phys. stat. sol. 26, 345 (1968)

Subject classification: 10.1; 21.1

Columbia University, New York

A Study of Quench Hardening in Copper[1])

By

J. L. DAVIDSON and J. M. GALLIGAN[2])

Quenching studies of copper, under clean conditions, have revealed a two stage hardening mechanism. The first stage corresponds to the formation of small vacancy clusters and occurs around room temperature, while the second stage is centered around 250 °C. Measurements of the dislocation loop density in quenched, aged specimens in the second stage of hardening, show that Frank vacancy loops are the major obstacle to dislocation motion. The temperature dependence of the critical resolved shear stress, in quenched specimens, was also measured throughout the aging process and compared with various expressions for the interaction of mobile dislocations with different obstacles. These results indicate quite clearly that Seeger's theory of obstacle shearing is favored over Fleisher's theory of asymmetrical distortion in this case. An experimental value of the cutting process is about 5 eV. In agreement with this mechanism, electron microscope observations show that Frank dislocation loops, within a slip plane, are removed during the first few percent of plastic deformation. Finally, the quench hardening is only removed at very high temperatures, in the same temperature range where the Frank loops are removed.

Abschreckungsuntersuchungen an Kupfer unter sauberen Bedingungen haben einen Zweistufenmechanismus für die Verfestigung ergeben. Die erste Stufe besteht aus der Bildung kleiner Leerstellenagglomerate bei Zimmertemperatur, während die zweite Stufe bei etwa 250°C erscheint. Messungen der Dichte der Versetzungsschleifen in abgeschreckten, gealterten Proben in der zweiten Stufe der Verfestigung zeigen, daß Franksche Leerstellenschleifen das Haupthindernis für die Versetzungswanderung sind. Die Temperaturabhängigkeit der aufgelösten kritischen Scherspannung in abgeschreckten Proben wurde ebenfalls während des Alterungsprozesses gemessen und mit verschiedenen Ausdrücken für die Wechselwirkung beweglicher Versetzungen mit verschiedenen Hindernissen verglichen. Diese Ergebnisse zeigen ganz klar, daß in diesem Falle die Seegersche Theorie der Hindernisscherung geeigneter ist als die Fleischersche Theorie der asymmetrischen Verzerrung. Ein experimenteller Wert für den Abschneideprozeß ist ungefähr 5 eV. In Übereinstimmung mit dem Mechanismus zeigen elektronenmikroskopische Beobachtungen, daß Franksche Versetzungsschleifen innerhalb einer Gleitebene schon während der ersten Prozente der plastischen Deformation beseitigt werden. Die Abschreckungsverfestigung kann nur bei sehr hohen Temperaturen beseitigt werden, im gleichen Temperaturbereich, wo die Frankschen Schleifen verschwinden.

1. Introduction

Many studies have been undertaken to determine the thermodynamic parameters associated with the formation and motion of single, di- and higher order vacancy complexes in quenched metals [1, 2]. The studies have mainly utilized resistivity for a variety of reasons, and such measurements have given extensive information on the kinetics involved in the motion and agglomeration of various defects [3]. In addition, previous studies of quenched metals [4 to 7]

---

[1]) Supported through the National Science Foundation.

[2]) Present address, Brookhaven National Laboratory, Upton, New York.

have also demonstrated large changes in mechanical properties are associated with non-equilibrium concentrations of clusters of vacancies or dislocation loops or stacking fault tetrahedra, formed from an excess of vacancies.

In particular, mechanical property measurements offer some additional pieces of information about specifically treated crystals [8]. The temperature variation of the yield stress of specifically treated crystals is dependent upon the size of the defects causing the hardening and upon the number of such defects per unit volume. The end point of a redistribution of vacancies among various clusters, prior to removal at "high" temperatures, should be large clusters [10], loops [11], or tetrahedra [12]. Such defects should be resolvable and countable, which allows an additional comparison with the above mentioned experiment.

A favorable material for the study of these problems is copper, since the energy of motion of single vacancies and of divacancies are thought to be sufficiently different [13] to allow a quantitative study of each defect. Secondly, the growth of dislocation loops is known to take place above room temperature in quenched copper crystals, which is not true, for example, in quenched aluminum, or gold [14]. Finally, previous quenching studies in copper were plagued by the presence of gaseous contaminants—oxygen or hydrogen—or slow quenching rates [15 to 17]. The present study is concerned with measurements of the kinetics of vacancy removal and the hardening introduced by various distributions of vacancies.

2. Experimental Procedure

2.1 Preparation of specimens and quenching procedure

The starting material was spectroscopically pure copper obtained from American Smelting and Refining Company, 99.999+% pure. After cleaning of the oxide, single crystal specimens were cast in high purity split graphite molds under a purified argon atmosphere. The argon was high purity gas, which was pre-dried and then passed over titanium chips, which were held at 800 °C, to remove oxygen and nitrogen. Since the specimens themselves were cut from the center section of the single crystal, some degree of purification could be expected from this process. The reproducibility of this phase of the procedure can be assessed from measurements of the critical resolved shear stress (C.R.S.S.) of annealed crystals, using the first departure from linearity on the load versus elongation curve. These measurements indicated a spread of less than 3% in this value on more than 5 separate crystals. Furthermore, the magnitude of this quantity, about 100 g/mm^2, is comparable to a large number of previous measurements in similar material [6, 18].

