range order they would tend to increase the concentration of quenched-in vacancies. The specimens were first annealed under argon at 1000°K for 30 min for the dual purpose of further homogenizing the specimens and providing a stable grain size. Next they were slowly cooled to 725°K (62°K above $T_c = 663^\circ\text{K}$) over 2 hrs, then held at 725°K for 15 min and finally quenched in water. After a week or more holding at room temperature, selected specimens were examined by Debye-Scherrer back-reflection x-ray diffraction. The efficiency of the quench is evident by the fact that in no case could even the faintest trace of superlattice lines be detected in the Debye-Scherrer photograms. The mean lineal grain diameter of selected specimens was determined by means of optical microscopy following etching of polished surfaces of selected specimens

with 50% aqueous solution of I_2 in KI. The results, also recorded in Table I, illustrate that both heats of Cu_3Au developed about the same grain size under the selected treatment.

Specimens were tested in tension after being held for one week or more at room temperature. All tensile tests were conducted on an Instron testing machine. Tensile tests at $273^\circ K$ were conducted with the specimens totally emmersed in ice-water bath. Over the range from somewhat above room temperature the tensile test specimens were completely immersed in agitated and thermostatically controlled silicone oil baths. Temperature remained with $\pm 1^\circ$ of the reported values during isothermal testing.

Tensile tests were conducted by rapidly elevating the controlled temperature baths so as to completely immerse the mounted tensile specimen and its fixtures. It took about 3 min for the specimens to heat to within $1^\circ K$ of the desired isothermal test temperature. One set of tensile tests were started 5 min after the isothermal control temperature was reached. Other isothermal tests were made following a series of larger hold times at constant temperatures.

Stresses were calculated from the tensile loads and cross sectional areas to an accuracy of $\pm 0.1 \times 10^8$ dynes/cm². Strains deduced from the elongation data and initial gage lengths are accurate to better than 0.002. Yield stresses were determined as the flow stress at 0.002 offset from the modulus lines. When required the shear stress was taken to be given by one half of the tensile stress.

III. EXPERIMENTAL RESULTS

Typical load-extension diagrams for Heat A following a 5 min isothermal hold for the series of tension tests at a machine cross-head speed of 0.02 in./min for temperatures from 299°K to 648°K are shown in Fig. 1a, 1b, and 1c. Completely similar load-extension curves were obtained for similar tests conducted at a cross-head speed of 0.001 in. per min. The following comments are pertinent to the thesis of this investigation.

(a) Yield points: Small yield points not always clearly discernible in the reduced charts of Fig. 1, were observed at all temperatures and strain rates that were investigated.

(b) Serrated stress-strain curves: (i) Tests at 299°K, 323°K, and 346°K exhibit serrated stress-strain curves only after preliminary extension of 0.14, 0.04, and 0.02 in. respectively. In general the amplitude of the serrations increased with increasing strain. (ii) Tests over the range from 374° to 533°K inclusive exhibited serrations from the beginning of yielding to the point of fracture. Again the amplitude of the serrations increased with increasing extension. (iii) The test at 556°K exhibited only a few irregular serrations and those over the range from 575° to 648°K inclusive remained unserrated over the entire range of extension.

(c) Correlation with x-ray photograms: Following testing, specimens were quenched in acetone (used to increase the cooling rate by dissolving the silicone oil), following which Debye-Scherrer back reflection photograms were taken using Cu radiation. No superlattice lines could be detected in the specimens tested at 414°, 475°, and

533°K. Very faint superlattice lines were noted in the specimen tested at 556°K, and faint superlattice lines were found in the specimens tested at 575° and 648°K.

(d) Yield stress versus test temperatures: The variation of yield strength of Heat A with temperature is documented in Fig. 2. Over the range from about 375° to 450°K, an athermal behavior was observed, the yield stress being insensitive to temperature and strain rate. From about 450° to 475°K the yield stress increased rapidly, and from about 475° to 610°K, it increased more slowly. A maximum value of the yield stress was obtained at about 630°K following which the yield stress decreased with increasing temperature. Over the range of increasing yield stress with increasing temperature, the yield stress was slightly higher for the specimens strained at the lower strain rate whereas the reverse occurred over the range where the yield stress was decreasing with increasing temperature. The fact that serrated stress-strain were obtained only when the superlattice lines could be detected in the Debye-Scherrer photograms is also documented in Fig. 2.

(e) Effect of time at temperature: The effect of the hold time at temperature preceding tensile testing on the plastic behavior of originally disordered Cu_3Au was investigated using Heat B. Figure 3 shows the experimentally determined flow stress versus isothermal hold time at 549°K for a cross-head speed of 0.02 in./min. A peak flow stress was found for an annealing time of 10.5 hr. A test for 5 min holding time gave completely serrated stress strain curves, while a test for 1 hr exhibited a few irregular serrations. Tests over

longer periods of time showed no evidence of serrations. Furthermore the Debye-Scherrer x-ray photographs, obtained for tested specimens in the same manner as previously described, showed no superlattice lines for specimens held for 5 min and very faint superlattice lines for specimens held for 1 hr. Specimens held for three and five hours gave faint superlattice lines and those held for 10 to 24 hrs gave increasingly stronger superlattice lines.

Additional tests conducted at 523°, 576°, and 603°K gave similar trends to those obtained at 549°K. The same states, however, were reached in a shorter period of time at the higher temperatures. In fact, as shown in Fig. 4, a single relationship is obtained when the yield stress is plotted as a function of $t e^{-E/RT}$, where t is the hold time (hr), RT is the gas constant times the absolute temperature and $E = 36 \pm 2$ kcal/mole is the activation energy.

IV GENERAL DISCUSSION

Above the curie temperature of $T_c = 603^\circ\text{K}$, the Cu and Au atoms are randomly positioned on the (000), $(0\frac{11}{22})$, $(\frac{1}{2}0\frac{1}{2})$ and $(\frac{11}{22}0)$ sites of the fcc lattice. When Cu_3Au is slowly cooled to below T_c , the structure orders in such a way that the Au atoms preferentially occupy one of the four equivalent fcc lattice sites and the Cu atoms preferentially occupy the remaining three sites, thereby producing the Li_0 ordered structure.⁷ Since only minor reshuffling of atoms from random to specified sites takes place, the ordering reaction occurs without necessitating long-range diffusion. Furthermore only a minor change⁸ in lattice parameter from 3.7538 \AA just above T_c to 3.7470 \AA just below T_c accompanies ordering in Cu_3Au .

Cowley's⁹ theories for short and long-range order will be employed to provide a basis of discussion and analysis of the experimental data. The selection of Cowley's theories in preference to other approximations such as given by the Gorsky¹⁰ and Bragg-Williams¹¹ zeroth-order approaches, Bethe's¹² concepts or the Guggenheim¹³ quasi-chemical method, is based on the fact that it is in best agreement with the experimental facts on ordering of Cu_3Au . To simplify the analysis, however, Cowley's theory will be couched in terms of only the nearest neighbor bonding.

