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THE MECHANICAL PROPERTIES OF METALLIC SOLID SOLUTIONS

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ABSTRACT. The theoretical relation between the lattice strains produced by precipitation in a metal and the corresponding increase in hardness is extended to the case of lattice strains in metallic solid solutions. The elastic limit of a single crystal of a solid solution is calculated on the assumption that the crystal will slip when the applied external stress is equal to the mean value of the internal stress. This mean is taken over the length of a dislocation, assumed to be 1000 atoms. The estimate agrees in order of magnitude with the experimental observations. Similar considerations are applied to the hardness of polycrystalline solid solutions. The theory is extended to cases in which the increase of hardness produced by alloying is not large in comparison with the hardness of the pure solvent.

§ 1. INTRODUCTION

It has long been known (Rosenhain, 1921) that the hardness of a metallic solid solution can be correlated with the distortion of the lattice caused by the presence of foreign atoms. A theory of precipitation hardening based on the concept of dislocations has already been given (Mott and Nabarro, 1940), and the aim of the present paper is to discuss the modifications in this theory which become necessary if it is applied to solid solutions in which the nuclei of strain are single atoms rather than aggregates of many atoms. These modifications are of two kinds. Firstly, it is no longer justifiable to estimate the strain in the matrix from purely elastic considerations of the atomic volumes of solvent and solute, and account must be taken of the binding forces between atoms of the solvent and of the solute. Secondly, even in solutions as dilute as 1%, the internal strains caused by the dissolved atoms change their directions over distances of a few lattice spacings, and it is to be expected that the opposed stresses acting on closely adjoining parts of a dislocation will largely cancel one another and so reduce the applied stress necessary to move the dislocation. It is apparently this effect which accounts for the great increase in mechanical strength produced by precipitation hardening.

§ 2. THE HARDNESS OF AN ALLOY CONTAINING A PRECIPITATED PHASE

According to the theory advanced by Mott and Nabarro, the elastic limit S of an alloy hardened by the precipitation of a second phase in roughly spherical particles should be given in order of magnitude by

$$S = E\epsilon f, \qquad \ldots\ldots(1)$$

where E is Young's modulus for the matrix (which to the order of accuracy required may be taken as the modulus for the pure solvent), f is the concentration

to $\alpha = 0{\cdot}056$. However, a large expansion of the lattice on adding Zn to Al is unexpected, and is not supported by the results of other workers. If Elam's figures for the lattice parameter are replaced by those of Owen and Iball (1934) (Al: 4·041 A., Al + 19% Zn: 4·0345 A.), the value of α becomes 1·05. Such a large value should be characteristic of precipitation hardening rather than solution hardening. The solubility of Zn in Al is not known beyond dispute, but Hansen (1936) considers the most reliable results to be those of Schmid and Wassermann, leading to a solubility of less than 2% at room temperatures. This gives considerable support to the suggestion that Elam's crystals were age-hardened.

(iv) *Cd in Zn*

In this system again the hardening found by Rosbaud and Schmid (1925) is remarkably great. Their values for the elastic limit may be combined with the value $E = 8 \times 10^{11}$ dynes/cm^2 for Zn. The value of ϵ may be estimated from the atomic volumes as $(13{\cdot}01 - 9{\cdot}16)/3 \times 9{\cdot}16$, and this leads to $\alpha = 0{\cdot}22$. This high value might be attributed to some peculiarity of the hexagonal lattice, but such an explanation seems unlikely, for in a single crystal specimen both hexagonal and face-centred cubic metals are known to slip on just one family of close-packed planes. A more likely explanation is that the specimens were precipitation hardened, since Hansen accepts the estimate of Boas that the solubility of Cd in Zn is less that 0·4% at 150° C. and unmeasureably small at 100° C. or below. Rosbaud and Schmid assume that the Cd is in solution because no eutectic is visible in the microstructure. On the other hand, the microphotographs of single crystals reproduced show large inclusions of some other phase or orientation. These may be twins (which would harden a single crystal of a hexagonal metal considerably), but are more likely to be laminar precipitates of another phase formed by diffusion.

