

STORED ENERGY AND SUBSTRUCTURE

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1. Introduction

1.1 Stored Energy and Substructure

The stored energy of cold work is the sum of the energy effects of the imperfections created by the deformation process and retained until the time of measuring. In view of the difficulty of differentiating between the effects of various structural elements, measurements of the stored energy may appear to hold little promise of contributing to the knowledge of substructure. Yet the stored energy of cold work not only has been interpreted in terms of variables of the deformation process and the deformed metal, but is becoming increasingly well understood in relation to structural factors. This paper will be concerned with the relation of the stored energy to the substructure on the basis of the pertinent literature.

1.2 Types of Substructure

In the broadest sense, the substructure comprises all imperfections present within the grain boundaries (large-angle boundaries) of a polycrystalline metal or present in a single crystal. This will be called here the "total substructure" without further differentiation. The subboundaries (low-angle boundaries), conventionally designated "substructure" are revealed at an intermediate level of resolution. They will be called "intermediate substructure". At the ultimate level, the substructure is composed of crystal imperfections such as dislocations, point defects, stacking faults, and twinning faults. Imperfections may occur individually or they may interact with other members of their own class or with members of one of the other classes. The imperfections will be classified here as "ultimate substructure".

In solid-solution alloys deformation may in addition to structural effects cause configurational effects, such as the destruction of short-range and long-range order and changes in the interaction of imperfections with solute atoms. These processes affect the stored energy, but the destruction of order is not normally considered as a change in substructure.

Metals in the as-solidified or annealed state contain some elements of substructure. A small part of this is an equilibrium feature, but most is due to non-equilibrium causes. However, the substructure present in as-solidified or annealed metals is of limited extent and its energy effects are so small that they can usually be ignored. Pronounced substructures are generated by cold work, irradiation, creep, cyclic loading, electrodeposition and thermal shock. This discussion will be limited to the substructure formed by cold work.

1.3 Measurement of the Stored Energy

The stored energy of cold work as a function of variables and its release during annealing have been subjects of extensive investigation. The energy expended in the deformation process and the ratio of the stored to the expended energy have attracted interest since the earliest investigations of the stored energy. More recently efforts have been made to relate stored energy measurements to changes during deformation and annealing in such properties, as hardness, electrical conductivity and density, and structural changes have been followed by light microscopy, electron microscopy and X-ray diffraction.

The methods of measuring the stored energy of cold work are of two types. Single-step methods determine the stored energy as the difference between the expended work and the heat evolved during deformation. The work is determined from stress-strain relations or by such means as a ballistic pendulum. The heat is determined from the adiabatic temperature rise of the specimen or by deformation inside a calorimeter. The single-step methods are unique in that they can supply information on the kinetics of heat evolution during and immediately after the deformation process.

In the two-step methods, the specimen is deformed and the stored energy is then measured calorimetrically. The calorimetric methods measure the heat effects of bringing the cold worked and a standard specimen to the same final state, such as the annealed state or solution in a solvent. Annealing methods also give information on the kinetics of energy release during the annealing of cold worked metals. Another two-step method involves metal solution calorimetry; for the required precision, special combinations of solutes and solvents have to be used, such as gold-silver alloys and a tin solvent.

In most methods, the enthalpy rather than the internal energy of cold work is measured. Their difference, however, is negligible.

2. The Total Stored Energy as a Function of Variables

The total stored energy, representing the total substructure, is a function of macroscopic variables which affect either the deformation process or the deformed metal. In the former category are the strain, the deformation temperature, the strain rate and the type of deformation. In the latter category are the nature and composition of the metal and its grain structure. The effects of these variables will be summarized in this section. A detailed account may be found in a review of the subject of the stored energy (Titchener and Bever, 1958)*.

2.1 Strain

The stored energy increases with strain at small and moderate strains. The results of several investigations of copper are plotted in Fig. 1 (Clarebrough

* The references are listed alphabetically at the end of this paper.

Hargreaves and West, 1955; Clarebrough, Hargreaves and Loretto, 1958; Gordon, 1955; figure after Titchener, 1961). The decrease in the rate of energy absorption with increasing strain should be noted. The energy stored by a gold-silver alloy deformed at room temperature and 78°K is shown in Fig. 2 (Appleton and Bever, 1963; Titchener and Bever, 1959). At room temperature, the energy stored by this alloy approaches a saturation value both in torsion and wire drawing. No decrease in the rate of energy absorption was observed at 78°K.

2.2 Temperature

As the temperature of deformation decreases, the stored energy increases. This relation, which is shown in Fig. 2 and more explicitly in Fig. 3 (Appleton and Bever, 1963) can be expressed by stating that the stored energy increases with a decrease in the ratio of the temperature of deformation T_w to the melting point T_m and the ratio of the temperature of deformation to the recrystallization temperature T_r .

2.3 Strain Rate

The strain rate can have an effect on the amount of energy stored. While at low and intermediate rates the energy stored by a gold-silver alloy is independent of strain rate, with further increases in strain rate it first increases and then decreases (Titchener and Bever, 1959). A maximum in the stored energy has been found at 4°K (Appleton and Bever, 1963). The decrease in the energy probably can be attributed to a rise in temperature of the specimens.

2.4 Deformation Process

Although the values for torsion and wire drawing in Fig. 2 are nearly equal, different deformation processes, under otherwise identical conditions, can lead to saturation values of the stored energy which differ appreciably (Titchener and Bever, 1959). This difference is probably at least in part due to differences in the temperature rise caused by the deformation process, but differences in microplastic behavior may also play a role.

2.5 Nature of Metallic Element

Knowledge of the dependence of the stored energy on the metal is limited. Most measurements have been made on face centered cubic metals. Also, a comparison of different metals is complicated by the effect of impurities on the stored energy. However, in general, the stored energy increases with the melting point and recrystallization temperature of a metal. This generalization is consistent with the increase in the stored energy as the ratios of the temperature of deformation to the melting temperatures (T_w/T_m) and to the recrystallization temperature (T_w/T_r) decrease.

2.6 Composition

The stored energy, in general, increases with impurity content. White and Koyama, 1962, discussed their observations and observations by Clarebrough et al., 1955, according to which impurities may either increase or decrease the amount of energy stored.

Larger concentrations of solute tend to increase the stored energy; as shown in Fig. 4 for the gold-silver system (Greenfield and Bever, 1957). At most, only a fraction of this increase (a maximum of about 30 cal/g-atom at 50 at. pct) is due to the destruction of short-range order. The increase of the stored energy is related to the increase of the recrystallization temperature with increasing solute concentration.

2.7 Grain Structure

At low strains, fine-grained copper under otherwise identical conditions stores a measurably larger amount of energy than coarse-grained copper, as shown in Fig. 1 (Clarebrough et al., 1958). This effect has also been observed by Loretto and White, 1961; White, 1962; and Williams, 1962.

2.8 The Ratio of the Stored to the Expended Energy

The expended energy has a bearing on the mechanisms of energy storage and work hardening. Fig. 5 shows the ratio of the stored to the expended energy E_s/E_w as a function of strain at room temperature and 78°K for a gold-silver alloy deformed in torsion (Appleton and Bever, 1963).

3. The Release of the Stored Energy

3.1 General

A cold worked metal is unstable and under favorable kinetic conditions returns to the annealed state by recovery and recrystallization. The driving force for these restoration processes is the free energy of cold work. In general, it is nearly equal to the internal energy, that is, to the stored energy of cold work usually measured.

The stored energy is released during the restoration processes and the kinetics of this release are indicative of the kinetics of these processes. The release of stored energy often takes place in well defined temperature ranges or time intervals; in some cases, it is possible to assign peaks in the release curves to a specific mechanism, such as the annealing out of vacancies or recrystallization. The energy released during prerecrystallization stages and the energy released during recrystallization, expressed as fractions of the total stored energy, E_p/E_s and E_r/E_s , are significant in interpreting the substructure.

The energy release can be investigated by

- (1) anisothermal annealing as a function of temperature during continuous heating
- (2) isothermal annealing as a function of time at constant temperature
- (3) isochronal annealing as a function of annealing for fixed times at different temperatures

A special mechanism of energy release involves mechanical deformation (work softening).

The literature on the release of the stored energy will be summarized briefly in this section. It has been reviewed extensively in several publications (Bever, 1957; Titchener and Bever, 1958; Clarebrough, Hargreaves and Loretto, 1962a).

3.2 Anisothermal Annealing

Following earlier investigations of the stored energy by anisothermal annealing, such as those of Sato, 1931, and Quinney and Taylor, 1937, a series of papers by Clarebrough, Hargreaves and their collaborators has made great contributions to the knowledge of the release of stored energy and the kinetics of the restoration of cold worked metals. Typical examples of their results will be presented.

The energy release by pure copper during continuous heating is shown in Fig. 6 (Clarebrough, Hargreaves and West, 1955). The release is almost entirely due to recrystallization which is represented by the peak in the curve. This is preceded by a small recovery effect. The decreases in hardness and electrical resistivity during recrystallization should be noted.

The energy release by copper containing 0.35% arsenic and 0.05% phosphorus is shown in Fig. 7 (Clarebrough et al., 1955). A plateau in the release curve preceding the recrystallization peak indicates the occurrence of prerecrystallization phenomena. Similar prerecrystallization processes probably take place in pure copper at or near room temperature, but impurities restrain these processes, which then occur at higher temperatures where they can be observed during annealing experiments.

The energy release by commercial nickel is shown in Fig. 8 (Clarebrough et al., 1955). The prerecrystallization phenomena include a small well developed peak, which is attributed to the annealing out of vacancies. Clarebrough, Hargreaves, Loretto and West, 1960, found such a peak also in nickel of higher purity, but the plateau was absent. Part of the release curve for commercial nickel has been explained by calculations of Nicholas, 1955, who assumed that point defects anneal out at the boundaries of subgrains. The first decrease in the resistivity curve shown in Fig. 8, which is not accompanied by a change in hardness, also indicates the annealing out of vacancies.

Michell and coworkers have combined measurements by anisothermal calorimetry of the energy stored in nickel with structural investigations by X-ray diffraction (Michell and Haig, 1957; Michell and Lovegrove, 1960).

Anisothermal annealing can be adapted to operation below room temperature. In an investigation of copper, deformed at 88°K, Henderson and Koehler, 1956, found several distinct annealing stages and substages. Van den Beukel, 1961, qualitatively confirmed these findings for copper and also reported results for gold, silver, and nickel.