Cowley's⁹ short-range order parameter, α , is defined by

$$P_{AB} = N_A(1-\alpha) \quad (1)$$

where P_{AB} is the observed probability that an A atom is coordinated about a B atom, and N_A is the atomic fraction of A atoms. For a random mixture of atoms $\alpha = 0$ and as short-range ordering takes place α becomes negative. The equilibrium degree of order for $N_A = \frac{1}{3}$,

appropriate for stoichiometric Cu_3Au , is given by⁹

$$\ln \frac{(\frac{1}{3} + \alpha)(3 + \alpha)}{(1 - \alpha)^2} = \frac{2\epsilon}{kT} \quad (2)$$

where k is the Boltzmann constant and ϵ is the bond reaction energy for destroying $\frac{1}{2}$ A-A bond and $\frac{1}{2}$ B-B bond and making an A-B bond, namely

$$\epsilon = \frac{\epsilon_{AA}}{2} - \frac{\epsilon_{BB}}{2} + \epsilon_{AB} \quad (3)$$

Both α and ϵ are negative for alloys that order.

Cowley's long-range order parameter, μ , for stoichiometric alloys of type Cu_3Au is defined by

$$\mu = \frac{3}{4} \frac{r_\alpha - \frac{3}{4}}{1 - \frac{3}{4}} + \frac{1}{4} \frac{r_\beta - \frac{1}{4}}{1 - \frac{1}{4}} \quad (4)$$

where r_α and r_β are the fractions of correct atoms, Cu and Au respectively on α and β sites. The equilibrium degree of long-range order is given by

$$\ln \frac{(\frac{1}{3} + \mu^2)(3 + \mu^2)}{(1 - \mu^2)^2} = \frac{-8 \mu^2 \epsilon}{kT} \quad (5)$$

which predicts a Curie temperature where $\mu = 0$ given by

$$\epsilon = \frac{-2 k T_c}{3} \quad (6)$$

The predicted variations of μ and $-\alpha$ with temperature are given by curves of Fig. 5. The datum points represent experimental results by Keating and Warren¹⁴ for long-range order below T_c and by Cowley⁹ for short-range order above T_c . The correlation between theory and experiment, although somewhat imperfect, is none-the-less good.

The curve for μ illustrates that a first-order thermodynamic reaction takes place during long-range ordering of Cu_3Au as the temperature is decreased below $T_c = 663^\circ\text{K}$. Over the range of temperature of major interest to this investigation from about 450° to 660°K , the equilibrium value of μ decreases only slightly from about 0.9 to about 0.8.

Only short-range order persists above $T_c = 663^\circ\text{K}$. The absolute degree of short-range order, $-\alpha$, also increases with decreasing temperature. The equilibrium curve for short-range order given in Fig. 5 has been extended to temperatures below 663°K . In this region short-range order is unstable and will, under favorable kinetic conditions, eventually transform toward the equilibrium degree of long-range order. The equilibrium curve for short-range order represents the upper bound values of $-\alpha$ that can be produced in this region.

As described under experimental results (Sec. III) no superlattice lines were detected at room temperature following quenching from 725°K . This observation is consistent with previously reported results³ on Cu_3Au . Consequently it can be inferred either that long-range order is not present or, if present that either μ is extremely small or the long-range ordered domains occupy only a very small fraction of the total volume of the alloy. It is possible that as-quenched specimens are completely free of long-range order since long-range ordering can take place only at temperatures below $T_c = 663^\circ\text{K}$. Since 663°K is also about one-half of melting temperature, the diffusive reshuffling of atoms required to produce long-range order is expected to be slow. Evidence in support of the concept that the quenching rates employed

in this investigation were sufficiently rapid to preclude the long-range order transformation will be presented later in this report.

Under ideally rapid rates of quenching to sufficiently low temperatures it might be possible to freeze-in the equilibrium degree of short-range order that prevailed at 725 °K from which the specimens were quenched. In general, however, $-\alpha$ at the quenching temperature represents a lower bound value of the short-range order that might be present in the as-quenched specimens: The absolute degree of short-range order can increase somewhat during quenching so as to approach the higher equilibrium values of $-\alpha$ that are obtained at the lower temperatures. The rates of such trends toward equilibrium will be increased above the usual isothermal rates as a result of migration of excess quenched-in vacancies.

Several resistometric studies¹⁵⁻²⁴ have been made on the kinetics of ordering in Cu_3Au following quenching. Minor discrepancies exist in some of the reported data and some differences in opinions have been expressed regarding interpretation of these data. Furthermore, several facets of the subject have not been adequately explored. Nevertheless there now appears to be fair agreement on all major issues. The research of Benci, et al.²⁴ is most pertinent to the present investigation: Following quenching thin wires 0.04 mm in diameter from a series of temperatures covering the range $T_c < T < 1073^\circ\text{K}$, they determined $(R_T - R_{T_c})/R_T$ where R is the resistivity measured at room temperature and the subscripts refer to the temperature from which the specimens were quenched. $(R_T - R_{T_c})/R_T$ decreased as T was first increased above T_c , reached a minimum value at about $T = 723^\circ\text{K}$, and

increased as T was increased above 723°K . Obviously at least two factors are responsible for the variation of the resistivity of quenched Cu_3Au as a function of the quenching temperature. The resistivity of Cu_3Au is known to increase with both increasing vacancy concentration¹⁵ and increasing absolute degree of short-range order,¹⁸ and it decreases with increasing degree of long-range order.²⁵ The possibility that increasing degrees of long-range order can account for the decreasing values of $(R_R - R_{T_c})/R_T$ with increasing values of T over the range $T_c < T < 723^\circ\text{K}$ can be disqualified on the basis of several observations, the most direct being the fact that isothermal annealing of quenched specimens at 438°K results first in a decrease in the resistivity followed by an increase in resistivity. The latter can only be due to predominance of short-range ordering over other factors. Furthermore as shown by Dugdale,¹⁶ specimens quenched from just below $T_c = 663^\circ\text{K}$ exhibit upon annealing only decreases in resistivity coincident with elimination of excess vacancies and long-range ordering. Consequently, the variations of $(R_T - R_{T_c})/R_T$ with quenching temperature must be ascribed to short-range order and vacancy effects. Over the lower range of quenching temperatures where $T_c < T < 723^\circ\text{K}$ the predominant factor appears to be the decreasing value of the quenched-in absolute degree of short-range order with increasing quenching temperature, whereas above 723°K the effect of increasing excess vacancies plays the predominant role. These conclusions are also in agreement with those presented earlier by Damask.²⁶ Thus Cu_3Au can be quenched sufficiently rapidly from above $T_c = 663^\circ\text{K}$ to avoid long-range ordering. Furthermore the absolute degree of short-range

order under equilibrium conditions at the quenching temperature must be frozen into the as-quenched Cu_3Au with no, or at most, negligible increases in value.