(v) *Ni in Cu, Cu in Ni*

This system was investigated by Osswald (1933). The curve relating elastic limit and concentration is distorted from the simple parabolic form which represents the results for the system Au–Ag. Osswald finds a negligibly low elastic limit for copper, rising to a maximum resolved shear stress of 3·0 kg./mm^2 at a concentration of about 60 atomic % Ni, and falling to 0·6 kg./mm^2 for pure Ni. For dilute solutions, the slopes of the curves may be estimated as 0·2 kg./mm^2 for 1% Ni added to Cu, and 0·17 kg./mm$_2$ for 1% Cu added to Ni. The Young's moduli are 11×10^{11} dynes/cm^2 for Cu and 21×10^{11} dynes/cm$_2$ for Ni. The lattice parameters are $a = 3{\cdot}608$ A. for Cu, $a = 3{\cdot}5175$ A. for Ni (Burgers and Basart, 1930; Owen and Pickup, 1934). Taking the mean of the results of the authors quoted, Δa for 1% addition is $-0{\cdot}0013$ A. for Ni added to Cu, 0·00078 A. for Cu added to Ni. These values substituted in equations (2) and (3) give $\alpha = 0{\cdot}049$ for Ni dissolved in Cu, and $\alpha = 0{\cdot}036$ for Cu dissolved in Ni.

(vi) ***Cu in Au, Au in Cu***

The elastic limits of polycrystalline alloys of copper and gold were determined by Broniewski and Wesolowski (1934). 1 atomic % Cu added to Au increases the elastic limit by 0·5 kg./mm^2, and 1 atomic % Au added to Cu increases the elastic limit by 0·7 kg./mm^2. The corresponding values of α are 0·073 and 0·066.

§ 5. APPLICATION TO HARDNESS MEASUREMENTS

A number of workers have measured the hardness of solid solutions (Goebel, 1922; Norbury, 1924; Frye and Hume-Rothery, 1942; Brick, Martin and Angier, 1943), and an interpretation of their results on the lines of the present theory would be of interest. However, in the Brinell test there is very heavy cold working of the metal close to the indentation: Norbury (1924) and Frye and Hume-Rothery (1942), by taking as their measure of hardness the " ultimate Meyer hardness ", measure a quantity which lies even farther from the initial elastic limit and closer to the limiting strength after heavy cold work than the Brinell number determined from a shallow impression. Attempts to extrapolate Frye and Hume-Rothery's results by Meyer's formula to give the hardness corresponding to an impression of diameter 1/10 of that of the ball lead to very irregular figures, as was to be expected from the work of Norbury (1923) on annealed copper and copper alloys. It appears that the experimental results measure the limiting strength after heavy cold work rather than the elastic limit. In general, dilute solid solutions work-harden under small strains less rapidly than does the pure solvent. Elam (1927) finds that in single crystals of brass this is also true for large concentrations and large strains, but Brick, Martin and Angier (1943) find that rolling reductions of 20% or more produce increases in the hardness of polycrystalline solid solutions in copper which are linearly proportional to the excess of the hardness of the annealed alloy above that of pure copper.

The reason for the abnormally small work-hardening of solid solutions under small strains is not known. It is presumably connected with the fact observed by Masima and Sachs (1928) that, whereas in single crystals of pure metals the active glide plane gives way to a new plane as soon as the resolved stress on the new plane exceeds that on the active plane, in solid solutions the original plane remains active until the stresses on the new plane considerably exceed those on the original plane. Possibly the slip process itself produces a type of ordering of the solid solution which is conducive to slip on the active plane. An alternative possibility is that the initial irregularity of the lattice of the solid solution causes small areas of lattice planes to buckle under small stresses, and so prevents the catastrophic rotations of large blocks of the lattice which lead to Laue asterisms in the early stages of slip in pure metals. It would be of interest to know if the early stages of slip in solid solutions, which are characterized by abnormally small hardenings, do in fact show abnormally little lattice distortion in Laue photographs.

Owing to this complicating factor, the analysis of hardness tests is not straightforward. It will be assumed that the Brinell or ultimate Meyer hardness exceeds the elastic limit of a single crystal by a factor β, so that the hardness is given by

$$H = \alpha\beta E\epsilon f. \qquad \ldots\ldots (4)$$

The numerical value of β is not known with any accuracy, nor (except in special cases) is it certain that the value of β remains roughly constant for a series of solutions in the same solvent. A rough estimate of the magnitude of β may be based on the consideration that in general the Brinell hardness of a pure annealed metal is of order 40 kg./mm^2 (e.g. Fe 67, Ag 30, Cu 45, Al 16), while the elastic limit for

a single crystal is of order 0·2 kg./mm^2 (e.g. Ag 0·06, Cu 0·1–0·4, Al 0·5), giving β about 200. Solid solutions showing little work-hardening would yield smaller values of β, and this estimate may be combined with one derived from a comparison of the measurements of Rosbaud and Schmid on the yield points of alloys of zinc and cadmium with the hardness measurements of Ludwik, which they quote. The two curves are not very similar in form, but the mean value of β is about 10. A figure of 80 will be taken as an estimate of the order of magnitude of β.