3.3 Isothermal Annealing

Measurements of the release of stored energy by isothermal annealing are of fundamental importance and have contributed much to the understanding of the kinetics of energy release. Borelius, Berglund and Sjöberg, 1952, applied isothermal calorimetry to measuring the energy stored by aluminum, copper and zinc and Gordon, 1955, using the same method, measured the energy stored in copper. Some of Gordon's results are shown in Fig. 9. Aström, 1955, annealed specimens of aluminum isothermally at progressively higher temperatures and followed changes in their substructure by metallography. Some of his results are shown in Fig. 10. Bailey and Hirsch, 1960, combined isothermal calorimetry of the stored energy in silver with electron transmission microscopy. The interpretation of their stored energy measurements in terms of the substructure observed by them has attracted particular attention.

3.4 Isochronal Annealing

The stored energy present in a gold-silver alloy after deformation at 78°K or room temperature and holding for various times at different temperatures is shown in Fig. 11 (Greenfield and Bever, 1956). After deformation at 78°K, two stages of release are indicated.

The curve in the lower part of Fig. 12 shows the energy release during isochronal annealing of filings of a gold-silver alloy (Averbach, Bever, Comerford and Leach, 1956). This curve is consistent with the corresponding curve in Fig. 11. The upper part of Fig. 12 shows results of a correlated X-ray investigation and hardness values, which will be discussed below.

3.5 Work Softening Effect

Observations of a work softening effect are shown in Fig. 13 (Titchener and Bever, 1960). A specimen cold worked at 78°K released energy when brought to room temperature as the thermally unstable imperfections annealed out. Additional deformation at room temperature caused a further decrease in the stored energy by the removal of mechanically unstable imperfections. This second decrease in stored energy was accompanied by a decrease in microhardness, which indicated that dislocations played a part in the process.

An appreciable decrease in the stored energy occurs when specimens of a gold-silver alloy deformed at 4°K are brought to 78°K (Appleton and Bever, 1963). No work softening was found to result from secondary deformation at 78°K after primary deformation at 4°K, but the strain levels as well as the temperatures were different from those of the earlier investigation.

4. Stored Energy and Total Substructure

Since the total stored energy represents the total substructure, the effects of variables on the stored energy are also indicative of their effects on the substructure. The conclusions which can be drawn on this basis will be summarized.

4.1 Strain

The increase in stored energy with increasing strain can be attributed to an increase in the number of imperfections and an intensification of their interaction as the deformation progresses. The increase in the energy also raises the question as to whether new types of imperfections are generated at higher strains. Under conditions where the stored energy attains saturation, the substructure reaches a steady state in the sense that as many imperfections are formed as are released by a work softening mechanism. In this connection, it is significant that measurements of the stored energy can be made after deformation to moderate and large strains at which the substructure is so highly developed and so complex that it cannot be observed directly in detail. Stored energy measurements because of their statistical or integrating nature, therefore, assume a particular usefulness at higher strains.

4.2 Temperature

The increase in stored energy with decreasing temperature suggests that the number of imperfections increases and that they may interact with each other more intensively. It is also known from other evidence that at low temperatures, additional types of imperfections are generated. The extent to which the increase in the energy is due to the suppression of thermally activated processes of energy release is not well known. The ratio of the stored to the expended energy may give some semi-quantitative information on this problem and some light may be shed on it by a suitable application of a single-step method of stored energy measurement.

4.3 Composition

The tendency of impurities and solute additions to increase the stored energy is connected with their tendency to cause the retention of imperfections.

4.4 Grain Structure

The increase in stored energy with decreasing grain size at small strains suggests that substructure forms more readily or is retained more completely in fine-grained metals. The elimination of this difference with increasing strain can be explained by the progressive accumulation of imperfections in the interiors of the grains regardless of their size.

Conrad and Christ, 1962, related the dependence of stored energy on grain size to the variation in dislocation density with the grain size of the deformed metal. They based their argument on the decrease in the average distance moved by a dislocation owing to the increase in the number of dislocation sources with increasing grain boundary area.

4.5 General

It has been shown in this section that four of the seven variables affecting the stored energy mentioned in Section 2 permit some conclusions to be reached concerning the substructure. Corresponding conclusions are also possible for the other variables. Further insight into the effects of variables can be gained from investigations of the stored energy in which simultaneous changes of other properties are investigated.

5. Stored Energy and Intermediate Substructure

The intermediate substructure, as defined in this paper, consists of the subboundaries. A correlation between the intermediate substructure and the stored energy, therefore, requires some coordinated knowledge of the subboundaries. Work involving both stored energy and substructure was carried out by Aström, 1955, who used light microscopy, and by Averbach et al., 1956, and Michell and co-workers, 1957 and 1960, who used X-ray diffraction methods.

Aström's values of the stored energy and hardness are shown in Fig. 10. He deduced from these data and his metallographic observations that (1) a recovery process (not involving detectable structural changes) occurred at about 80°C, (2) the substructure underwent a change between 180 and 250°C and (3) the metal recrystallized at 350°C. He did not definitely identify the process involving the substructure, but suggested that it was either subgrain growth or polygonization, or both.

Averbach et al., 1956, measured by calorimetry the energy stored in filings of a gold-silver alloy in the deformed state and after annealing at different temperatures between room temperature and 500°C (Fig. 12). They measured the elastic strain energy and the short-range order parameter. From the latter, they calculated by the quasi-chemical theory energy values after different annealing treatments. No stacking faults or twin faults were observed. Averbach et al. subtracted the energy effects due to strain and changes in short-range order from the stored energy measured calorimetrically and considered the remainder to be interfacial energy. They estimated the total interfacial area from the particle size measured by X-ray diffraction and from this derived a specific interfacial energy. The results, recalculated after some corrections, arising from a discussion by Michell, 1958, appear to be reasonable; in particular, they show an upward trend after annealing above 250°C (Averbach, Bever, Comerford and Leach, 1958).

In the cold worked specimens approximately two-thirds of the stored energy was accounted for by interfacial energy, only 5% by elastic strain and the balance by the destruction of short-range order. During recovery, the subgrain size increased slightly, a small amount of stored energy was released, presumably due to this subgrain growth, but the specific interfacial energy changed little. A partial relief of local strains occurred. During recrystallization, the subgrain size increased rapidly, the specific interfacial energy increased, presumably to a value of the random grain boundary energy, and the remaining local strains disappeared.

Michell and Haig, 1957, combined a structural investigation by X-ray diffraction of nickel grindings before and after annealing with measurements of the stored energy. The apparent particle sizes of the deformed powder extended over an appreciable range depending on the manner of analysis and the energies calculated from them showed a corresponding range. Also, the calculated values of the energy were lower than the measured value. The authors discussed this discrepancy in terms of the assumed distribution of strains. Two stages in the relief of strain were observed. The first, which did not involve a change in particle size, was attributed to recovery and the second occurred during recrystallization with an attendant increase in apparent particle size.

Michell and Lovegrove, 1960, reported a similar investigation of the annealing of bulk specimens of nickel. The stored energies derived from various methods of analysis of particle size were spread over a large range. Best agreement with the measured energy values was obtained by assuming a Gaussian distribution of the strain.

The importance of the interfacial energy of subparticles, which is brought out by the X-ray diffraction investigations, raises the question as to how changes in the stored energy resulting from changes in variables are related to the interfacial energy. As an example of this problem, it may be considered whether the change in the stored energy with composition is associated with a change in the interfacial energy and if so, whether this is due to a change in the total interfacial area or in the specific interfacial energy.

In concluding this section, a consequence of the method of finding interfacial energy of subboundaries by subtracting the energies of all other mechanisms from the total measured energy should be emphasized. This method tends to overstate the interfacial energy, which will be reduced as energies attributable to other mechanisms are considered. In general, however, these energies are likely to be small.

6. Stored Energy and Ultimate Substructure

6.1 Dislocations

Dislocations, in addition to making up the subboundaries, constitute other elements of substructure. They may occur in random arrangements or in regular networks and groups such as pile-ups, in which they interact with each other.

The simplest analysis of the stored energy in terms of dislocations assumes individual non-interacting dislocations. The measured stored energy, or that part of it which can be attributed to dislocations, is divided by the estimated value of the specific energy of a dislocation in order to find the dislocation density. Alternatively, if the dislocation density is known or can be estimated, the specific energy of a dislocation can be found.

Seitz and Read, 1941, Koehler, 1941, 1942, and Bragg, 1945, calculated a dislocation density of 10^{12} per cm^2 after cold work from values of the stored energy

reported by Taylor and Quinney, 1934, 1937. This high value of the density can be explained by the low specific energy values assumed by these authors.

In more recent investigations, dislocation densities derived from stored energy values have been compared with densities derived from changes in other properties measured on identical samples. Table 1 reports the results for copper of Clarebrough, Hargreaves and West, 1957. The dislocation densities obtained by them from changes in the hydrostatic density, $\Delta D/D$, are larger than those obtained from the stored energy, E_s ; the incremental resistivity, $\Delta\rho$, gave even larger values. Clarebrough et al. discussed this discrepancy and Boas, 1957, commented on a similar discrepancy in nickel. Seeger, 1957, pointed out that the dislocation density based on hydrostatic density changes, recalculated on a different basis, agreed satisfactorily with the value derived from the stored energy. He also suggested that the dislocation density derived from the resistivity change might be reduced if stacking faults contributed to the resistivity change.

Clarebrough et al., 1962b, reported dislocation densities derived from stored energy and hydrostatic density changes for silver and gold, together with the values for copper based on the investigation by Clarebrough, Hargreaves and West, 1957 (see Table 2). The discrepancy had been reduced substantially by the use of a new figure for the effect of a dislocation on the density (Stehle and Seeger, 1956). Since the effects of dislocations on the resistivity of copper, silver and gold were almost identical, in spite of the difference in the stacking fault energies of these metals, the possibility that stacking faults make significant contributions to the resistivity of a dislocation seemed to be ruled out.

Bailey and Hirsch, 1960, from dislocation densities measured by electron microscopy and calorimetric values of the stored energy, obtained a specific energy of a dislocation of approximately 8 ev/atom plane in polycrystalline silver deformed in tension. Electron microscope observations showed a cellular structure. No change was observed in dislocation densities or distribution during recovery, but the energy remaining after recovery, E_r (released during subsequent recrystallization), was only about half the total stored energy, E_s , except at high strains. Pertinent data are given in Table 3.

Bailey and Hirsch calculated stored energies of dislocations occurring singly (E_1) and in groups of two, three, and four dislocations (E_2 , E_3 , and E_4). Table 4 lists these energies for different values of the radius, R , of the stress field. The agreement of the calculated values with the measured value is satisfactory, especially for the largest value of R and groups of three or four dislocations. The authors concluded that the interaction energy can be accounted for by groups of this size, the long range stresses of which do not cancel. They explained the decrease in stored energy during recovery by a small rearrangement of dislocations in the cell boundaries. They concluded that the stored energy values were compatible with the observed dislocation distribution and that the long-range stresses were at most accounted for by groups of three or four dislocations in the cell boundaries; also, after recovery, the dislocation energies were within a factor of 2 of the theoretical value of the self-energy. In particular, they believed that no pile-ups needed to be postulated and they also did not observe them by electron microscopy.