Estimates of the energy of formation of monovacancies deduced from resistivities investigations have been reported by several investigators.^{16,24,27}

Whether excess quenched-in vacancies can be retained over several days in as-quenched specimens might be estimated from annealing kinetics. In the light of the previous discussion the early stages of annealing could involve two simultaneous trends, a decrease in resistivity arising from migration of excess vacancies to sinks and an increase in resistivity due to short range ordering. Since the resistivity is more sensitive to vacancy concentration, this effect will predominate at first, resulting in a decrease in resistivity, followed subsequently, when the excess vacancy concentration is small, by an increase in resistivity due to an increase in the absolute degree of short-range order. Only following much longer times will the resistivity decrease again as a result of transformation from short-range to long-range order. Such general trends upon annealing have been reported by Binci et al.²⁴ and Brinkman et al.¹⁵

Annealing data at a series of temperatures from 363°K to 473°K were obtained by Binci et al.²⁴ following quenching from 803°K . The ratio R/R_0 , of the instantaneous to initial resistivity initially decreased rapidly, reached a minimum value and then increased very slowly with time. Obviously over the initial stages of annealing the decrease in resistivity due to migration of excess quenched-in vacancies to

sinks predominated over the minor concomitant increase in resistivity resulting from short-range ordering, whereas in the final stage the excess vacancy concentration was so low that the effects of short-range ordering on the resistivity predominated. The fact that about the same minimum value of R/R_0 was obtained regardless of the annealing temperature can be attributed to the fact that the differences in the equilibrium concentration of vacancies over the range of annealing temperatures was negligibly small in contrast to the excess quenched-in vacancy concentration. Since both the migration of excess vacancies to sinks and short range ordering are dependent on the migration of vacancies, the annealing data for all temperature should correlate as shown in Fig. 6 to give a single curve in terms of the temperature compensated time, $t e^{(E_m/RT)}$, where $E_m = 16.6$ kcal/mole is the activation energy for migration of vacancies. Similar values for E_m have been obtained by a number of investigators.^{16,24, 28} The upper scale in Fig. 6 gives an extrapolation of these data in terms of the time of anneal at 290°K. Assuming that most of the excess vacancies have been eliminated when R/R_0 reaches its minimum value, it is noted that the excess vacancy concentration in quenched Cu_3Au becomes small after a 3000 hr hold at room temperature.

It is well-known that following the previously described initial period of adjustment, Cu_3Au quenched from above T_c , can be held for very long periods of time at room temperature without material changes in its ordering-sensitive properties. This shows that the equilibrium concentration of vacancies is so low and their rate of migration at room temperature is so slow as to provide infinitely slow rates of short-range

ordering. Consequently the terminal slow increase in resistivity documented in Fig. 6 must be due to excess vacancies. Such order will continue until the excess vacancy concentration reaches some terminal residual value.

Long-range ordering in Cu_3Au is the result of a first-order thermodynamic phase transformation and therefore should be initiated as a result of nucleation followed by phase growth. Data by Lord²⁸ on the variation of Young's modulus with time of anneal following quenching seems to follow the sigmoidal trend characteristic of this process. The necessity for nucleation can also be inferred from data reported by Dugdale,¹⁶ who found that higher temperatures were needed to promote long-range ordering in specimens quenched from just above T_c , where nucleation of domains acts to precede ordering, than in those quenched from just below T_c where ordered domains were already present. As might be expected, however, most of the evidence suggests that nucleation of long-range ordered domains is so highly favorable energetically and therefore takes place so readily at many centers of the volume of the crystal that it is very difficult to detect and thus isolate.

Long-range order domains undoubtedly nucleate at favorable sites of short range order and spread therefrom. As they spread, the degree of long-range order at the domain centers increases from its initiating value toward the equilibrium value resulting in a range in degree of order over the spreading domain. In each domain the Au atoms occupy one of the four equivalent sites on the fcc lattice. When they meet domains in which the same site is occupied by Au atoms coalesce to form a single domain. Upon meeting, antiphase domains in which the

Au atoms occupy different fcc lattice sites produce antiphase-domain boundaries, APB. Each domain of Cu_3Au can form three kinds of APBs with neighboring domains. Since long-range order does not extend across APBs, the average degree of long-range order is somewhat less than the ideal equilibrium value. The energy of APBs depends on the number of "wrong" bonds per unit APB area. Consequently antiphase domains in Cu_3Au are separated by APBs that form a foam-like structure, in some respects not unlike that for grain-boundaries in polycrystalline aggregates of pure metals. When APDs first contact each other, the shape and arrangement of the APBs are dictated by the geometrical statistics of nucleation and growth. Readjustments follow so as to reduce the energy of the APBs and produce a somewhat metastable APD size. Complete stability, however, is only achieved upon elimination of all SPBs. Therefore, as shown by Rudman,²⁹ slow growth of APDs takes place at ever-decreasing rates producing larger APDs and more stable APBs.

V. ANALYSIS AND DISCUSSION OF RESULTS

The plastic behavior of quenched and subsequently annealed Cu_3Au that was reported under Experimental Results can now be discussed in terms of short and long-range ordering phenomena. The observations suggest that this discussion can best be presented in four parts, namely:

- (a) The behavior after annealing for five minutes at temperatures below about 550°K
- (b) The behavior after annealing for five minutes above 550°K
- (c) The trends following increasing annealing times
- (d) Serrations at low temperatures.

(a) Plastic properties following five minutes annealing below 550°K

As shown by Fig. 2, a thermally-activated mechanism of deformation becomes operative below about 370°K . Langdon and Dorn³ have associated this thermally activated behavior with the Peierls mechanism. The introduction over this temperature range of serrations in the stress-strain curve following prestaining will be described later.

The plastic behavior following a five minute anneal at the testing temperature over the range from about 370°K to 550°K can be ascribed to short-range ordering phenomena. This interpretation is consistent with the following observations:

(1) The absence of superlattice lines in the Debye-Scherrer X-ray photograms following tensile testing at temperature.

(2) The presence of a yield point, which can be ascribed to an avalanche of dislocations sweeping across a slip plane due to introduction of disorder across it.

(3) The presence of serration in the stress-strain curves due to re-ordering that can occur at these temperatures as promoted by migration of vacancies.

(4) The trend of increasing yield stress with increasing temperature from 370°K to 550°K due to increasing absolute degrees of short range order as dictated by ordering kinetics.

(5) The magnitude of the yield stress.

(6) The athermal plastic behavior over this range of temperatures.

In the following analysis it will be assumed that effects arising from Cottrell atmospheres and Suzuki locking are small relative to those due to mutual interactions of dislocations and the effects of short range order. On this basis the yield stress τ_y is determined by the sum of the stress, τ_G , needed to move dislocations past their mutual long-range interaction fields and the stress, τ_s , described by Fisher,³⁰ that is needed to disorder the crystal across its slip plane. As shown by Flinn,³¹ this can be estimated in terms of the product of the number of bonds crossing a unit area of the slip plane and the average energy per bond, $2 N_A N_B \alpha \epsilon$, in the ordered alloy. Thus for slip on the {111} planes by the $\frac{a}{2} \langle \bar{1}10 \rangle$ Burgers vector, the work done in disordering a unit area across the slip plane is

$$\tau_s \frac{a}{\sqrt{2}} = 3 \frac{4}{\sqrt{3}} \frac{1}{a^2} \cdot 2 N_A N_B \alpha \epsilon \quad (7)$$

Introducing $a = 3.75 \times 10^{-8}$ cm, $N_A = \frac{3}{4}$, $N_B = \frac{1}{4}$, and the value of ϵ given by Eq. (6) reveals that

$$\tau_s = -42 \alpha \text{ dynes/cm}^2 \quad (8)$$

If for example the equilibrium degree of short-range order at 725°K taken from the curve of Fig. 6 could have been quenched-in, τ_s should have equaled about 7.6×10^8 dynes/cm² at 430°K. At this temperature τ_y was observed to be 6.9×10^8 dynes/cm². In view of the admitted crudity of the analysis, the above calculations merely reflect that the basic concept of ascribing the mechanical behavior to short-range ordering effects cannot be disqualified. A more reliable support for the hypothesis of short-range ordering effects can be obtained by eliminating the effect of τ_G . For example the maximum value of τ_y corresponding to short-range order was 9.24×10^8 dynes/cm² obtained at 550°K. Assuming that this value pertains to the maximum absolute degree of short-range order at 550°K and that τ_y of 7.6×10^8 dynes/cm² at 430°K refers to the quenched in degree of order for equilibrium indicates that

$$\begin{aligned}\tau_y(550^\circ\text{K}) - \tau_y(430^\circ\text{K}) &= -42(\alpha_{550^\circ\text{K}} - \alpha_{725^\circ\text{K}}) \\ &= 1.69 \times 10^8 \text{ dynes/cm}^2\end{aligned}$$

whereas the experimentally determined value is 1.8×10^8 dynes/cm².