§ 6. SUMMARY OF THE EXPERIMENTAL OBSERVATIONS ON HARDNESS

Norbury (1924) examined the hardness of solid solutions of Ni, Zn, Al, Mn, Ag and Sn in copper, and similarly analysed the results of Goebel (1922) on solid solutions of Bi, Sn, Hg, and Cd in lead. In both cases the hardening effect is very roughly a linear function of the difference in size of the atoms of the solute and the solvent. In each series of experiments there was one anomaly, the solid solutions of Si in Cu and Na in Pb both being abnormally hard. Norbury attributes this to the formation of intermetallic compounds, so that the dissolved atom no longer has twelve symmetrically-placed nearest neighbours, but is closely bound to a smaller number of solvent atoms. This introduces stresses into the lattice which are more complicated than those which occur in other cases. Similar results have been obtained by Frye and Hume-Rothery (1942) on the hardness of solid solutions of Cd, In, Sn, Sb Mg, Al and Zn in silver. The solution of Al and Zn in silver decreases the lattice constant, whereas the other solutes increase the lattice constant. In all cases the hardness of solid solutions of various concentrations of these seven elements in silver is roughly a linear function of the change in lattice spacing (without regard to sign). Solutes which decrease the lattice spacing appear in general to produce a greater increase in hardness for a given change of lattice spacing than those which increase the lattice spacing. Frye and Hume-Rothery show that if the observations are grouped into series in which the dissolved atoms belong to the same row of the periodic table, and are present in the same concentration (2·4 atomic per cent or 5·0 atomic per cent), then the hardness in each series is very closely given by a linear function of the square of the change in lattice constant. The disagreement of the square law with the linear law originally suggested is discussed below. Finally, results by Brick, Martin and Angier (1943) for Si, Ni, Zn, Al, Mn, As, Sb and Sn dissolved in copper largely confirm the work of Norbury. Cobalt has an atomic volume slightly less than that of copper, and its solid solutions are very hard. The change in lattice parameter caused by adding Mg is not known, but the point for Mg falls on the curve relating hardening effect and difference of atomic volume.

A close connection between hardness and internal stress has recently been demonstrated by Frye, Caum and Treco (1944).

§ 7. EFFECT OF RESIDUAL STRESSES DUE TO OTHER CAUSES

The theory originally proposed led to a hardness of the alloy directly proportional to the deformation of the lattice, whereas the measurements of Frye and Hume-Rothery show a linear relation between hardness and the square of the deformation. These are in fact both limiting cases of the same general formula, and are obtained when the increase in hardness caused by the presence of the dissolved atoms is very large or very small in comparison with the hardness of the pure solvent.

Whether the dislocation is imagined as rigid or as flexible, the stress required to cause slip in a metal by moving an appreciable number of dislocations in it is determined less by the extreme values of the internal stress than by the average fluctuations of stress in the material. These are conveniently measured by the mean square stress, since the mean stress over the whole body must be zero.

Consider a pure metal containing random internal stresses (due to misfits at grain boundaries or imperfect annealing) of mean square value S_0^2. The hardness of this metal is given by

$$H_0 = \alpha\beta S_0, \qquad \ldots\ldots(5)$$

where α is a pure number, the value of which, according to the previous arguments, must be about 1 if dislocations are flexible and about 1/20 or less if dislocations are rigid, and β is the ratio of the hardness to the elastic limit, and is of order of magnitude 50 to 100. If foreign atoms are now dissolved in the metal they give rise to a further random distribution of stress of mean square value $(E\epsilon f)^2$. The hardness of the solid solution is now given by