Bailey and Hirsch also calculated the stored energy from the flow stress assuming a pile-up model. The values are shown in Table 5. Since they were an order of magnitude larger than the experimental values, the authors concluded that the pile-up model did not account satisfactorily for the flow stress and stored energy. They found fairly close agreement between the experimental values and values calculated by the forest theory. They attributed the remaining discrepancy to some long-range stresses or a contribution of point defects to the stored energy. Since the dislocation arrangements observed in nickel, copper, gold, and aluminum were similar to those in silver, Bailey and Hirsch concluded that the same work hardening mechanism operated in these metals. However, since pile-ups had been observed in stainless steel and alpha brass, they admitted the possibility that long-range stresses might be important in them.

Clarebrough, Hargreaves, Head and Loretto, 1961, criticized the equation used by Bailey and Hirsch for the calculation of the energy from the flow stress. In particular, they stated that the outer cut-off radius should not appear in it. They derived an equation for the stored energy from an analysis due to Stroh, 1953. They calculated values for several metals; that for silver is included in Table 5. Clarebrough et al. concluded that the pile-up theories could not be dismissed on the basis of the measurements of the flow stress and the stored energy alone, but also emphasized that the agreement should not be taken as proof of their correctness.

Clarebrough et al. pointed out that earlier results for nickel (Clarebrough et al., 1955) which showed a large energy evolution during recovery ($E_p/E_s = 0.70$) was similar to the observations for silver by Bailey and Hirsch. They agreed in attributing a large part of this release to a rearrangement in the cell boundaries during recovery. They also mentioned the possibility of loss of dislocations during thinning in the preparation of electron microscope specimens.

Seeger and Kronmüller, 1962, stated that the equation used by Bailey and Hirsch for connecting the flow stress and the energy incorrectly assumed that a group of n dislocations can be treated as a superdislocation of dislocation strength (nb) and that this overestimates the energy stored in the stress fields between the dislocations. The stored energy connected with the overlap of the stress fields is only slightly larger than the stored energy due to stress fields of individual dislocations. They used a dislocation model developed for stage II of the stress-strain curve of face-centered metals and calculated the energy of pile-ups and the work expended in the deformation of a single crystal. From this they calculated a value of the ratio of the stored to the expended energy, E_s/E_w . They considered the agreement of the experimental values for copper, gold, and nickel with the calculated ratio as satisfactory. They also calculated stored energies for the specimens of silver deformed by Bailey and Hirsch, which are included in Table 5. Seeger and Kronmüller concluded that their theory accounted reasonably well for the experimental results, except at the highest strains, where work softening effects could be expected.

Faulkner and Ham, 1962, reported data for aluminum in which the dislocation density was determined by electron microscopy. The specific energies derived from the stored energy were surprisingly large. They concluded that the density of dislocations in thin films of aluminum differs systematically from the bulk values, probably owing to losses during thinning.

Li, 1960, analyzed the elastic properties of a dislocation wall and concluded that its strain energy is smaller than that of a set of dislocations of the same sign distributed within a circle, the diameter of which is approximately equal to the height of the wall. He called attention to the fact that local groupings of dislocations of the same sign generated by a deformation process such as bending interfere with the method of measuring the dislocation density by the amount of stored energy.

Li, 1961, showed that a release of an appreciable amount of energy may occur, as observed by Bailey and Hirsch during the recovery of polycrystalline silver, without an observable change in the dislocation distribution if low-angle twist boundaries are formed by a crossed grid of screw dislocations. This would cause a large energy difference with only a slight rearrangement of dislocations. Li suggested that the kinetics of this rearrangement probably require some thermal activation and that it, therefore, takes place during recovery. The large energy change with only minor visible rearrangement according to Li places the method of determining dislocation densities from stored energy in jeopardy. It should be recognized, however, that the occurrence of the grids has not been demonstrated. Also, the difficulties of evaluation would arise from difficulties of measuring the dislocation density rather than of the energy.

6.2 Point Defects

The estimated values of the energy of point defects and aggregates of point defects in face-centered cubic metals published in the literature appear to be satisfactory. It is, therefore, possible to arrive at estimates of the concentration of these defects, if the energies attributable to them are known from measured values of the stored energy. However, it is often difficult to separate the effects of point defects from those of other imperfections and to differentiate between the effects of different aggregates of point defects.

Point defects are particularly important at low temperatures. This lends interest to the work of Henderson and Koehler, 1956, van den Beukel, 1961, and Greenfield and Bever, 1956. In particular, Henderson and Koehler estimated a vacancy concentration of 1.6×10^{-4} from the stored energy release by a specimen compressed 65%.

The temperature range for the annealing out of point defects in nickel is higher than in the other face-centered cubic metals investigated to date. This permits the energy effect of point defects in cold worked nickel to be measured above room temperature. The results of an investigation by Clarebrough et al., 1960, summarized in Table 6, include concentrations of interstitials and vacancies, as well as the concentration of dislocations, which is derived from recrystallization.

A recent finding by Appleton and Bever, 1963, suggests that, at least in gold-silver alloys, point defects play less of a role at 78°K than has been assumed. They found that between room temperature and 78°K, the stored energy, E_s , increased, but the ratio E_s/E_w increased little more than the stored energy, E_s . This indicates that the expended energy also increased, which is in accord with the measured stress-strain curves at room temperature and 78°K. These observations can be explained by an increase in the density of dislocations and an

intensification of their interaction. Between 78° and 4°K, however, the stored energy and the ratio E_s/E increased appreciably, while the stress-strain curve changed much less. This suggested strongly an increase in the concentration of point defects generated during deformation at 4°K over that generated at 78°K.

6.3 Other Imperfections

The relation of other imperfections, such as stacking faults or twinning faults, to the stored energy seems to have received little consideration in the literature. However, data on their concentrations and specific energy are becoming available and this will make it possible to include them in the evaluation of stored energy measurements.

7. Conclusion

It has been shown that the stored energy of cold work can be related to the total substructure, the intermediate substructure and the ultimate substructure. The detailed interpretations possible for the various investigations differ considerably. The statistical nature of the stored energy has been shown to be advantageous in revealing certain features of the total substructure. On the other hand, under favorable conditions, it has been possible to differentiate between elements of substructure on the basis of stored energy values.

Additional investigations of the stored energy are needed. In particular, further investigations combining stored energy measurements with the measurement of changes in other properties should be made. Also, research should be extended to body-centered cubic and hexagonal close-packed metals. In this way, it will become possible to partition the stored energy, even in complex cases, by allocating specific energies to all operative mechanisms.

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Table 1

Deformation, % Compression	Density of Dislocations in Copper, N lines/cm ²		
	From E _s	From ΔD/D	From Δρ
30	8.5 x 10 ¹⁰	4 x 10 ¹¹	5 x 10 ¹²
55	1.1 x 10 ¹¹	6 x 10 ¹¹	7 x 10 ¹²
70	1.3 x 10 ¹¹	8 x 10 ¹¹	9 x 10 ¹²

Clarebrough, Hargreaves and West, 1957

Table 2

Metal	Deformation, % Compression	Density of Dislocations, N lines/cm ²		Δρ/N,
		From E _s	From ΔD/D	μΩcm/d.line/cm ²
Cu	70%	1.33 x 10 ¹¹	2.8 x 10 ¹¹	28 x 10 ⁻¹⁴
Ag	75%	1.50 x 10 ¹¹	2.8 x 10 ¹¹	34 x 10 ⁻¹⁴
Au	75%	0.74 x 10 ¹¹	1.4 x 10 ¹¹	35 x 10 ⁻¹⁴
Ni	70%	1.06 x 10 ¹¹	—	94 x 10 ⁻¹⁴
Al	75%	0.40 x 10 ¹¹	—	33 x 10 ⁻¹⁴

Clarebrough, Hargreaves and Loretto, 1961 and 1962b

Table 3

Deformation %	Measured Dislocation Density N lines/cm ²	E _s [*] cal/g-a	E _r [*] cal/g-a	E _s /N _s eV/at.pl.
11	2.2 x 10 ¹⁰	2.70	1.25	9.1
21	5.2 x 10 ¹⁰	5.10	2.83	7.3
32	6.8 x 10 ¹⁰	7.75	4.9	8.4
43	—	7.27	6.03	—
			Avge.	8.3

Polycrystalline silver, deformed in tension
Bailey and Hirsch, 1960

Table 4

Stress Field R, A.U.	Calculated Stored Energy (eV/at. plane)				
	E ₁ (1)	E ₁ (2)	E ₂ (1)	E ₃ (1)	E ₄ (1)
200	2.66	1.90	—	—	—
1,000	3.38	2.61	4.1	4.62	5.16
10,000	4.4	3.63	6.16	7.7	9.3

(1) Bailey and Hirsch, 1960

(2) According to Schoeck and Seeger, 1953

Table 5

Deformation, %	Stored Energy, cal/g-a			
	Exptl.	Calculated from Flow Stress		
		(1)	(2)	(3)
11	2.7	21.2	—	3.0
21	5.1	37.0	—	5.6
32	7.8	54.0	—	8.2
43	7.3	64.0	9.6	9.71

Polycrystalline silver, deformed in tension

- (1) Bailey and Hirsch, 1960
- (2) Clarebrough et al., 1961
- (3) Seeger and Kronmüller, 1962

Table 6

Annealing Stage	Energy Evolved E_s , cal/g-a	Defect Assumed	Concen- tration from E_s	Assumed Specific Energy
→ 200°C	2.58	Interstitials	2.2×10^{-3} at. %	5 eV
200-350°C	3.28	Vacancies	9.5×10^{-3} at. %	1.5 eV
Recrystal- lization	11.78	Dislocations	1.06×10^{11} cm/cm ³	4.4×10^8 eV/cm