The agreement between the theoretically estimated and the experimentally determined value is excellent especially considering that the theoretically calculated value represents the upper bound.

Short range ordering rates at temperatures below about 440°K are so slow that no change takes place in the degree of short range order following five minutes anneal. From about 450°K to 490°K the absolute degree of short range order increases abruptly. The slower increase in short-range order between 490°K and 550°K is undoubtedly attributable to the fact that the equilibrium value for each temperature is now being approached. As will be shown, the yield stress for the slower strain rates

falls above those for the faster rates merely because of the longer times of anneal and the corresponding increase in short-range order.

(b) Plastic properties following five minutes anneal between 550°K and 650°K

Tensile tests on quenched specimens following a five minute anneal over the range of 550°K to 650°K differed from those tested in the lower temperature range by the complete absence of serrations in the stress-strain curves and by the presence of superlattice lines in the Debye-Scherrer X-ray diffraction photograms. Thus it becomes evident that the serrations in the stress-strain curves are associated only with the short-range and not long-range ordering phenomena. The yield stress increased to a maximum value at about 630°K and decreased at higher temperatures. Below 630°K the tests at slower strain rates gave slightly higher yield stresses and above 630°K the reverse was observed. This can be explained in terms of strengthening during the initial stages of long-range ordering followed by softening upon annealing for five minutes at temperature. Over the range of temperatures from 550°K to 650°K, however, the equilibrium degree of long range order μ decreases uniformly and only slightly from about 0.93 to 0.84. Obviously the observed trends cannot be ascribed to the equilibrium degree of long-range order and must therefore be associated with the kinetics of ordering. This will be shown in the next section of this report.

Theories of order strengthening have been offered by many investigators,³¹⁻³⁵ but each model was devised to explain the behavior of a particular alloy. Since there is no change in the shape of the Cu_3Au

unit cell on ordering, the strengthening effects cannot be attributed to the internal strains set up by the ordered phase in the disordered matrix.³⁶ In the Cu_3Au superlattice, a superdislocation,³⁷ composed of pairs bound together by a strip of APB, could move through an ordered region more easily than an ordinary dislocation. An ordinary dislocation creates a complete sheet of APB when it passes through an ordered region. On the other hand as the dislocation pair moves, the disorder created by the leading dislocation is erased by the trailing dislocation.

Flinn³¹ pointed out that, the lowest energy configuration for two partial dislocations connected by a strip of APB may be such that their common plane is not the slip plane. This suggests that, if we have a superdislocation lying on the slip plane, the leading superpartial should climb to another plane and leave the trailing component on the former slip plane. When this occurs the dislocations become much more difficult to move, since each one now leaves an antiphase boundary in its wake. In order to move the dislocation, the stress must be large enough that the work it does is at least equal to the energy of the antiphase boundary produced. Since Fisher's³⁰ idea can be applied to the case of the production of APB by the passage of a single dislocation, as well as to the case of the destruction of short-range order, the required stress is given by

$$\tau = \frac{\gamma}{b}, \quad (9)$$

where γ is the APB energy and b the magnitude of the Burgers vector. As shown by Flinn,³² the γ_{APB} on $\{111\}$ planes of the lattice is given by

$$\gamma_{APB} = \frac{-2 \epsilon \mu^2}{a \sqrt{3}} = \frac{4 K T_c \mu^2}{3 \sqrt{3} a^2} = 50 \mu^2 \text{ dynes/cm}^2, \quad (10)$$

where μ must now be interpreted as an average degree of long-range order over the specimen. From Eqs. (9) and (10) and introducing value of Burgers vector = $\frac{a}{2} \sqrt{2}$

$$\tau = 19 \times 10^8 \mu^2 \text{ dynes/cm}^2$$

The experimental data reveal that the maximum yield strength for the ordered alloy is greater than any value achieved in the disordered state. It is significant to note that this is in agreement with theory. For example

$$\tau_y(630^\circ\text{K}) - \tau_y(430^\circ\text{K}) = 2.65 \times 10^8 \text{ dynes/cm}^2$$

represents the difference $\tau(630^\circ\text{K}) - \tau_s(550^\circ\text{K})$. Upon introduction of $\alpha(430) = \alpha(725)$, and taking $\mu(630) = 0.87$ as a reasonable value of

$$\begin{aligned} \tau(630^\circ\text{K}) - \tau_s(430^\circ\text{K}) &= (11.4 - 7.6) \times 10^8 \\ &= 3.8 \times 10^8 \text{ dynes/cm}^2 \end{aligned}$$

in good agreement with the experimental results. Above the temperature of the peak a large volume of the material is ordered; it will be energetically favorable for the dislocations to move in pairs. Fisher³⁰ suggested that the long-range order itself provides the driving force for grouping dislocations into pairs. At this stage the tendency will be

for the material to soften. Therefore the peak in strength corresponds to transition from deformation by unit dislocations to deformation by superlattice dislocation.³⁵

(c) Effects of annealing time

The effects of annealing time at temperature preceding tensile testing are in complete agreement with the preceding discussion with the exception that these data were obtained on Heat B which seems to have had slightly higher yields strength than Heat A. The reason for this minor difference is not known. Tests designated by the solid points in Fig. 4 gave serrated stress-strain curves whereas all other stress-strain curves were free from serrations. Whereas specimens exhibiting serrations did not exhibit superlattice lines following testing, those that were free from serrations showed evidence of long-range ordering. The single activation energy of 36 ± 2 kcal/mole seemed to be appropriate for correlation of all data. This value is only slightly less than the sum of $E_p + E_m = 39$ kcal/mole for motion and migration of vacancies.^{16,24,28} Since the same trends were obtained over all temperatures, it follows that the mechanical behavior was athermal. For short annealing times over the lower range of test temperatures, deformation depends principally on the degree of the short-range order. For higher temperatures and longer annealing time, the yield stress depended principally on transition from deformation by unit dislocation to deformation by superlattice dislocation.

(d) Serrations at low temperatures

The lowest temperature at which the stress-strain curves were completely serrated was found to be 374°K. It must be presumed that at this temperature the vacancy concentrations and their mobility is just adequate for restoration of short-range order. As a basis of analysis the parameter P might be defined as

$$P = (C_{\epsilon_v} - C_{q_v}) e^{-E_m/RT} \quad (11)$$

where C_{q_v} is the concentration of quenched-in vacancies, C_{ϵ_v} is the concentration of those generated during straining, and E_m is the energy for vacancy migration. At the temperature T_1 where the serrations just started after yielding, the equation becomes

$$P_1 = C_{q_v} e^{-E_m/RT_1} \quad (12)$$

For lower temperatures than T_1 , where the serrations start after straining,

$$P_2 = C_{\epsilon_v} e^{-E_m/RT_2} \quad (13)$$

putting

$$P_1 = P_2$$

$$C_{\epsilon_v} = \frac{C_{q_v} e^{-E_m/RT_1}}{e^{-E_m/RT_2}} \quad (14)$$

Since C_{q_v} is unknown, $C_v(\epsilon)$ should be replaced by the ratio C_v/C_q

$$\frac{C_{\epsilon_v}}{C_{q_v}} = \frac{e^{-E_m/RT_1}}{e^{-E_m/RT_2}} \quad (15)$$

When the estimated values of C_{ϵ_v}/C_{q_v} were plotted versus ϵ^2 , where ϵ is the strain required before the serrations appear, they gave straight line (Fig. 7). This indicates that the concentration of vacancies

produced by straining is proportional to the square of strain.