The quenching procedure involved specifically isolating the quenching medium from the specimen by using a thin glass membrane at the end of a tubular furnace. The quenching medium was a brine solution. In order to minimize accidental deformation in the quenching operation due to breakage of the glass membrane, which separated the furnace and the quenching medium, a massive copper cylinder surrounded the specimen. This copper cylinder also served as a radiation shield in the quenching operation. A magnet release system allowed the hot copper specimens to fall from the hot zone, the massive copper cylinder breaking the glass membrane and specimen quenching would then take place. The estimated quenching rate was 3×10^4 °C/s.

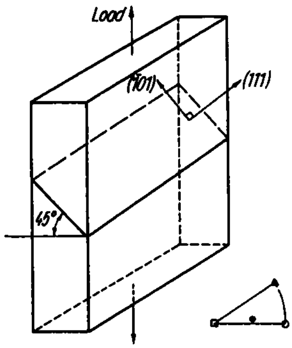


Fig. 1. Orientation of tensile axis of specimens used

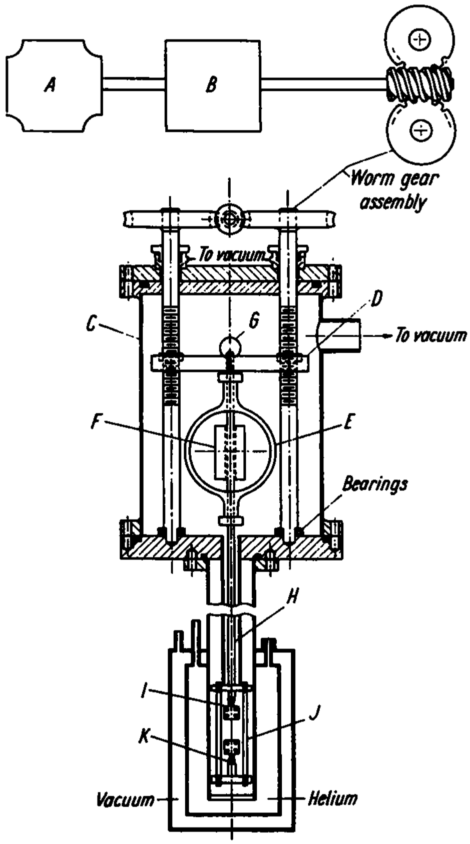


Fig. 2. Schematic diagram of tensile machine. A drive motor, B reduction gear box, C vacuum jacket, D moveable crosshead, E proving ring, F linear variable differential transformer, G precision ground bearing, H stainless steel pulling rod, I top specimen grip, J cage for specimen, K bottom specimen grip

Some measure of the success of this operation in keeping copper clean during the quench is indicated by the fact that a neutron activation analysis indicated a net loss of oxygen in quenched crystals. This analysis was performed on "as received" specimens and quenched single crystals. The "as received" material had approximately 12 parts per million oxygen.

2.2 *Mechanical property tests*

The single crystals, grown as described above, were all of the same orientation, which is compared to a standard stereographic triangle in Fig. 1. Specimens were flat sheets 1.25 cm wide by 0.06 cm thick. This orientation favors a single slip system, with an extensive amount of easy glide at low temperatures. Critical resolved shear stress measurements were usually performed on specimens, after appropriate quenching and aging treatments, at 80 °K. The apparatus used for these measurements is shown schematically in Fig. 2. Fixed temperature baths were used for measurements at temperatures intermediate between 80 °K and 300 °K, and a previously calibrated gold (2.1% Co) versus copper thermocouple was used to check these temperatures. Aging treatments were performed in the same furnace as in the quenching experiments, except a magnet system allowed manipulation of the specimen into and out of the hot zone, without any breaking of the gas seals. In order to test the relative error involved in heating-up and cooling-down in this aging treatment, a chromel-alumel thermocouple was attached to a blank copper specimen and the heat-up time and cool-down time measured. For short times, a correction for this was used, as outlined by Shewmon [19].

2.3 Transmission Electron Microscopy

Copper crystals, which were given parallel treatments to those used in the mechanical property measurement sections, were examined by standard transmission electron microscopy in a Siemens Electron Microscope. These specimens were examined after quenching from a fixed temperature, 1030 °C, and aged at various temperatures for fixed times between 23 and 850 °C. The quenching temperature was again measured with a calibrated chromel-alumel thermocouple adjacent to the specimens. Thin foils were made from quenched crystals, for examination in Siemens Elmiskop IA, in a manner similar to that described by Bell et al. [17]. In these foils, specific sections were examined, which allowed a determination of the loop concentration. The thickness was determined by careful analysis of thickness fringes. All counting was carried out with an operating reflection in which all loops were visible. The values obtained are averages of various sections of the foil (20) for a minimum of 2 quenched specimens.