Nickel (99.85%) compressed 70% and annealed

Clarebrough et al., 1960

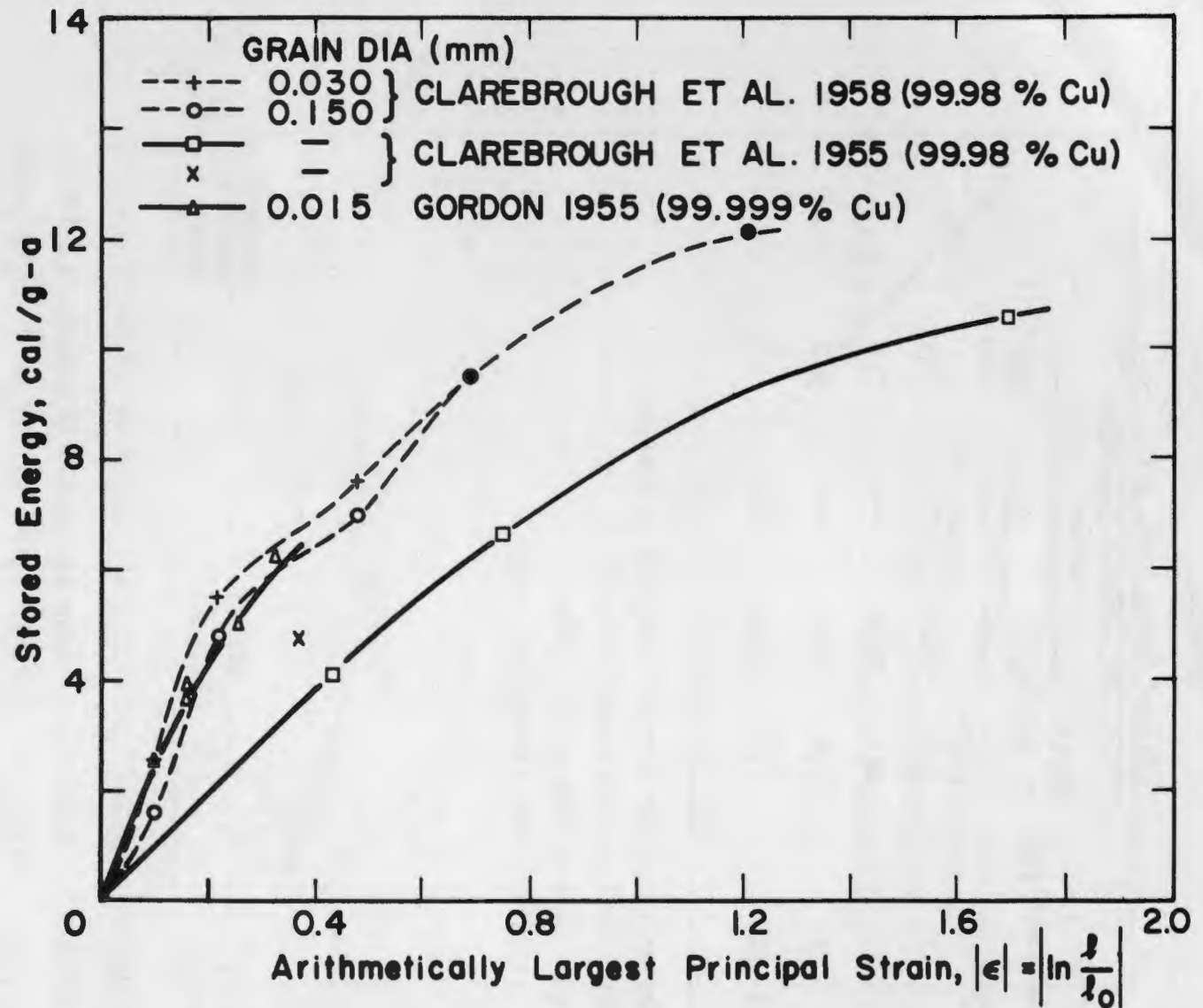


Fig. 1 Energy Stored in Copper as a Function of the Arithmetically Largest Value of Logarithmic Strain in Tension and Compression. (After Titchener, 1961)

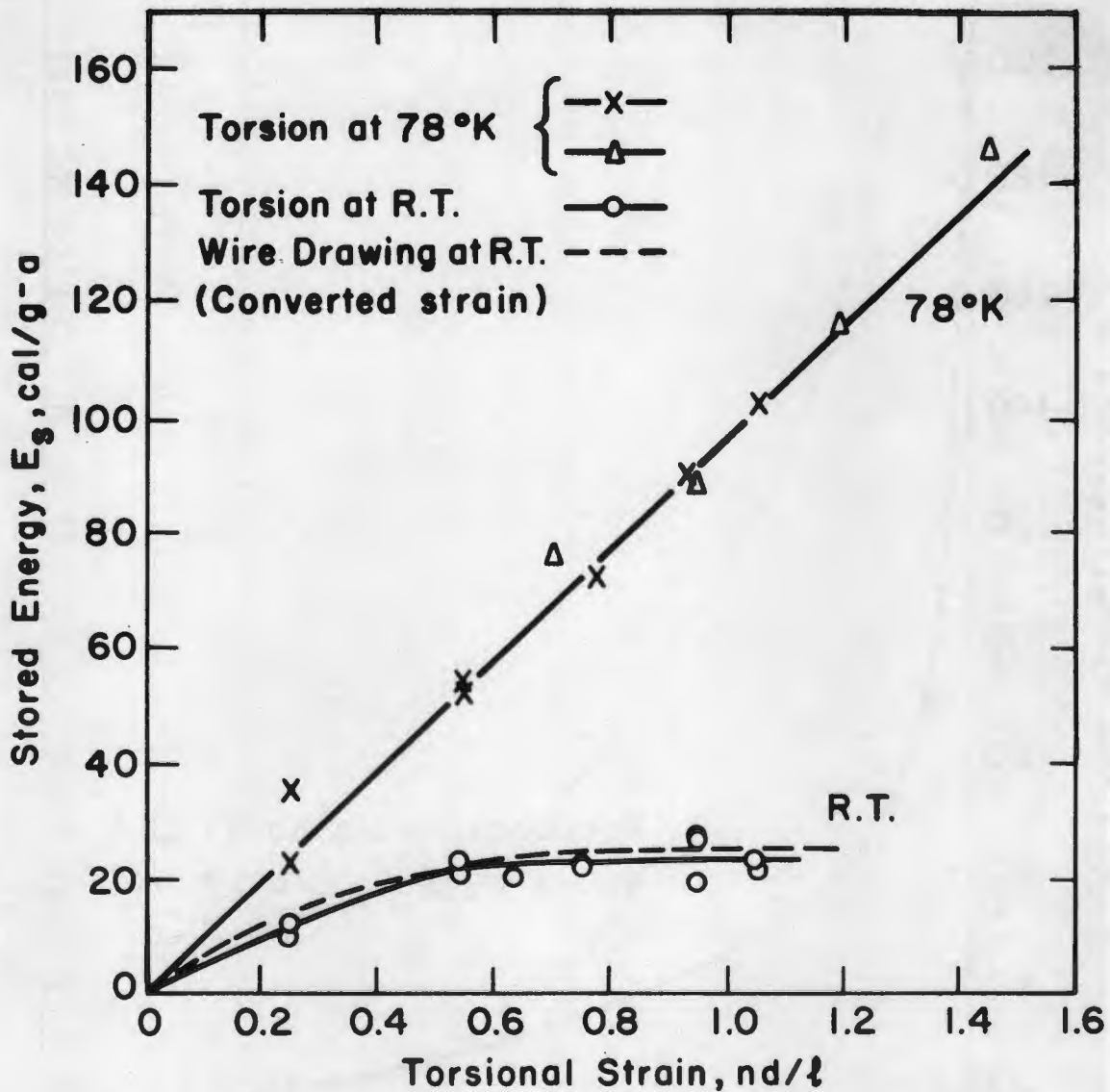


Fig. 2 The Energy Stored by an 82.6% Au-17.4% Ag Alloy at Room Temperature and 78°K as a Function of Strain. (Appleton and Bever, 1963; Titchener and Bever, 1959)

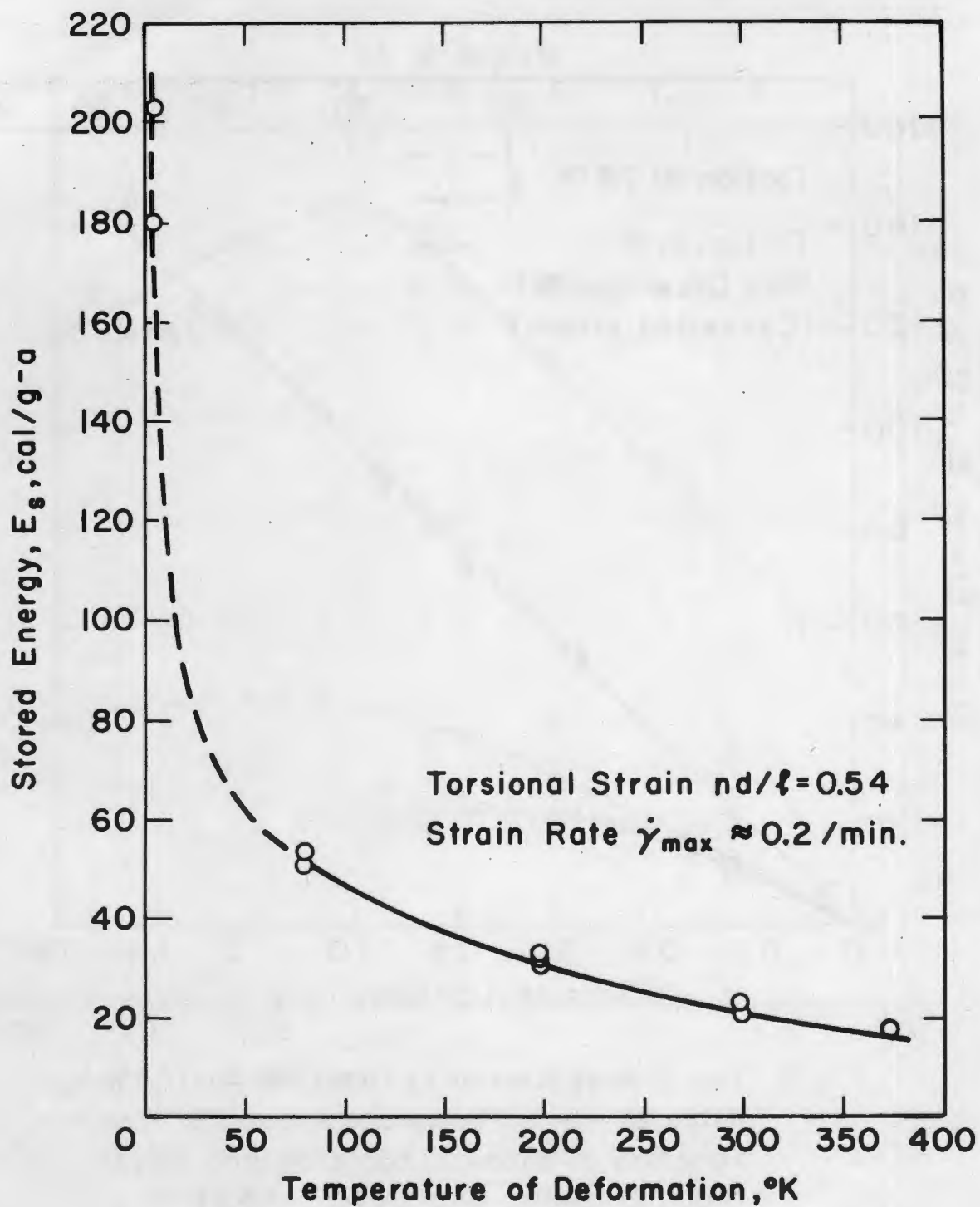


Fig. 3 The Energy Stored by an 82.6% Au-17.4% Ag Alloy at Constant Strain as a Function of the Temperature of Deformation by Torsion. (Appleton and Bever, 1963)