Cottrell⁴ supposed the vacancies created by deformation increases with the strain according to

$$C_{\epsilon_v} = B\epsilon \quad (16)$$

Our result can be proved if the following assumptions are considered.

$$\frac{dC_{\epsilon_v}}{d\epsilon} = A\rho \quad (17)$$

$$\rho = K\epsilon, \quad (18)$$

where ρ is the density of dislocation, A and K are constants. Solving Eqs. (17) and (18) for C_{ϵ_v}

$$\frac{dC_v}{d\epsilon} = AK\epsilon \quad (19)$$

integrating and putting $C_{\epsilon_v} = C_{q_v}$ at $\epsilon = 0$

$$C_{\epsilon_v} = C_{q_v} + \frac{AK\epsilon^2}{2} \quad (20)$$

At larger values of strain, C_{q_v} is negligible compared to C_{ϵ_v} and Eq. (20) approximates to,

$$C_{\epsilon_v} \approx AK\epsilon^2 \quad (21)$$

VI. CONCLUSIONS

1. A mechanism is proposed to explain the serrated stress-strain curves obtained in originally disordered Cu_3Au , in which the serrations are associated with dynamic reordering of short-range order.
2. The activation energy determined ($\sim 36 \pm 2$ kcal) is thought to be the activation energy required to produce and move a vacancy in Cu_3Au .
3. The concentration of vacancies created in deforming Cu_3Au alloy is proportional to the square of plastic strain.

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Table I. Composition and grain size.

Heat No.	Final analysis (at.%)		Mean grain diameter (grains/cm)
	Cu	Au	
A	74.94	25.06	630
B	74.86	25.14	660

Figure Captions

Fig. 1. a, b, and c. Load curves of disordered Cu_3Au strained in tension at crosshead speed 0.02 in./min.

Fig. 2. Flow stress (0.02%) vs temperature for two different cross-head speeds.

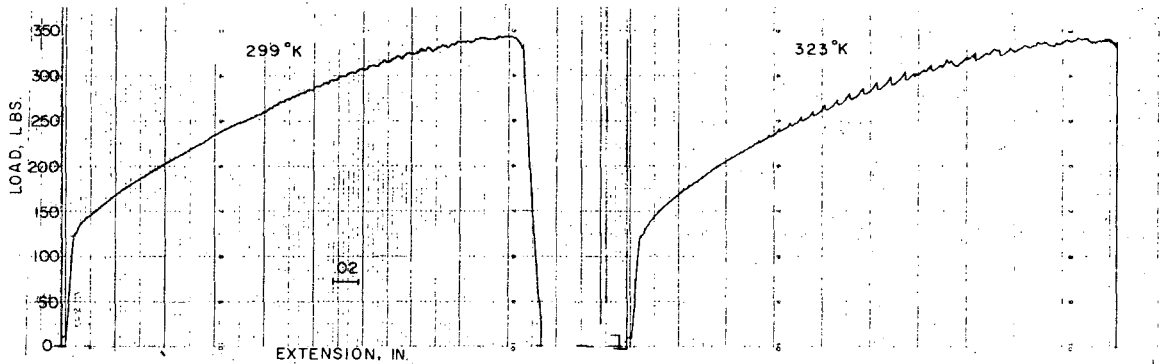
Fig. 3. The flow stress (0.02%) as a function of annealing time at 549°K.

Fig. 4. The flow stress (0.02%) as a function of $t e^{-E/RT}$.

Fig. 5. Short-range order parameter (α) and long-range order parameter (μ) vs temperature.

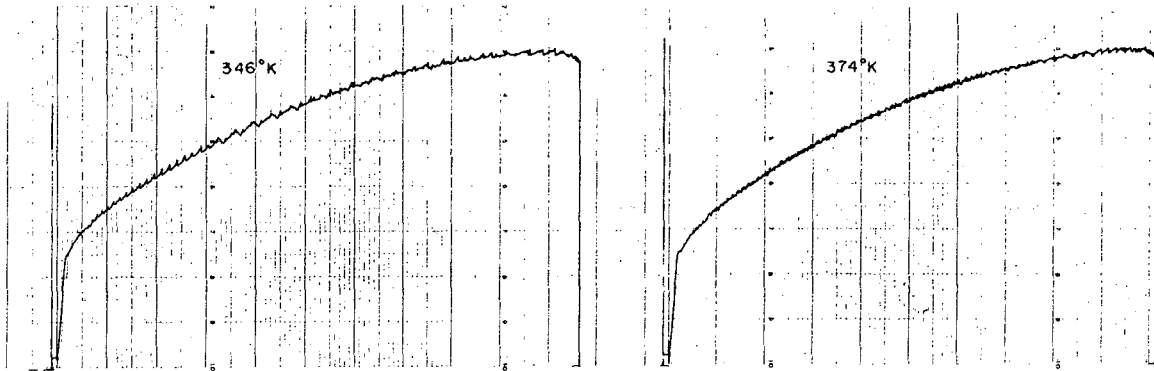
Fig. 6. Ratio of instantaneous to the initial resistivity vs $t e^{-E_m/RT}$.

Fig. 7. Ratio of concentration of vacancies produced by straining to the concentration produced by quenching vs square of strain (ϵ^2).



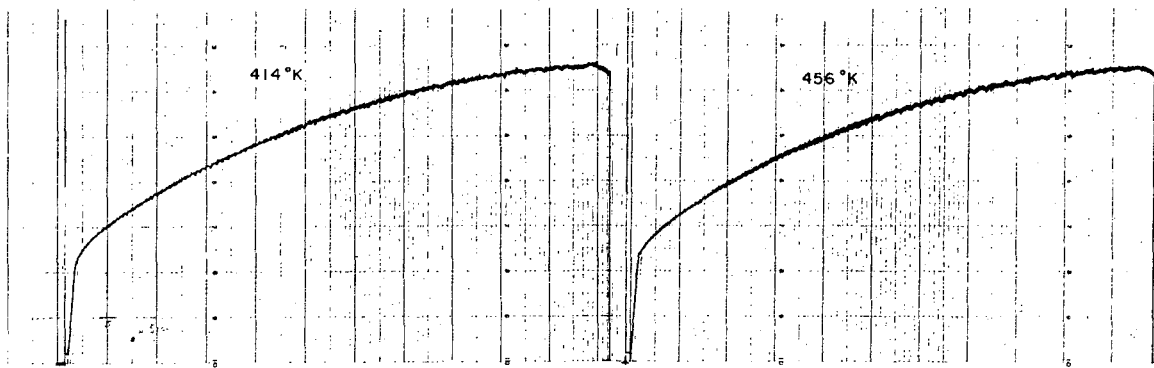
Diam: 0.0856 in.

Diam: 0.0852 in.



Diam: 0.0857 in.

Diam: 0.0861 in.



Diam: 0.0852 in.

Diam: 0.0853 in.

XBL 6911-6513

Fig. 1a. Load-extension curves of disordered Cu₇Au strained in tension at crosshead speed 0.02 in./min. (Heat A). Scale is shown in the first graph.