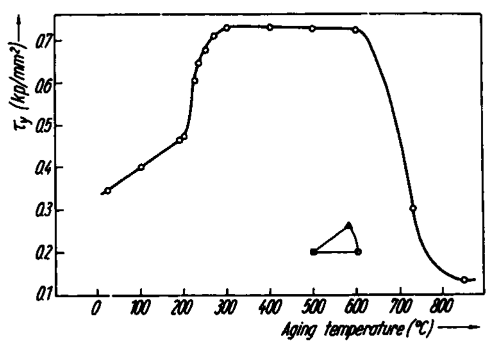


Fig. 3. Critical resolved shear stress of quenched copper crystals, measured at 78 °K, after aging for one hour at various temperatures, $\dot{\varepsilon} = 10^{-4}\ s^{-1}$, deformed at 78 °K, —○— aged for 7 min at 23 °C, —⊖— annealed

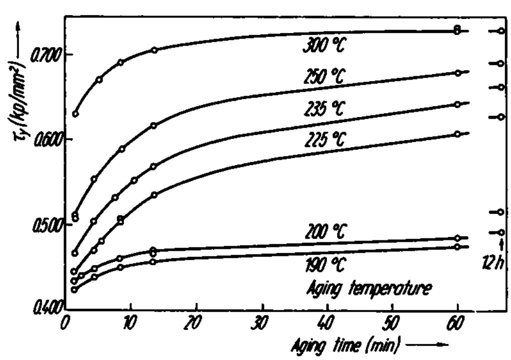


Fig. 4. Observed variation of the critical resolved shear stress of quenched specimens aged for various times for various aging temperatures

3. Experimental Results

After growth of the copper crystals, all of the same orientation, these crystals were quenched, as outlined above, from a fixed temperature of 1030 °C. The measurements made on these crystals were primarily measurements of the mechanical properties of the quenched crystals after various aging treatments.

Measurements of the C.R.S.S. of quenched specimens were undertaken at 80 °K after aging specimens one hour at temperatures between 25 and 830 °C. These results, which are summarized in Fig. 3, show two distinct aging reactions take place below 300 °C and a final removal of the quench-hardening in the temperature range around 750 °C. Isothermal measurements were undertaken around 220 °C, in order to obtain information about the nature of the growth process. These results are shown in Fig. 4.

In addition to measurements of the C.R.S.S. of quenched and aged specimens, the temperature dependence of the C.R.S.S. for various aged specimens was measured between 80 and 300 °K, Fig. 5, in order to compare the observed dependence of the C.R.S.S. upon temperature with various theories.

Another measurement of interest is the observation of the temperature at which we first see observable dislocation loops and their subsequent growth at various aging temperatures, Fig. 6. We have observed the presence of dislocation loops, using transmission electron microscopy techniques only, at aging temperatures of 250 °C and above. This is in contrast to previous observations and undoubtedly has something to do with the slower quenching rate used in previous quenching studies in this material.

The nature of the dislocation loops were determined as follows: By tilting a foil containing dislocation loops, it was observed that the electron beam axis was nearly parallel to the [111] direction, it was observed that some of the loops were symmetrical in shape, with their sides parallel to the $\langle 110 \rangle$ directions. These loops then lay on the (111) plane. A further tilting of the foil gave operating reflections, $\boldsymbol{g}$, of the type $\{\bar{2}24\}$. The loops, whose habit planes were (111), disappeared under these diffracting conditions, requiring that $\boldsymbol{g} \cdot \boldsymbol{b} = 0$, where $\boldsymbol{b}$ is the Burger's vector of the dislocation loop. The possible values of

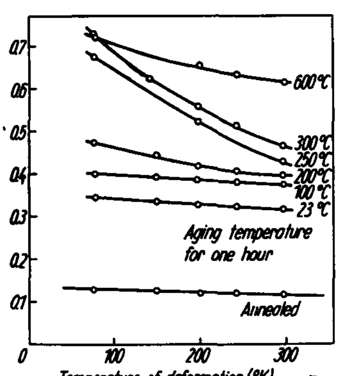


Fig. 5. Temperature dependence of the critical resolved shear stress for quenched crystals given various aging treatments

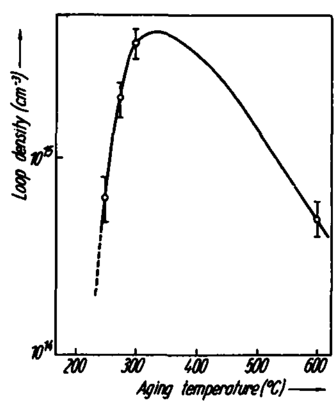


Fig. 6. A comparison of the observed density of Frank vacancy loops as a function of aging temperature, aged for one hour