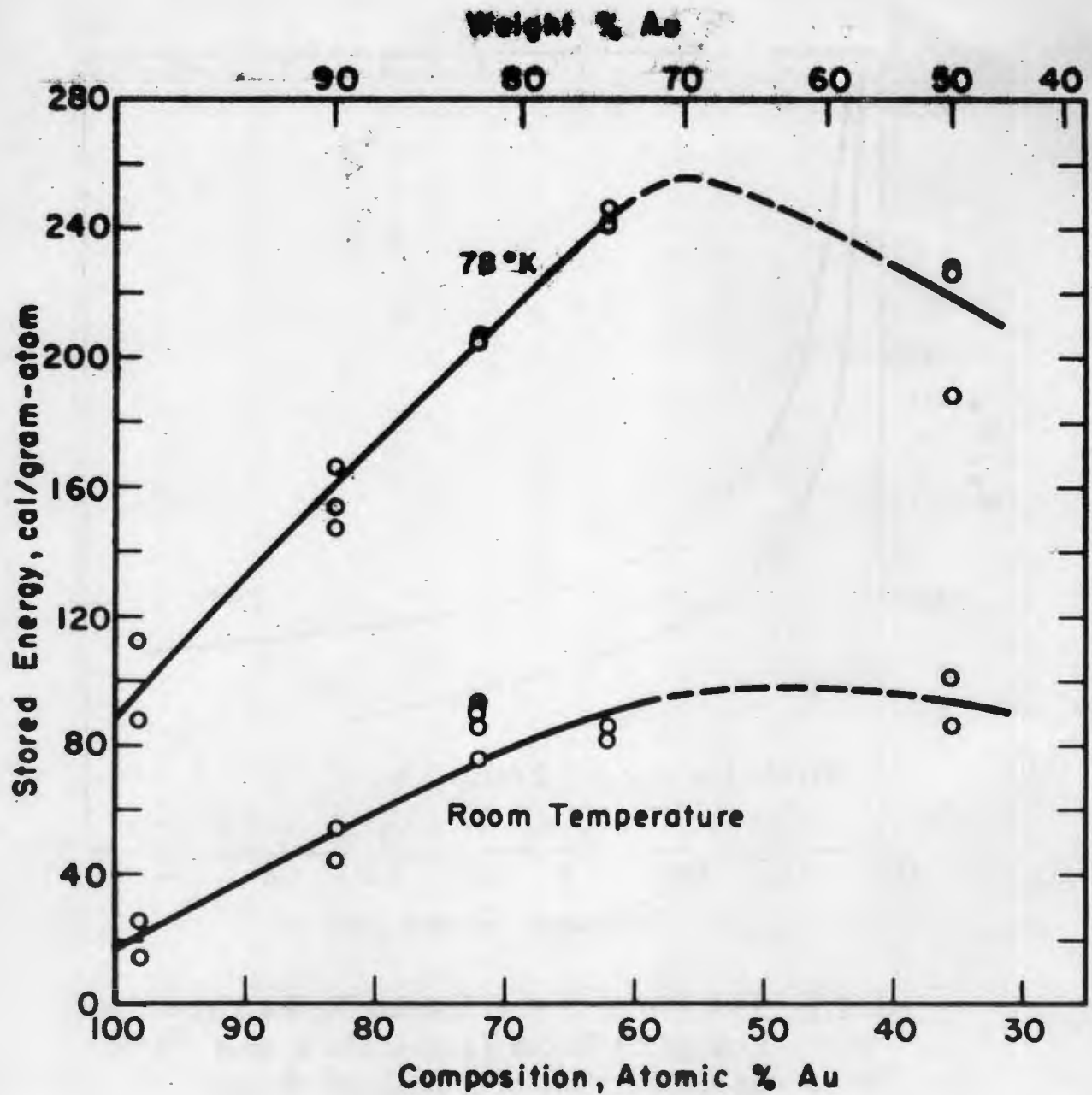


Fig. 4 The Energy Stored by Gold-Silver Alloys Cold Worked at Room Temperature and 78°K. (Greenfield and Bever, 1957)

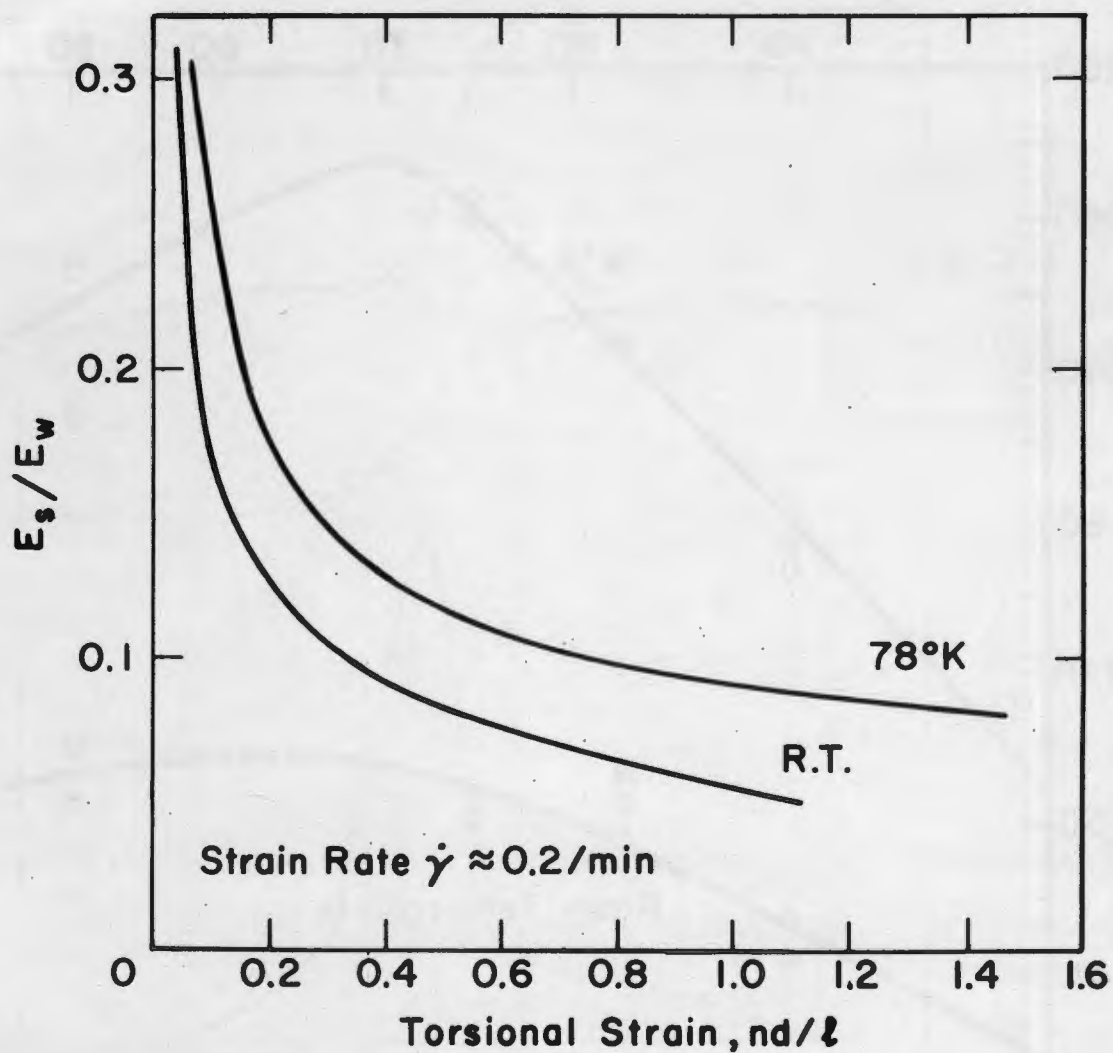


Fig.5 The Ratio of the Stored to the Expended Energy at Room Temperature and 78°K as a Function of Torsional Strain. (Appleton and Bever, 1963)