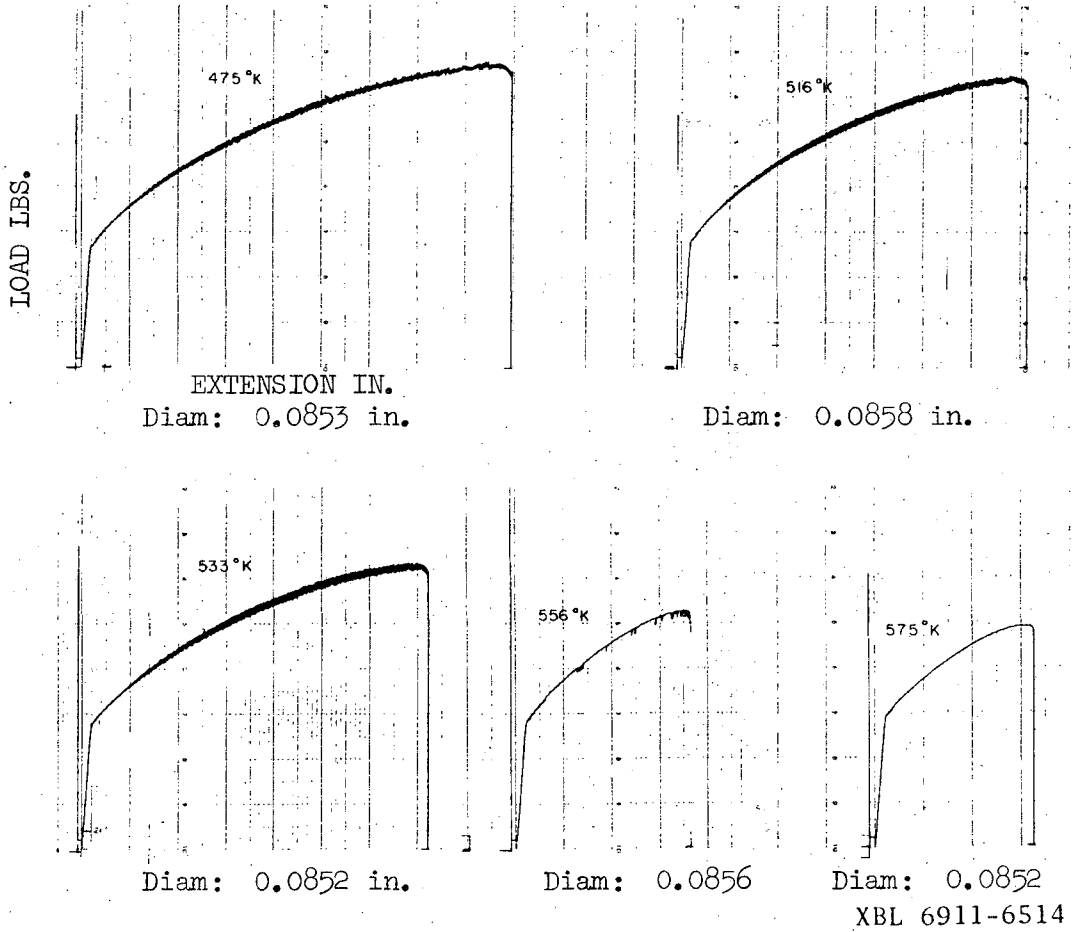


Fig. 1b. Load-extension curves of disordered Cu_3Au strained in tension at crosshead speed 0.02 in./min. (Heat A) Scale is shown in Fig. 1a.

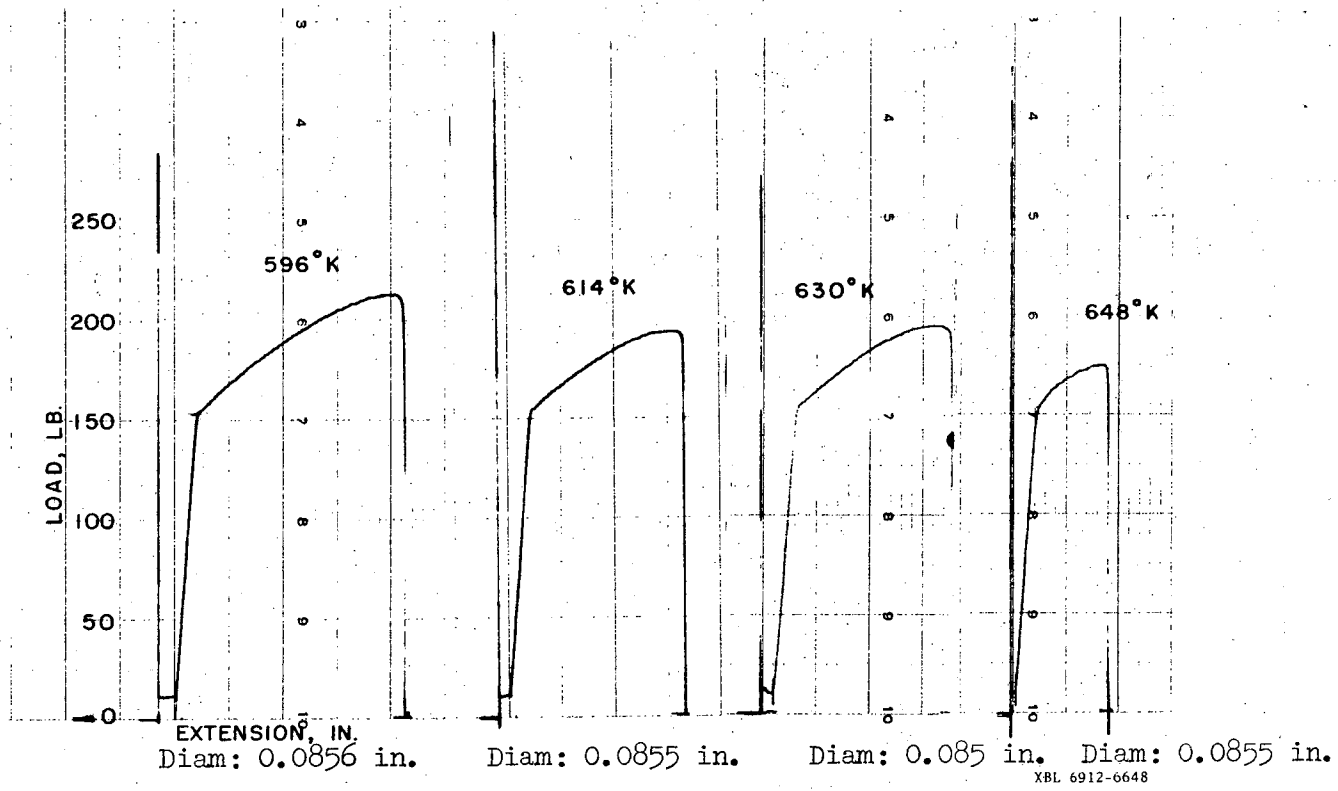


Fig. 1c. Load-extension curves of disordered Cu_3Au strained in tension at crosshead speed 0.02 in./min. (Heat A).