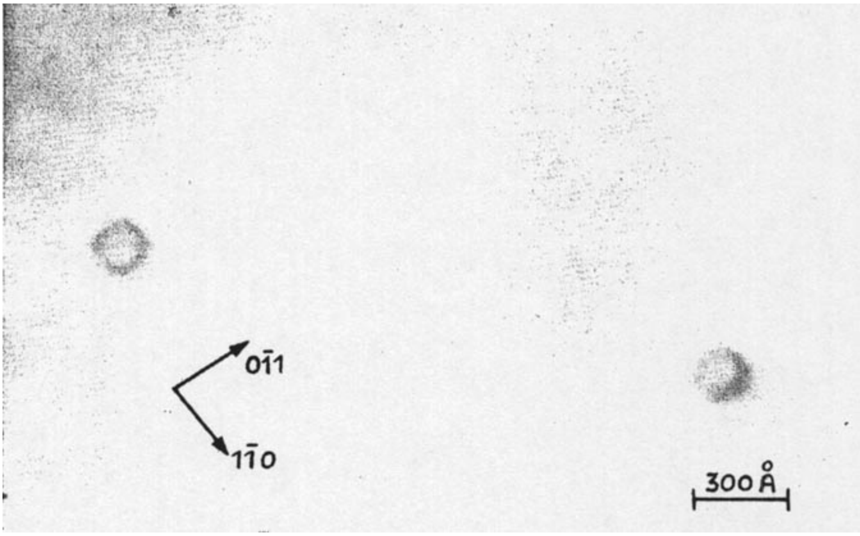


Fig. 7a. Frank dislocation lops in quenched copper

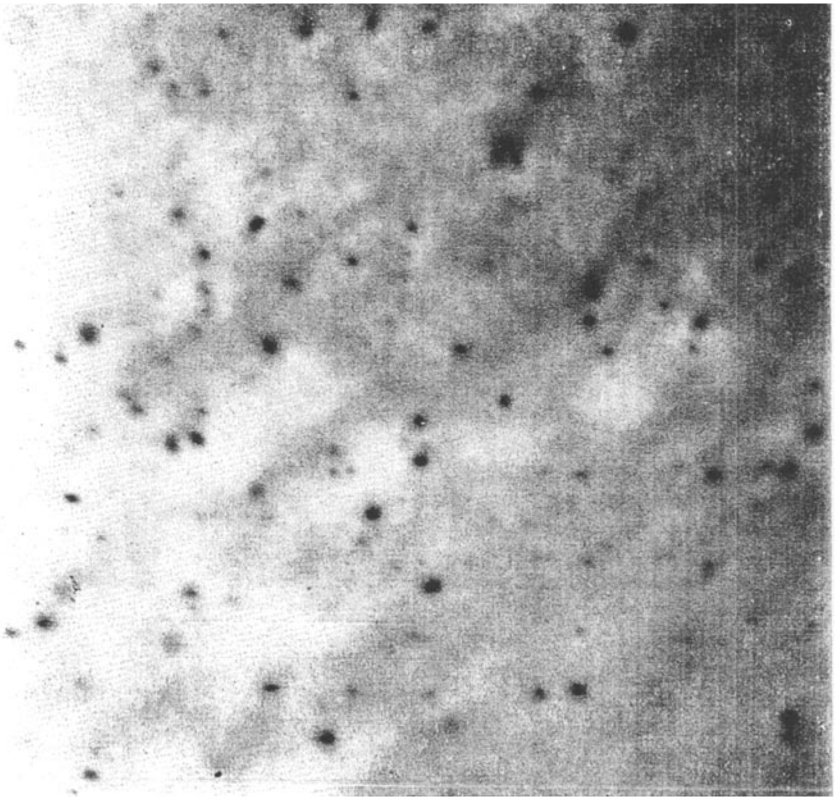
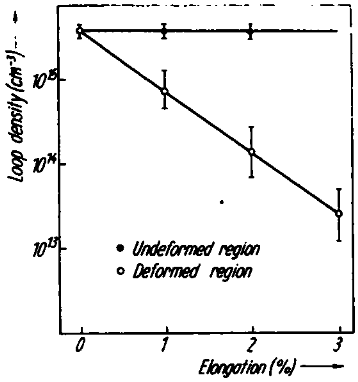


Fig. 7b. An example of a Frank dislocation loop in specimen quenched from 1030°C and aged at 600°C

Fig. 8. Measured rate of removal of Frank dislocation loops, within slip traces, compared to density outside slip traces, after various plastic strains, quenched—aged at 300 °C for one hour, deformed at 78 °K



$b = a/6\,\langle 112\rangle$ preclude $g \cdot b = 0$ for this reflection and only $b = a/3\,\langle 111\rangle$ satisfied the condition. Thus the loops are of the Frank type. Some examples are shown in Fig. 7.

Another interesting observation was the rate of removal of dislocation loops in quenched and aged specimens, as a function of plastic strain. Quenched and aged specimens were deformed and thin foils prepared for examination. The loop density, within a slip trace, was determined on various specimens after fixed amounts of plastic deformation. The results are shown in Fig. 8. In addition, two further observations are of interest on this point, firstly, if the foils are accidentally deformed or heated such as to establish a temperature gradient, prismatic dislocation loops are observed. Secondly, we observed an increased density of retained screw dislocations in the deformed samples, which have been quenched and aged to produce Frank dislocation loops.

4. Discussion

It is convenient to consider the kinetics of the reactions observed after which a discussion of the various hardening mechanisms will be given.

4.1 Isothermal studies between 190 and 300 °C

In quenched specimens, aged in this temperature range, a fairly pronounced increase in critical resolved shear is observed, Fig. 4. The apparent kinetics of the reactions are complicated but they can quite reasonably be interpreted with reference to the observed growth of dislocation loops as well as the observed changes in the mechanical properties of quenched crystals. First, though, it is of interest to consider the general annealing behavior around 200 °C, in light of the fact that after extensive annealing of quenched specimens, no dislocation loops are apparent at this aging temperature. On the other hand, after annealing quenched specimens at, say, 250 °C for comparatively short times (compared on the basis of an activation energy of 1 eV) dislocation loops do appear. Furthermore, the saturation of the C.R.S.S. for a given aging temperature is further evidence that loop growth is temperature dependent. The activation energies for the process between 190 and 300 °C were obtained by the standard cross-cut method and they show an apparent increase from about 1.1 to about 1.4 eV, which indicates that more than one process is occurring in the temperature range under consideration.