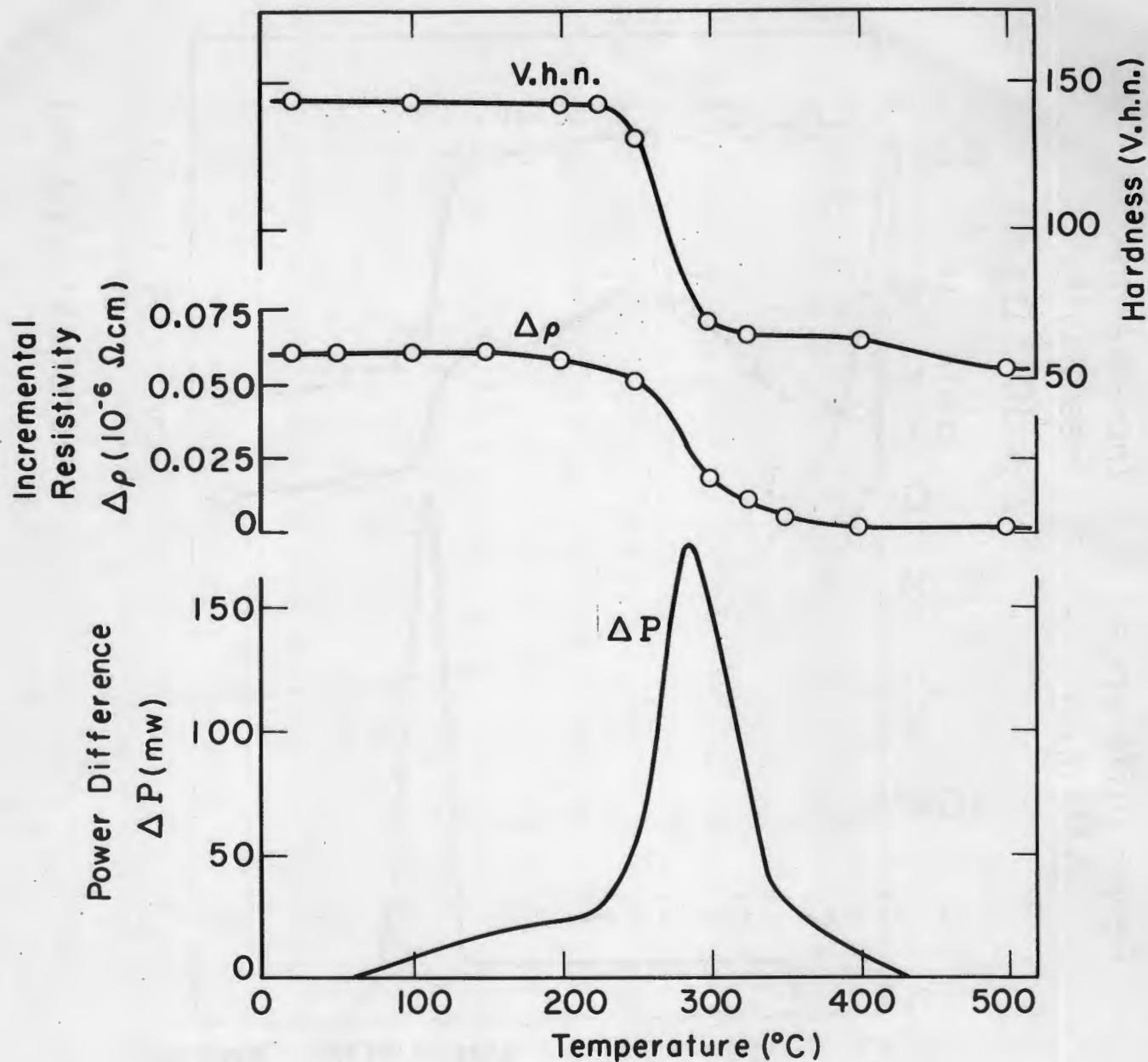


Fig. 6 Rate of Energy Release by Cold Worked Copper as a Function of Annealing Temperature. Incremental Resistivity and Hardness also Shown. Specimen Deformed in Torsion to $nd/l = 1.87$. (Clarebrough et al., 1955)

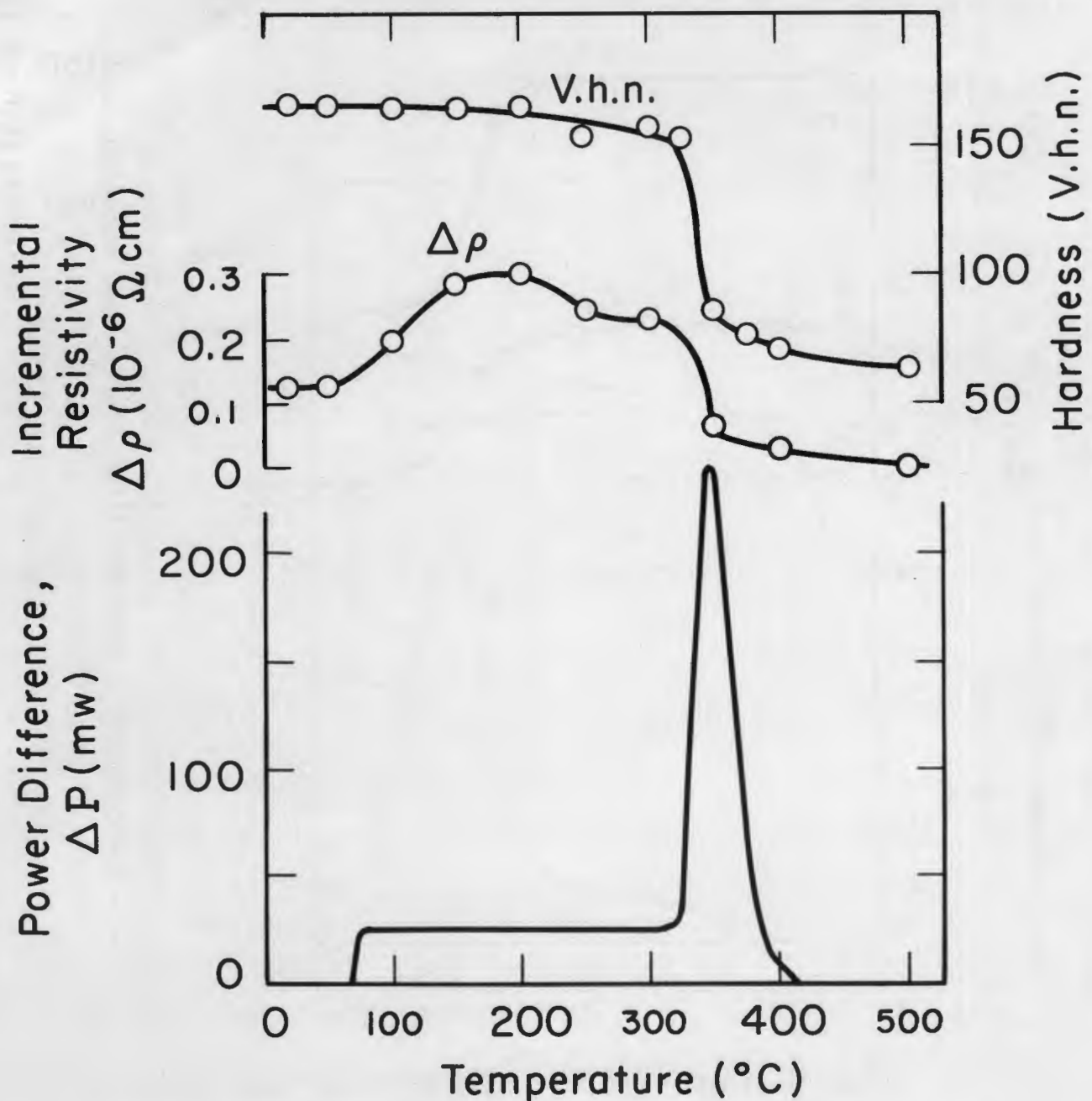


Fig. 7 Rate of Energy Release by Cold Worked Copper Containing Arsenic and Phosphorus as a Function of Annealing Temperature. Incremental Resistivity and Hardness also Shown. Specimen Deformed in Torsion to $nd/l = 1.87$. (Clarebrough et al., 1955)

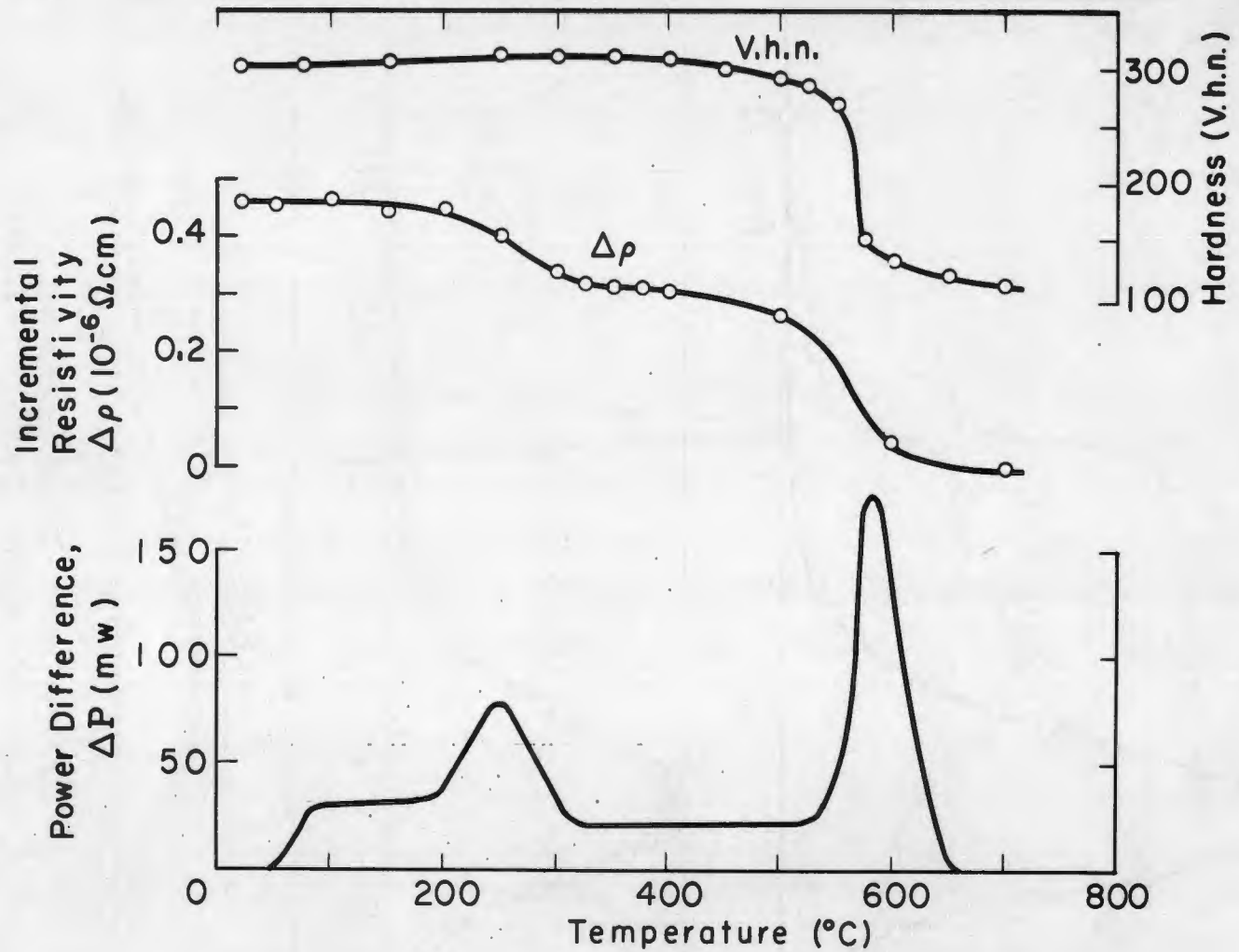


Fig 8 Rate of Energy Release by Commercial Nickel Deformed in Torsion as a Function of Annealing Temperature. Incremental Resistivity and Hardness also Shown. Specimen Deformed in Torsion to $nd/l = 2.34$. (Clarebrough et al., 1955)