$$H = \alpha\beta\sqrt{(S_0^2 + E^2\epsilon^2 f^2)}. \qquad \ldots\ldots(6)$$

Eliminating S_0 between (5) and (6) gives

$$H^2 = H_0^2 + (\alpha\beta E\epsilon F)^2. \qquad \ldots\ldots(7)$$

The original theory, which neglected H_0, made H a linear function of $E\epsilon f$, and Goebel's results for solutions in lead, where the initial hardness is small, show a roughly linear dependence of hardness both on concentration (except where the solute is Hg) and on difference of atomic volume (except in the case of Na, which has already been attributed to the formation of a chemical bond).* Norbury's solid solutions in copper and Frye and Hume-Rothery's solutions in silver showed only small increases in hardness above that of the pure solvent. For such cases equation (6) may be written approximately as

$$H - H_0 = (\alpha\beta E\epsilon f)^2/2H_0. \qquad \ldots\ldots(8)$$

Norbury's results show an increase in hardness which for dilute solutions of a given element varies more rapidly than a linear function of the concentration in the cases of solutions of Si, Al, Ni and Zn. The effect is not shown in solutions of Sn, Ag, and Mn, but in the cases of Sn and Mn he states that " there are reasons for thinking that . . . . the results really lie on a curve bending upwards initially ", and in the case of Ag " it is possible that . . . . the results lie on a curve bending upwards and not on a straight line ". The results of Brick, Martin and Angier on 1% solutions in copper are well represented (except for Si) as a function of ϵ by a formula of type (7), and finally the quadratic law of Frye and Hume-Rothery is in agreement with the form of equation (8).

However, the dependence of hardness on concentration in the results of Brick, Martin and Angier for solutions in copper is linear even for small concentrations which increase the hardness by an amount less than the initial hardness of pure copper, and it seems in general that the hardening effects of solution and of other causes combine sometimes linearly and sometimes as independent random factors. It is to be expected that the small-scale strains due to solution will combine in a random manner with other small-scale strains, but will add linearly to the hardness produced by large-scale strains.

* Kurnakow *et al.* (1940) have confirmed that small additions of Na harden lead appreciably, while altering the lattice parameter very little.

§ 8. ANALYSIS OF EXPERIMENTAL HARDNESS MEASUREMENTS

As a check on the order of magnitude of the effect, the quantity $\alpha\beta$ of equation (8) may be estimated from the results of Frye and Hume-Rothery. They give $H_0 = 43$ kg./mm.$^2 = 4{\cdot}2 \times 10^9$ dynes/cm.^{2} and E for silver is $7{\cdot}7 \times 10^{11}$ dynes/cm.^{2} The lattice spacing a in silver is 4·1 A., and so $\epsilon f = \Delta a/4{\cdot}1$. For $f = 5\%$. Frye and Hume-Rothery give two lines, one of slope $\Delta H/(\Delta a)^2 = 2{\cdot}4 \times 10^5$ kg./mm.^{2}/A.^{2}, the other of slope $0{\cdot}45 \times 10^5$ kg./mm.^{2}/A.^{2}. (The factor 10^5 appears in their paper as 10^7, but this is an error in computation.) These correspond respectively to $\Delta H/\epsilon^2 f^2 = 4 \times 10^{14}$ dynes/cm.^{2} and $0{\cdot}74 \times 10^{14}$ dynes/cm.^{2} So the value of $\alpha\beta = (2H_0 \Delta H/\epsilon^2 f^2)^{\frac{1}{2}}/E$ is 2·4 or 1·0.

It is also possible to estimate $\alpha\beta$ from Goebel's results on solutions in lead, which give hardening as a linear function of the distortion of the lattice. Norbury's plot of Goebel's results is expressed in arbitrary units, which appear to be hardening h in tenths of a kilogram per square millimetre and difference of size of solvent and solute atoms e in cubic centimetres per gram atom. This gives $H = 0{\cdot}981 \times 10^7 h$ dynes/cm.^{2}, $\epsilon = e/3 \times 18{\cdot}27$. For $f = 0{\cdot}01$, the points plotted by Norbury show $h/e = 2{\cdot}7$, corresponding to $H/\epsilon = 1{\cdot}45 \times 10^9$ dynes/cm.^{2} Taking E for lead as $1{\cdot}6 \times 10^{11}$ dynes/cm.^{2} gives $\alpha\beta = H/E\epsilon f = 0{\cdot}9$. This value of $\alpha\beta$ is consistent with that deduced from the results of Frye and Hume-Rothery. Combining these results with the rough estimate $\beta = 80$ gives values of α of the order of 0·02, in agreement with the estimates from the yield points of single crystals.

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