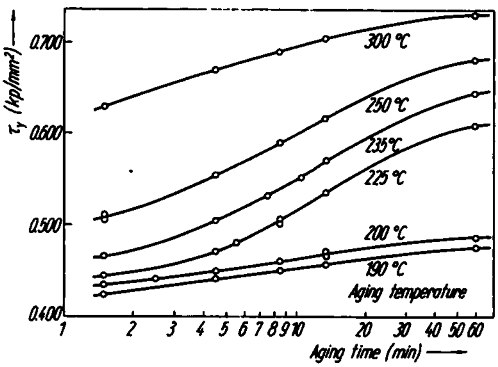


Fig. 9a. Critical resolved shear stress as a function of log of aging time in quenched specimens

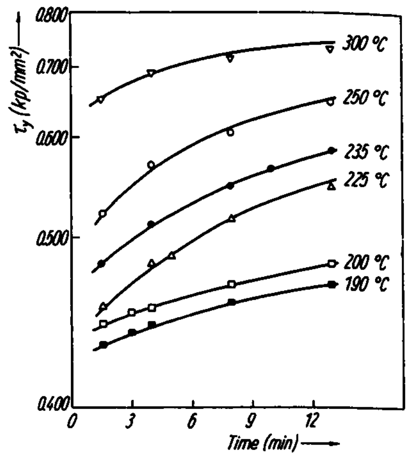


Fig. 9b. A comparison of the log of the critical resolved shear stress for quenched specimens aged various times at temperatures indicated

In the higher temperature range, 250 to 300 °C, dislocation loop growth must be taking place at the expense of either small dislocation loops or small vacancy clusters. The activation energy, which would limit such a process, must be the emission of a vacancy from a small cluster and its eventual trapping at a larger sink, i.e.

$$E = E_{\mathrm{IV}}^{\mathrm{M}} + E_{\mathrm{IV}}^{\mathrm{B}} \,, \tag{1}$$

where E observed activation energy, $E_{\mathrm{IV}}^{\mathrm{M}}$ energy of motion of single vacancy, $E_{\mathrm{IV}}^{\mathrm{B}}$ binding energy, since it is expected that the binding energy of a divacancy to a cluster would be higher than that of a single vacancy. If we argue further that $E_{\mathrm{IV}}^{\mathrm{B}}$ is an increasing function of the size of the cluster from which it is emitted then we expect

$$E_{\mathrm{IV}}^{\mathrm{B}} = A\, r^{\gamma} \,, \tag{2}$$

where A and γ are adjustable parameters and r is the size of the cluster which has emitted a vacancy.

This simple model suggests that for a distribution of small clusters, growth is limited by the diffusion of single vacancies, which allows the eventual growth of dislocation loops. Again the kinetics have been analyzed by the cross-cut method, Fig. 9a. Also, an analysis of the data using a diffusion controlled mechanism, as suggested by Flynn [20], is shown in Fig. 9b. Since some curvature is indicated in the data plotted either way, this indicates that the process would be best considered as one with a variable activation energy. The measured activation energy of (1.1 ± 0.1) eV which is associated with the temperature range around 200 °C, corresponds to the second stage of annealing in quenched copper, as measured by resistivity changes [21], and is, accordingly, assigned to single vacancy motion.

It is important to emphasize that the error associated with this measurement is an upper limit, the reproducibility being such that the total changes in yield stress between 190 and 200 °C are of the order of 50 g/mm², while the sensitivity of the measurement is about $1\frac{1}{2}$ g/mm². Also, we have repeatedly measured the magnitude of the hardening—throughout the observed range of hardening at selected points—and the reproducibility is within the above stated sensitivity.

If we consider the behavior of quenched crystals, aged at temperatures between 250 and 300 °C, we must conclude, in view of the observed activation energy and the reasonable correlation of mechanical properties with observable dislocation loops, that there exists a distribution of cluster sizes. This again indicates that smaller clusters or loops are emitting vacancies and allow the growth of larger loops, in density as well as size.

If the smaller, vacancy emitting defects are dislocation loops, then they must climb in the emission process and, then, the emitted defect must migrate to a larger loop. Then, the activation energy for the process E, would be given by

$$E = E_{\mathrm{m}} + E_{\mathrm{f}} = E_{\mathrm{SD}} ,$$

where E_{m} the migration energy of a single vacancy in copper, E_{f} the formation energy of a single vacancy in copper, E_{SD} the self diffusion energy of copper. Measured values [22] of E_{SD} clearly rule out a vacancy emission process. We are led to the conclusion that clustering of vacancies is a necessary step in the aging process in quenched copper.

An equation, which approximately describes the condition of transformation from cluster to Frank loop, is

$$\frac{4}{3}\,\pi\, R_{\mathrm{V}}^{2}\,\gamma \approx \frac{1}{2}\, G\, b^{2}\, \pi\, R_{\mathrm{L}} \ln \frac{R_{\mathrm{L}}}{r_{0}} + (\text{ST fault energy})\, \pi\, R_{\mathrm{L}}^{2} ,$$

where we neglect volume strain associated with the cluster of vacancies from which a dislocation loop grows

An estimate of the stacking fault energy, assuming known values of the surface energy of copper [23] and estimating the vacancy cluster size from the work of Galligan and Washburn [24] and Seeger et al. [25], the stacking fault energy is found to be of the order of 50 ergs/cm².