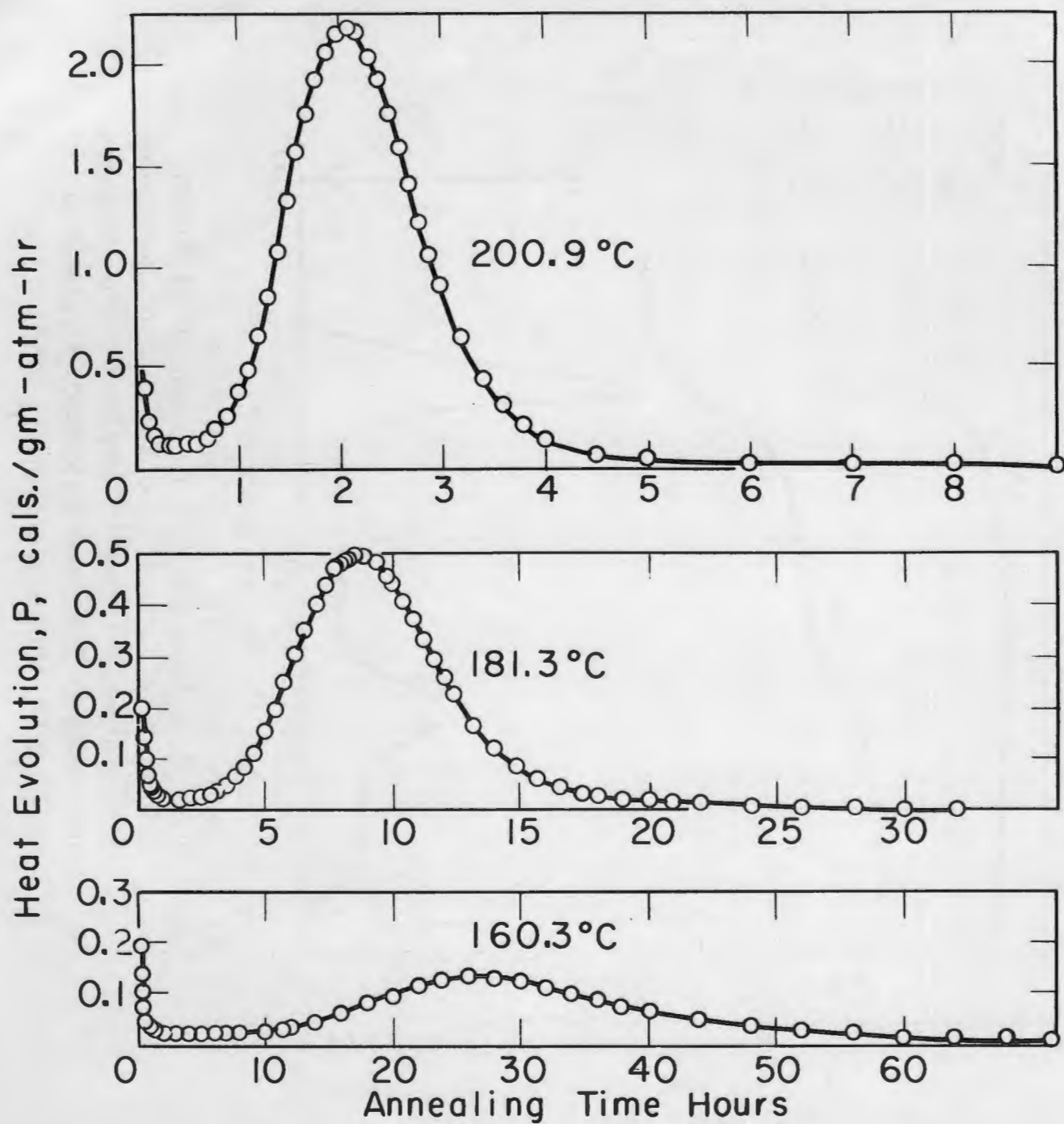


Fig. 9 Rate of Energy Release by Copper Extended 17.7% as Function of Annealing Time at Constant Temperature. (Gordon, 1955)

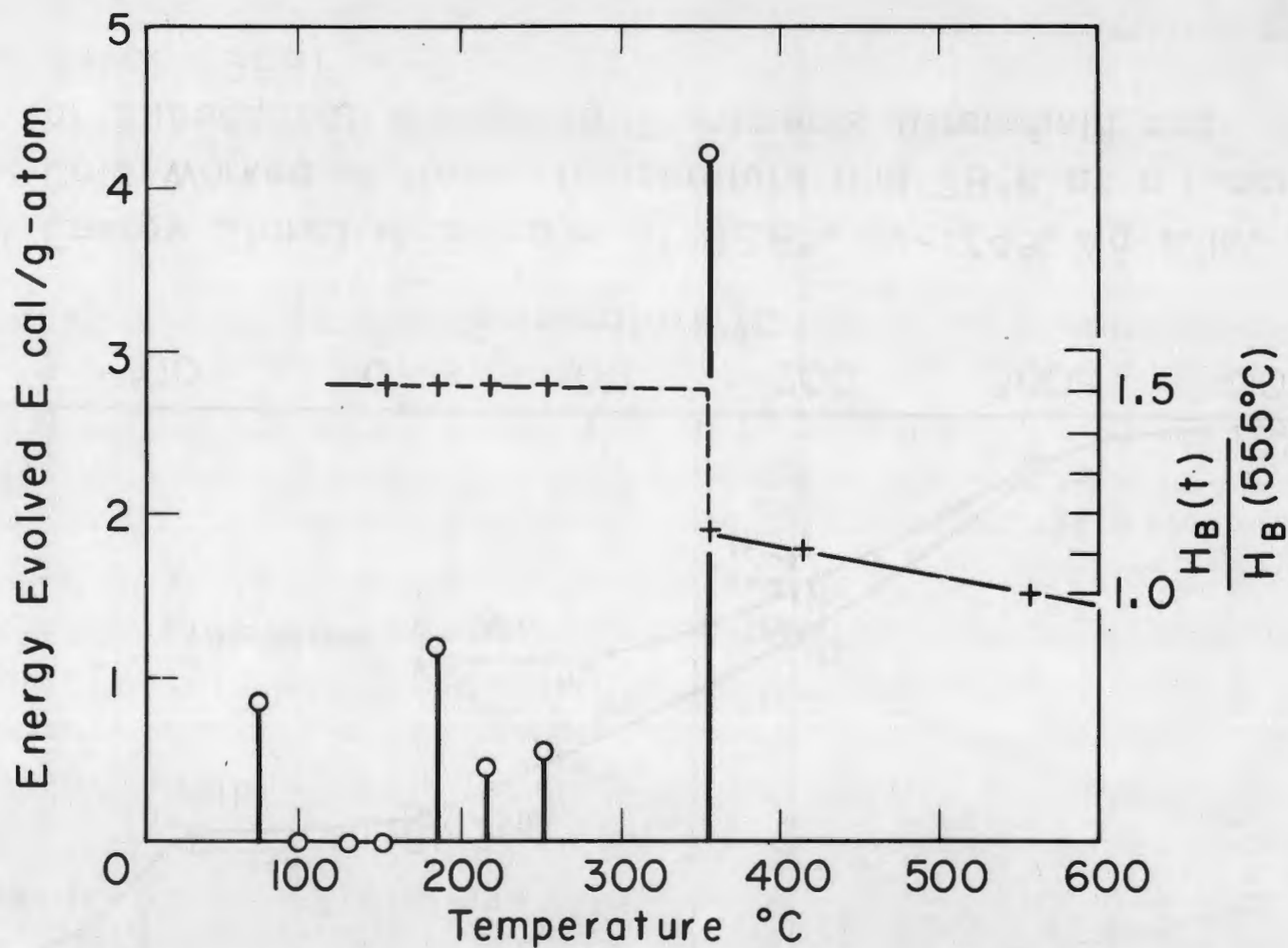


Fig.10 Energy Release by Aluminum Compressed 45% as Function of Annealing Temperature. Relative Hardness also Shown. (Åstrom, 1955)

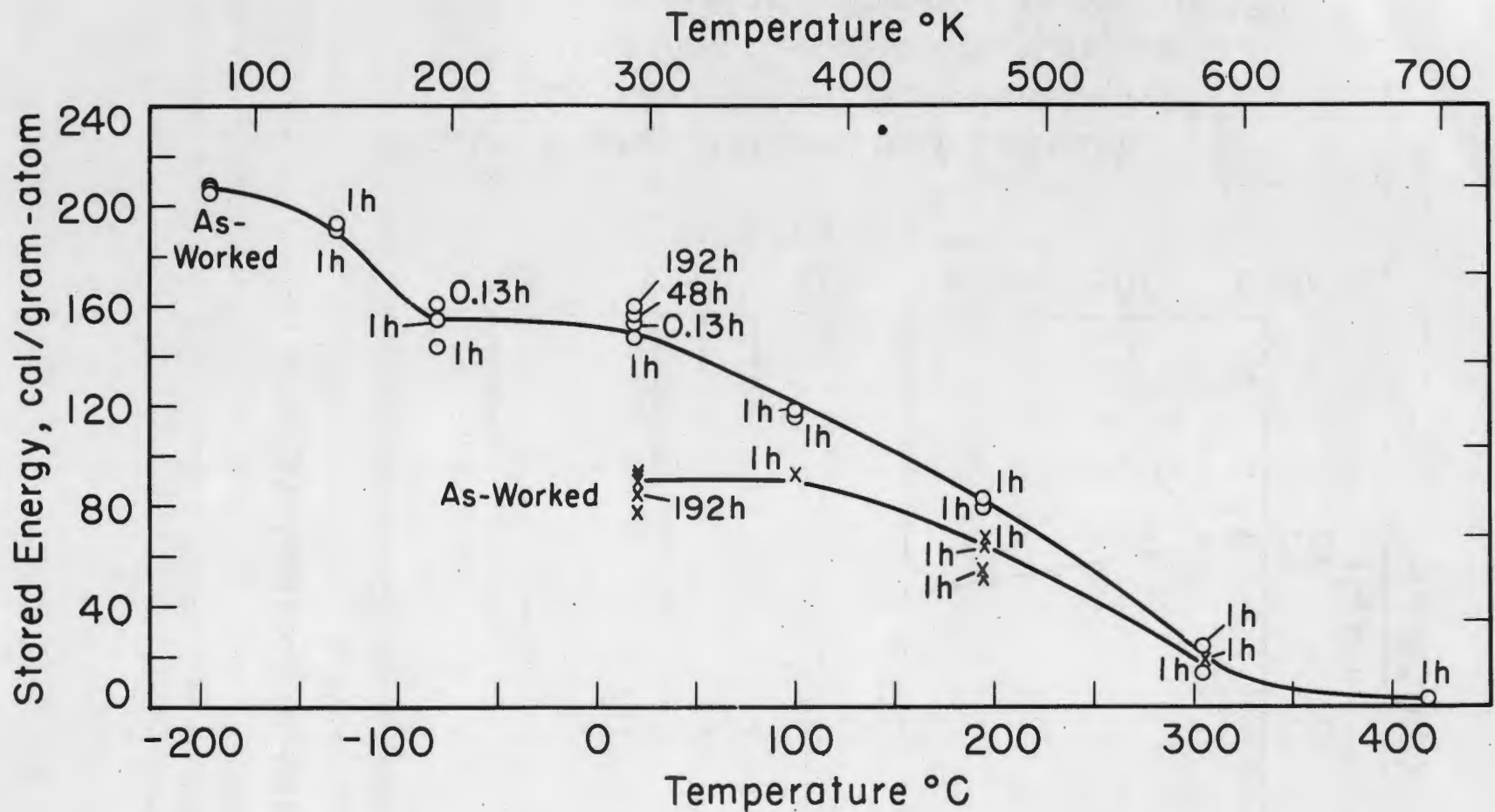


Fig. II Energy Stored in Samples of 82.6% Au-17.4% Ag Alloy Cold Worked at Room Temperature and 78°K as a Function of Subsequent Annealing Treatments. (Greenfield and Bever, 1956)