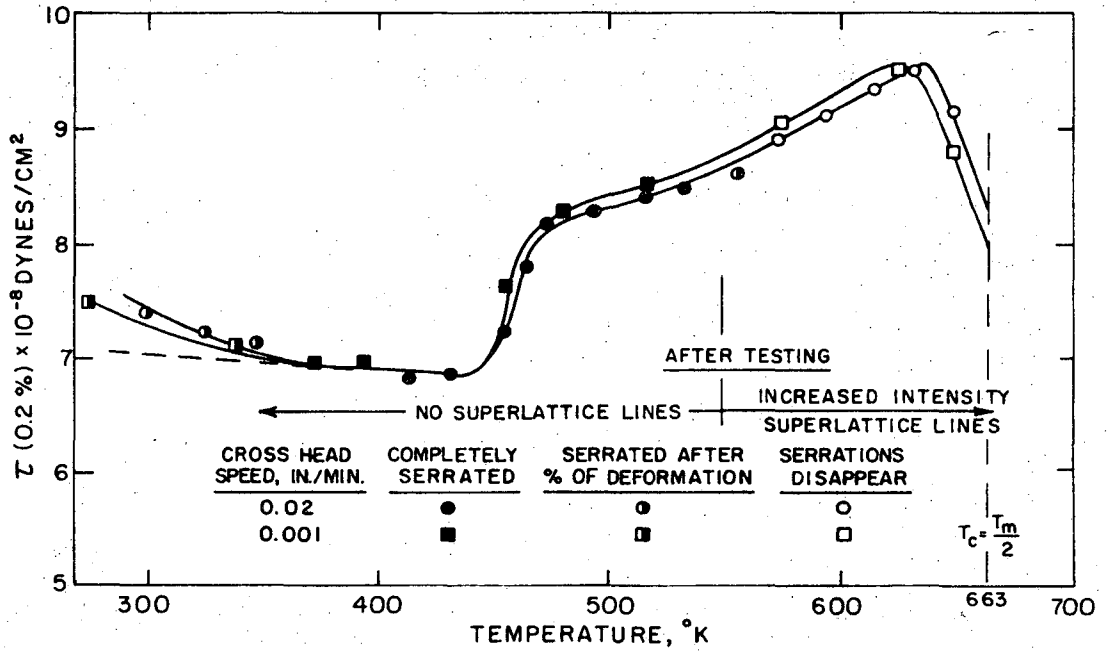


FIG. 2 0.2 % FLOW STRESS vs. TEMPERATURE. (HEAT A.)

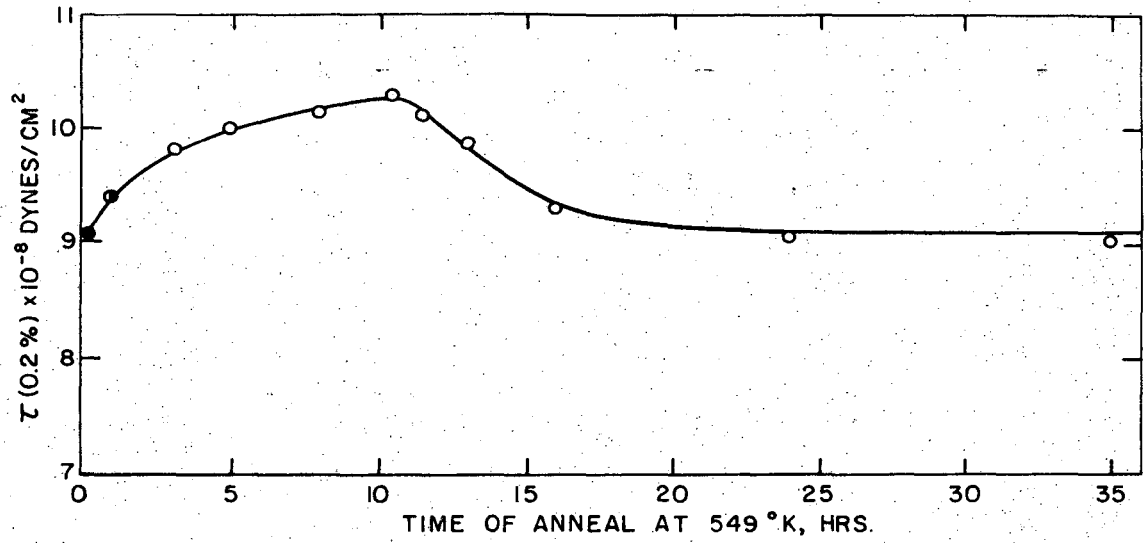


FIG. 3 FLOW STRESS AS A FUNCTION OF ANNEALING TIME. (HEAT B.)

XBL 701-195

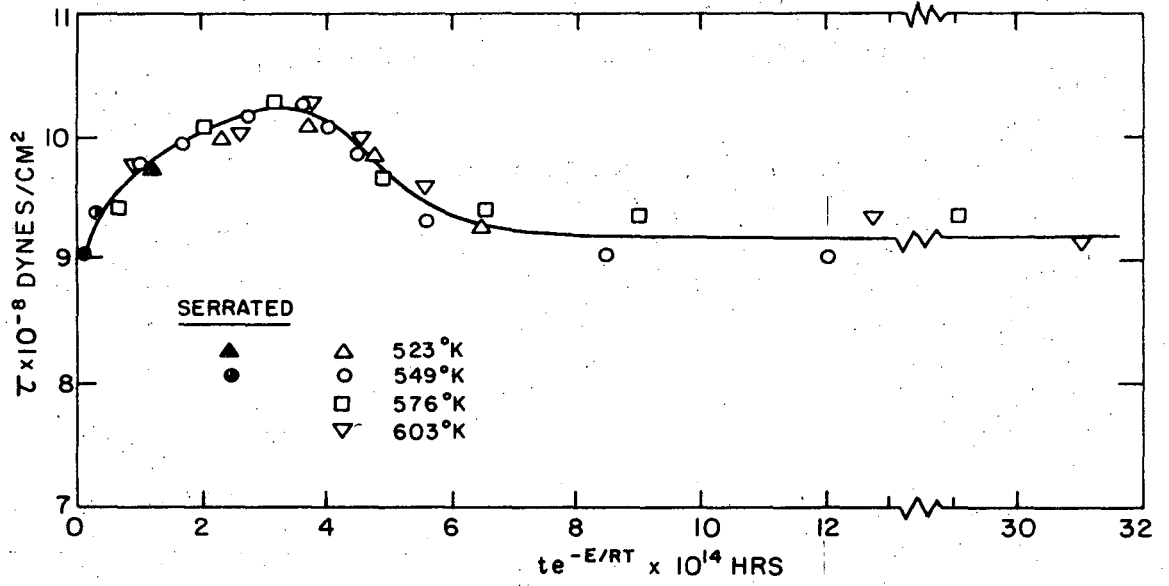


FIG. 4 FLOW STRESS AS A FUNCTION OF $te^{-E/RT}$ (HEAT B.)