4.2 Consideration of the density of retained vacancies

In light of the assignment of an energy of motion of 1.1 eV to the single vacancy in the present work, it is quite important to examine this assignment with respect to various measurements of the energy of formation of vacancies in copper. The direct measurements of Simmons and Balluffi [27] give a value of 1.17 eV for the energy of formation of a vacancy while the energy of motion is of the order of 1 eV [28, 29]. If we consider the number of single vacancies required to produce the number of observed vacancy loops, in conjunction with a formation energy of 1.17 eV, no agreement is obtained, there being more vacancies observed than predicted. A consideration of the various errors in such a determination, such as measurement of temperature, measurement of loop size and density measurement of the thickness of foils and magnification factors in the electron microscope, do not seem sufficiently large to seriously change the result. For example, we have calibrated the thermocouple in various fixed temperature baths and the error in this instance is less than 2 °C. Measurement of the density of loops has been made by determination of the foil thickness in two ways, which agree within 5%. Furthermore, since it is quite probable that some loss of vacancies occurs in the quench, then the observed density of loops provides a lower limit in such an estimate. We also neglect plastic deformation, since the dislocation density is so low in the as quenched samples. The observed vacancy concentration present in quenched samples would, accordingly, be less than the actual high temperature value. A consideration of the loop character — Frank vacancy loops — as well as the observed temperature dependence of the growth, quite clearly rules out prismatic punching of loops, due to oxide particles or hydrogen gas.

These arguments indicate that the vacancy formation energy is, indeed, lower than that indicated by the measurements of Simmons and Balluffi and favor the assignment of 1.1 eV to the single vacancy migration.

4.3 Temperature dependence of the critical resolved shear stress after various aging treatments

In quenched specimens, those aged between 100 and 600 °C, an interesting change in the temperature dependence of the C.R.S.S. occurs, which reveals, again, a growth of large loops at the expense of small clusters. It is interesting, therefore, to compare the present results with the various theoretical considerations of the interaction of mobile dislocations with voids and small dislocation loops. Since a temperature independent and a temperature dependent C.R.S.S. is observed, depending upon the aging conditions, a clear distinction as to the applicability of various theoretical expressions for the temperature dependence of the C.R.S.S. can be given.

In the region where little or no temperature dependence of the C.R.S.S. is observed, two models are applicable, the first due to Kroupa and Hirsch [30] and the second due to Coulomb [31]. The Kroupa and Hirsch model suggests that the effective void spacing depends on the interaction energy of the void and the dislocation line, which gives an increase in C.R.S.S.

$$\Delta\tau = G\,b\,d\,N^{2/3}/\gamma,$$

where G shear modulus, b absolutely value of the Burgers' vector, d diameter of the obstacle, N the number of obstacles per unit volume, and γ is a constant which characterizes the distribution and is equal to eight for a random distribution of obstacles [32]. If we assume that the voids at this aging temperature have a size of about 10 Å, we can then estimate the density from the initial concentration C_v of vacancies as

$$C_v \approx K\left(\frac{R}{r}\right)^3 N\,,$$

where R radius of void, r atomic radius, K a conversion factor, then $N \approx \approx 2\times10^{16}/\mathrm{cm}^3$, for $C_v = 10^{-4}$ atom fraction. Upon insertion of these values, the change in C.R.S.S. is observed to be about 0.3 kg/mm^2, which is in reasonable agreement with observation. Similarly, if we use appropriate values in the expression given by Coulomb, $\Delta\tau$ is estimated at about 7 kg/mm^2. These estimates indicate that the Kroupa and Hirsch model is more applicable than the Coulomb model to the present problem.

In contrast to the temperature independent C.R.S.S., the observed temperature dependence in specimens aged between 200 and 600 °C can be directly related to an observed defect and, thus, a more critical comparison with various theories can be given. Of these theories which predict a strong temperature dependence of the C.R.S.S., two appear applicable to the present problem: Fleischer's [33] theory of asymmetrical strain and Seeger's [8] theory of obstacle cutting. We can directly compare these theories with the present results,

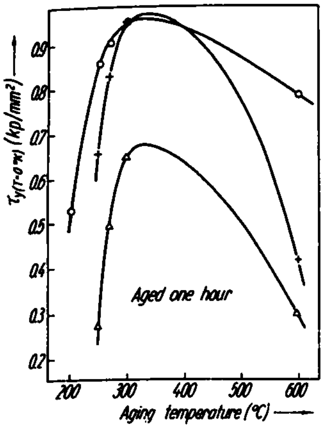


Fig. 10. The observed critical resolved shear stress of the quenched and aged crystals compared with the predicted values. Values for the C.R.S.S. are computed on the basis of the observed size and defect density.