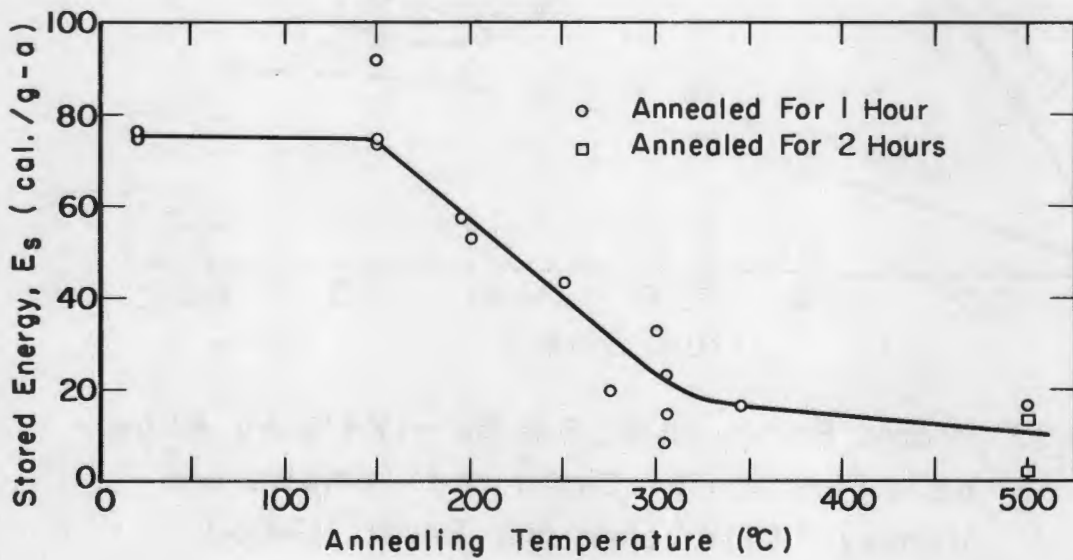
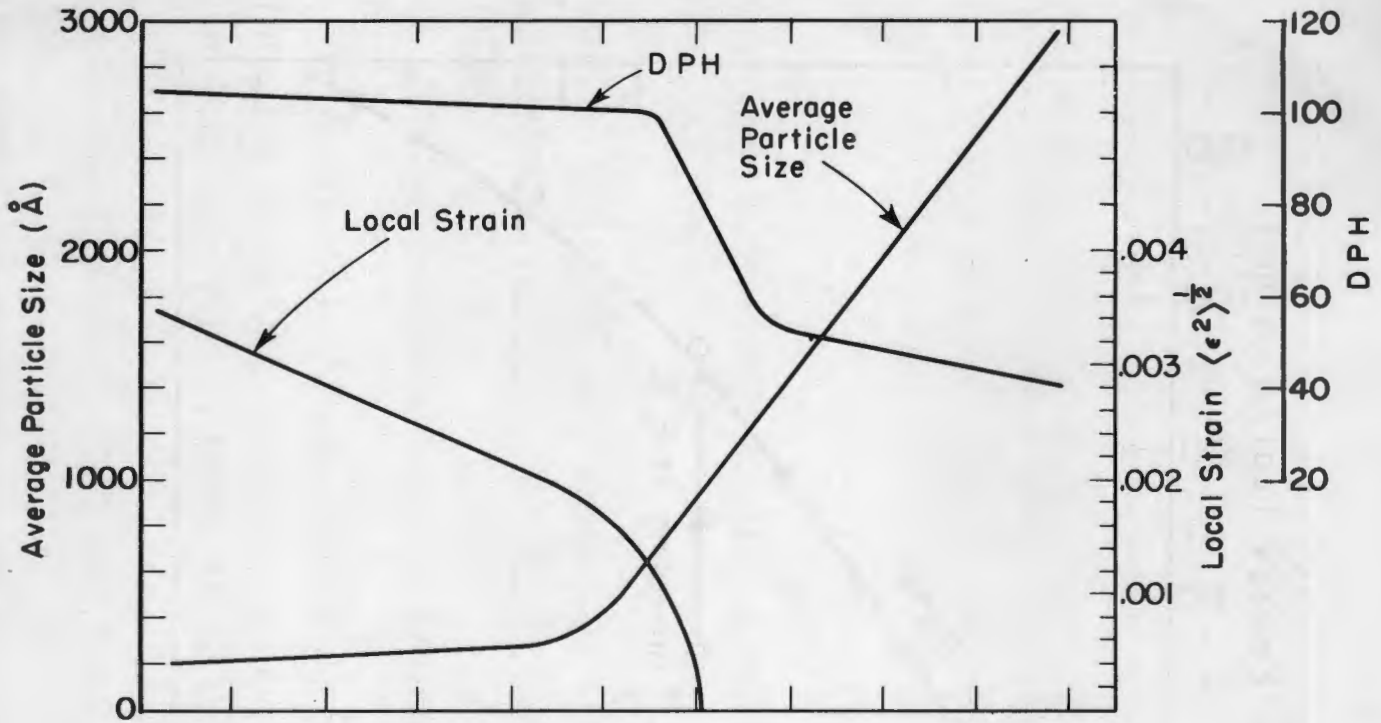


Fig. 12 Stored Energy, Particle Size, Strain and Hardness of 75%Au-25%Ag Alloy as a Function of Annealing Treatment. (Averbach, Bever, Comerford and Leach, 1956)

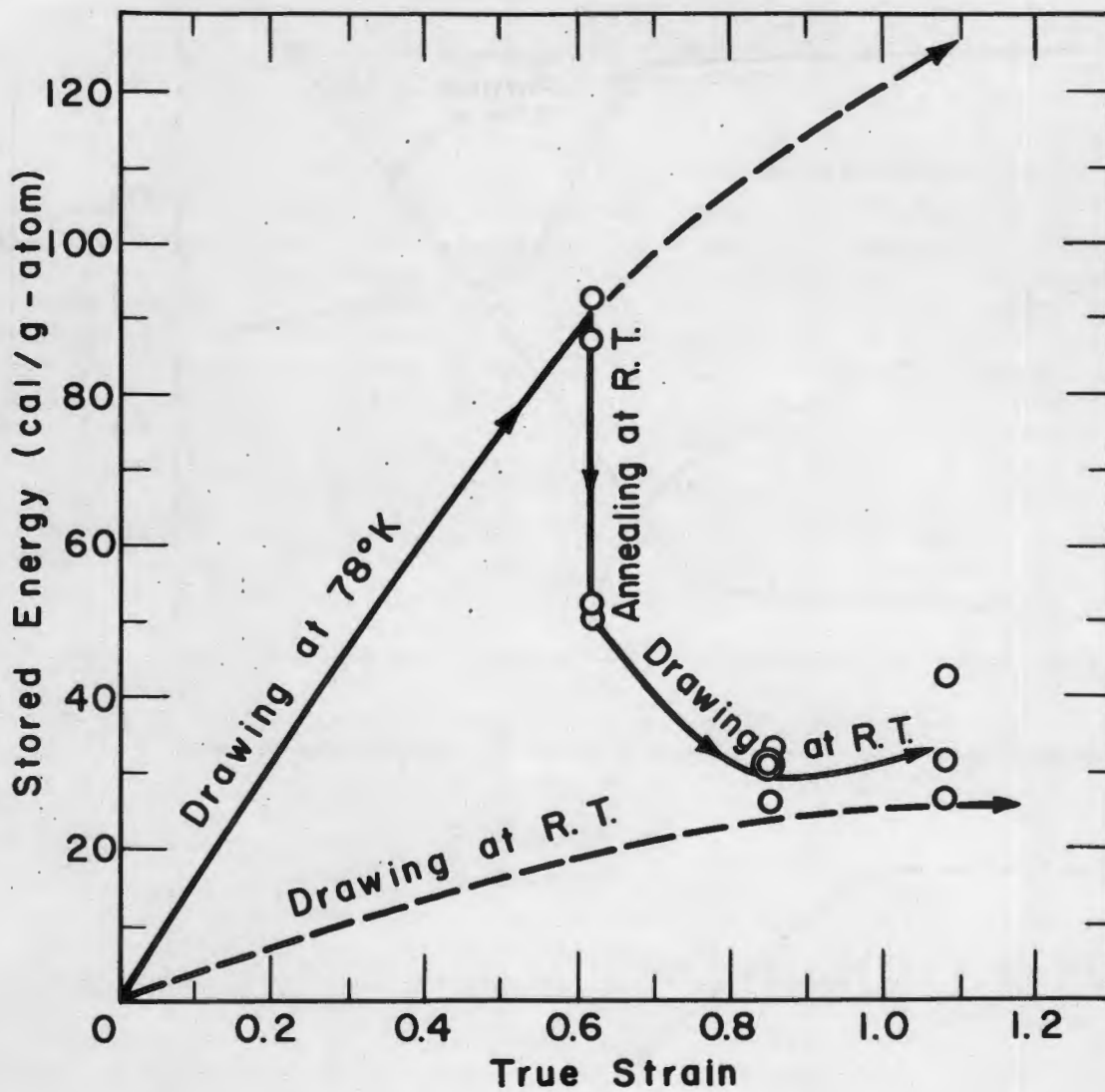


Fig. 13 Stored Energy in 82.6% Au - 17.4% Ag Alloy as a Function of Strain and Temperature History. (Titchener and Bever, 1960)