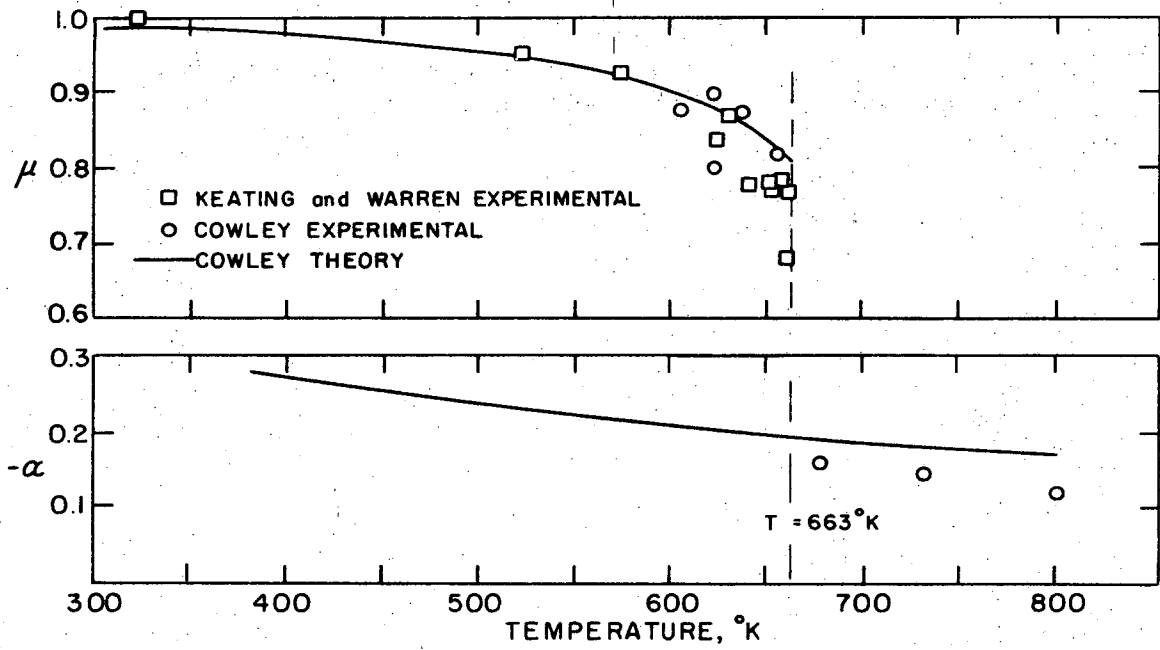


FIG. 5 VARIATION OF SHORT-RANGE ORDER PARAMETER (α) AND LONG - RANGE ORDER PARAMETER (μ) vs. TEMPERATURE.

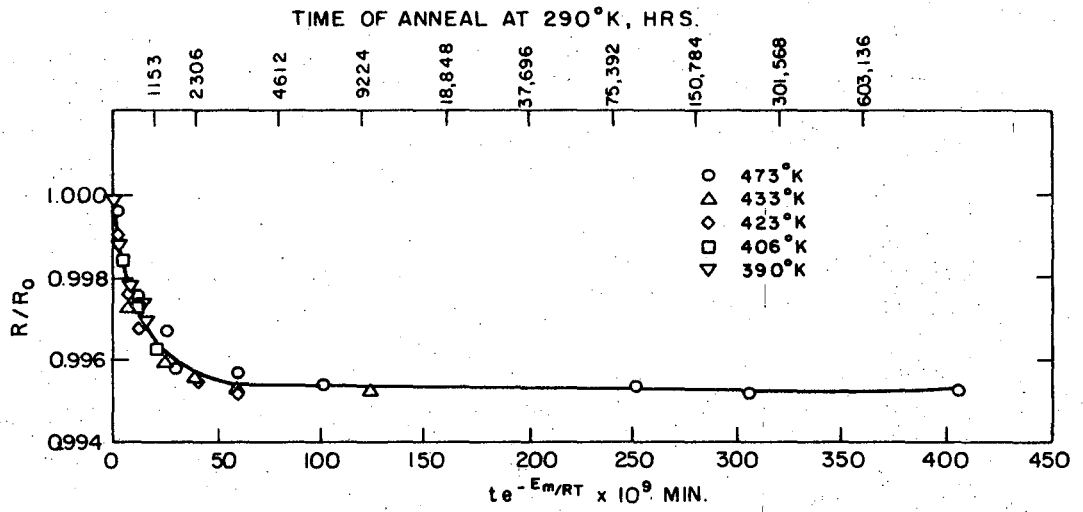


FIG. 6. RATIO OF THE INSTANTANEOUS TO INITIAL RESISTIVITY vs. $te^{-E_m/RT}$

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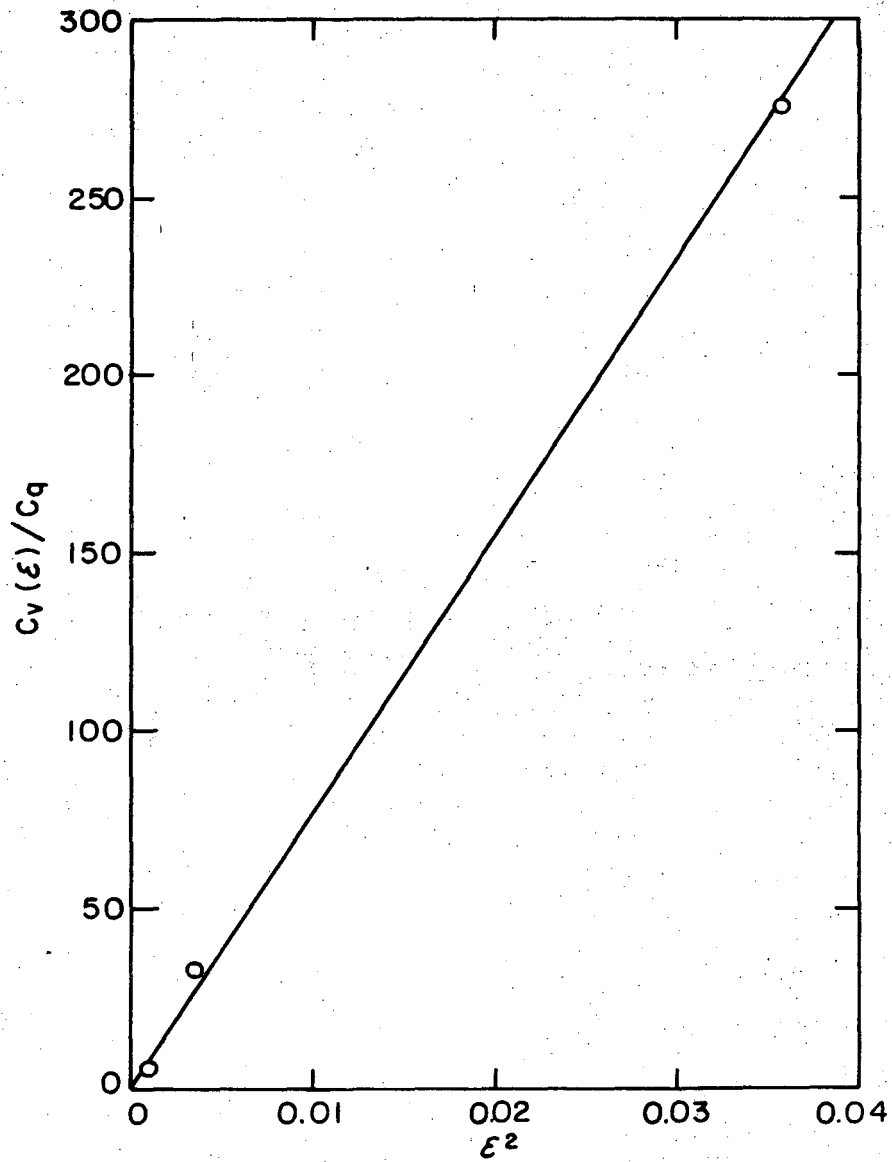


FIG. 7 RATIO OF CONCENTRATION OF VACANCIES PRODUCED BY STRAINING (C_v) TO THE CONCENTRATION PRODUCED BY QUENCHING (C_q) vs. SQUARE OF STRAIN.

XBL 701-199

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