○ – $\tau_y (T = 0\ °K)$ observed
+ – $\tau_y (T = 0\ °K)$ Seeger ($U_0 \approx 4.3$ eV)
△ – $\tau_y (T = 0\ °K)$ Fleischer (τ_y to be multiplied by 10)

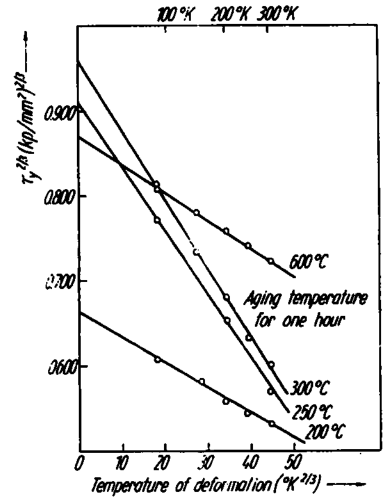


Fig. 11. The measured critical resolved shear stress versus temperature plotted according to the behavior expected on the basis of Seeger's theory

by first considering the measured size of the loops and their density, with predicted values of the C.R.S.S. based on these measured parameters. This is shown in Fig. 10. We first note that we must assume a value of 4 eV for the activation energy associated with the cutting process, as given, in the Seeger model, (A value originally suggested by Seeger. We will show below that this value is in very reasonable agreement with a measured value.) Quite clearly, the Fleischer theory does not adequately describe the present results, since the predicted C.R.S.S. is about ten times larger than the observed C.R.S.S.

An additional consideration of the applicability of the Seeger model, which we have undertaken, is a comparison of the observed and predicted temperature dependence of the C.R.S.S. This is shown in Fig. 11, where clearly a very reasonable fit is obtained. Another test of Seeger's theory is to compare the measured activation energy for the cutting process with the value originally

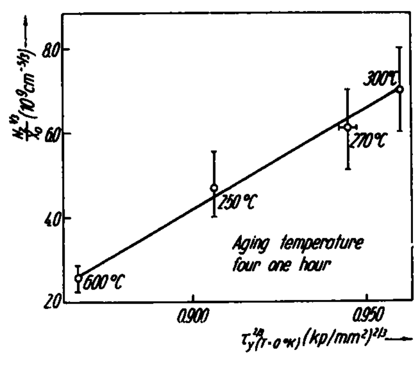


Fig. 12. The critical resolved shear stress, raised to the 2/3 power, obtained from extrapolation of the data in Fig. 11, compared to the density of loops to the one third power divided by the defect size. The comparison is made from the observed defect density after specimens are aged at various temperatures

suggested by Seeger. In Seeger's formulation $\tau^{2/3}$ is given by

$$\tau^{2/3} = A\,(1 - B\,T^{2/3})\,.$$

where A is given by

$$A = \left(\frac{N_z}{G\,b}\right)^{1/3} \frac{U_0}{4\,X_0\,b}\,, \quad \text{and} \quad B = \frac{K}{U_0}\left(\frac{N_b\,\nu_0}{N_z\,A'}\right).$$

Here N_z the number of zones in the slip plane and we assume X_0 is the size of the obstacle, U_0 the activation energy of the cutting process at 0 °K, A' the strain rate, N the number of dislocations held up at obstacles and ν_0 the attempt frequency for the dislocation overcoming the obstacles. This has been considered in two ways, first we obtain values of A from extrapolation of the temperature dependence of the C.R.S.S. to 0 °K and secondly, we measure N_z and X_0 from the observed density of obstacles in the micrographs of appropriately aged specimens. These values can then be directly compared, Fig. 12, and a value of the activation energy, U_0, obtained. The activation energy obtained in this way is about 5 eV which is in extremely good agreement with an obstacle cutting process, as given by Seeger. We assume in this, as was originally done by Seeger, that the parameter X_0 is proportional to the diameter of the defect involved. Furthermore, the observed temperature dependence and intercept of the $\tau^{2/3}$ versus $T^{2/3}$ plot, are consistent with a proportionality constant of unity. In any case, the present method of approach presents a method of establishing such a proportionality. A future paper will deal with this question.

4.4 The role of impurities in quench hardening

In the present copper, 99.999 + % pure, impurities would be expected to play a minor role in the hardening for a few reasons. Firstly, the whole of the quench hardening is recoverable. Secondly, the recovery of the quench hardening occurs when the dislocation loops are removed. Some crystals have been repeatedly quenched and the quench hardening is reproducibly the same. This last point indicates that, if impurities are involved they are within the specimen and not introduced by the quenching. The impurity level of the as quenched copper is small compared to the total number of vacancies retained in the quench. It is important to emphasize, that the whole of the observed hardening is directly related to an *observable defect*.

4.5 Consideration of the rate of removal of dislocation loops

As shown in the results section, the rate of removal of dislocation loops occurs very rapidly within a slip trace — after a few percent strain — while the density outside a slip trace is experimentally the same as the undeformed samples. This indicates that new dislocation sources are not operating, but the source density remains constant throughout the deformation. This directly shows, that the hardening mechanism involves a lattice hardening, rather than a source hardening mechanism. Another consideration which indicates a lack of source hardening is the observation that vacancies have certainly had time to reach grown-in dislocations at, say 200 °C, where helical dislocations are observed, but the hardening is not as pronounced as at 300 °C. The most important point is, however, that loops are swept up by mobile dislocations and some interaction between loops and mobile dislocations is taking place.

5. Conclusions

The following conclusions can be drawn from this work:

A) Quench hardening in copper, in which oxygen contamination is avoided, occurs in two stages. The first stage is centered around room temperature, while the second is centered around 250 °C.

B) Frank dislocation loops are observed to grow in the same temperature range where the second stage of hardening takes place.

C) Isothermal measurements of the kinetics associated with the second stage of hardening reveal that two distinct processes are taking place: the first occurs with an activation energy of 1.1 eV, consistent with an assignment of single vacancies. The second occurs with a variable activation, energy, 1.3 eV to 1.4 eV.

D) A model, which accounts for a variable activation energy, is proposed in which large loops grow at the expense of small clusters.

E) A comparison of the temperature dependence of the C.R.S.S. in quenched specimens, which are aged around 100 °C, indicates the applicability of the theory of Kroupa and Hirsch to the observed hardening in this range.

F) On the other hand comparison of the temperature dependence of the C.R.S.S. in quenched specimens, aged above 235 °C, with the theories of Fleischer and of Seeger, quite clearly indicates the applicability of Seeger's theory to the present results.

G) A quantitative measurement of the density and size of Frank loops, and the temperature dependence of the C.R.S.S. in quenched specimens, aged above 235 °C, gives a value of $\approx$ 5 eV for the cutting of a loop by a mobile dislocation.

H) The removal of the hardening in quenched crystals takes place around 800 °C, coincidental with the removal of Frank dislocation loops.

I) Since complete removal of the hardening occurs in quenched samples — after aging at 830 °C — impurity effects are probably of little significance.

J) Dislocation loop removal in quenched and deformed crystals occurs in a few percent strain, within a slip region. Outside the slip region, the density of loops remains fairly constant throughout the first few percent strain.

K) Prismatic dislocation loops are only observed in specimens which have been intentionally (or unintentionally) deformed.

References

[1] A. Seeger and D. Schumacher, Lattice Defects in Quenched Metals, Ed. R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii, Academic Press, New York 1965.
[2] R. W. Balluffi, J. S. Koehler, and R. Simmons, Recovery and Recrystallization in Metals, Ed. L. Himmel, Interscience Publishers, New York 1962.
[3] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. 107, 1499 (1957).
[4] R. Maddin and A. H. Cottrell, Phil. Mag. 46, 735 (1955).
[5] M. Meshii and J. W. Kauffman, Phil. Mag. 5, 939 (1960).
[6] J. Galligan and J. Washburn, Phil. Mag. 8, 1455 (1963).
[7] H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, Acta metall. 7, 154 (1959).
[8] A. Seeger, Proc. 2nd UN Internat. Conf. Peaceful Uses of Atomic Energy 6, 250 (1958).
[9] K. H. Westmacott, Phil. Mag. 14, 239 (1966).
[10] L. M. Clarebrough. P. Humble. and M. H. Loretto, Acta metall. 15, 1007 (1967).
[11] W. L. Bell and G. Thomas, Phil. Mag. 13, 395 (1966).

[12] J. SILCOX and P. B. HIRSCH, Phil. Mag. 4, 72 (1959).
[13] A. C. DAMASK and G. J. DIENES, Point Defects in Metals, Gordon and Breach, New York 1963.
[14] M. MESHII, ob. cit. Ref [1] (p. 387).
[15] G. LAMPERT, ob. cit. Ref [1] (p. 54).
[16] C. BUDIN, F. DENAYRON, A. LUCASSON, and P. B. LUCASSON, C. R. Acad. Sci. (France) 256, 1518 (1963).
[17] W. BELL, D. M. MAHER, and G. THOMAS, ob. cit. Ref [1] (p. 739).
[18] J. W. STEEDS, Relation between Structure and Mechanical Properties of Metals, Nat. Phys. Labor. Symp., No. 15 (1963).
[19] P. G. SHEWMON, Diffusion in Solids, McGraw-Hill, New York 1963, (p. 31).
[20] C. P. FLYNN, Phys. Rev. 134A, 587 (1964).
[21] F. RAMSTEINER, G. LAMPERT, A. SEEGER, and W. SCHULE, phys. stat. sol. 8, 863 (1965)
[22] A. KUPER, H. LETAW, L. SLIFKIN, E. SONDER, and C. T. TOMIZUKA, Phys. Rev. 96, 1224 (1954).
[23] H. UDIN, A. J. SCHALER, and J. WULFF, J. Metals 1, 1936 (1949).
[24] J. GALLIGAN and J. WASHBURN, Phil. Mag. 8, 1455 (1963).
[25] A. SEEGER, V. GEROLD, and M. RUHLE, Z. Metallk. 54, 553 (1963).
[26] H. KUMURA, R. MADDIN, and D. KUHLMANN-WILSDORF, Acta metall. 7, 154 (1959).
[27] R. O. SIMMONS and R. W. BALLUFFI, Phys. Rev. 129, 1553 (1963).
[28] R. R. HASIGUTI, Y. NAKAO and H. KIMURA, J. Phys. Soc. Japan 20, 553 (1965).
[29] D. M. MAHER, Ph.D. Thesis, Univ. of California (1966).
[30] F. KROUPA and P. B. HIRSCH, Disc. Faraday Soc. 38, 49 (1964).
[31] D. COULOMB, Acta metall. 7, 556 (1959).
[32] K. H. WESTMACOTT, Phil. Mag. 14, 239 (1966).
[33] R. L. FLEISCHER, J. appl. Phys. 33, 3504 (1967).

(Received January 8, 1968)