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MECHANICAL EFFECTS OF CARBON IN IRON

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ABSTRACT. Snoek has shown that when carbon atoms move from one possible set of interstitial sites in the lattice of α-iron to another set they cause shear strains. Cottrell has shown that the stress around a dislocation may be relieved by the migration of solute atoms in its neighbourhood, and that the dislocation is then bound to its present position. By combining these theories with the usual theory of age-hardening it is possible to explain the existence of a yield point, quench aging, strain aging, delayed yield and blue brittleness as consequences of the presence of carbon in iron. A rough quantitative theory of the time-aging effects is given, and shown to agree with experiment. The need for further xperiment is emphasized.

§1. INTRODUCTION

A. H. Cottrell (1948) has recently pointed out that in the stress field surrounding an elastic dislocation there will be regions in which the strain energy of a foreign atom in solid solution is greater than the energy of the same atom dissolved in an unstrained lattice, and regions in which the energy is less. Foreign atoms tend to diffuse to the regions where their strain energy is lowest, and a pattern of high and low concentrations is set up near each dislocation. Once the diffusion of foreign atoms has established this pattern, the force required to move the dislocation from its position in the lattice is larger than the force which would have been required before the pattern was formed.

If the dislocation is torn from its position by a sufficiently large force, it can continue to move across the crystal under the influence of a smaller force. This corresponds to the phenomenon of a sharp yield with continuing flow under a load less than the yield stress. If the load is now removed, the material is in an "overstrained" condition; the dislocations are free to move and plastic flow occurs under stresses less than the yield stress. If the material is allowed to rest without load for a considerable time, foreign atoms again diffuse to form atterns round the dislocations. The process of diffusion is principally one of e-adjustment of concentrations within the pattern, not one in which the concentration averaged over the whole pattern alters. It follows that the time τ taken to achieve equilibrium in a pattern of linear dimensions x is of order

$$\tau=x^2/2D, \qquad \ldots\ldots(1)$$

where D is the diffusion coefficient of the dissolved atoms, and is independent of the distance between neighbouring dislocations, provided this is much greater than x.

Snoek (1941 b) has shown that iron containing less than 0·0001 % of carbon by weight does not show a yield point with fall of load, while the addition of 0·003 % of carbon leads to a clear yield point. Snoek (1941 a, 1948) and Polder (1945) have also shown that the diffusion coefficient of carbon in α-iron is unusually large, being given by the formula

$$D=5{\cdot}2\times10^{-4}e^{-9000/T}\ \mathrm{cm^2 sec^{-1}}, \qquad \ldots\ldots(2)$$

where T is the temperature. This may be compared with the formula $D=10^{-3}e^{-18000/}T$ for the diffusion of copper in nickel, a metal of lower melting point.

Atoms forming dilute substitutional solid solutions can only relieve the stress round a dislocation by diffusing between regions where the lattice is compressed and regions where the lattice is expanded. They cannot relieve shear stresses. (Zener (1947) has shown that this is not true in more concentrated solutions, where a solute atom may have another solute atom as a nearest neighbour). Carbon in interstitial solution also increases the atomic volume of iron, and so carbon can contribute to the development of a yield point by concentratingin those regions near a dislocation which are dilated. This, however, is not likely to be the most important effect. The insterstitial positions at which carbon atoms may be found are the face centres and mid-points of the edges of the body-centred iron lattice. If the carbon atoms lie all at the centres of (001) faces and at the mid-points of edges perpendicular to (001), the lattice becomes tetragonal with (001) as the square base. If the carbon atoms jump to neighbouring (010) interstitial sites, the lattice becomes tetragonal with (010) as the square base. It follows that, whereas substituents in dilute solution in the lattice can relieve only hydrostatic stresses, and must travel distances comparable with the dimensions of the pattern to do so, interstitially dissolved carbon atoms can relieve shear stresses by migrating to neighbouring interstitial positions at a distance of only $\sqrt{3}d/2$, where a is the side of the elementary cell. This mechanism forms the basis of Snoek's analysis (1941 a) of internal friction in iron. The anchoring of dislocations by the migration of carbon in iron should therefore occur much more readily than the corresponding process in substitutional solid solutions, both because the carbon is very mobile and because carbon can relieve the stress by moving a very short distance.

It follows that the diffusion of carbon in iron can affect the mechanical properties by three mechanisms. The first mechanism is that of ordinary precipitation hardening, in which particles of cementite (Fe_3C) are formed. This manifests itself as quench aging. The second is the release of hydrostatic stresses around dislocations by local variations in the concentration of carbon. This we believe to be the cause of strain aging. The third mechanism is the release of shear stresses around dislocations by an ordering of carbon atoms among the possible sets of interstitial sites. We believe that this explains the phenonenon of delayed yield under constant load. The evidence for each of these effects is discussed below.

§2. QUENCH AGING

Suppose a specimen of ordinary iron is annealed at a temperature at which austenite is not formed, and then cooled rapidly to room temperature. The hardness of this specimen increases steadily with time as it remains at room temperature. At higher temperatures the hardening is accelerated, and is followed by softening. This phenomenon of quench aging was attributed by Davenport and Bain (1935) to the precipitation of cementite. They pointed out that decarburized iron does not show quench aging. The effect is also reduced if the carbon content is large enough for some cementite to remain undissolved at the quenching temperature, for precipitation on aging then occurs by the growth of these particles and not by the formation of fresh nuclei. From their graphical results we obtain table 1.

Table 1.

Temperature °(c.)	20	40	60	80	100
Time τ to reach maximum hardness	650 hrs.	140 hrs.	12 hrs.	2·9 hrs.	45 mins.

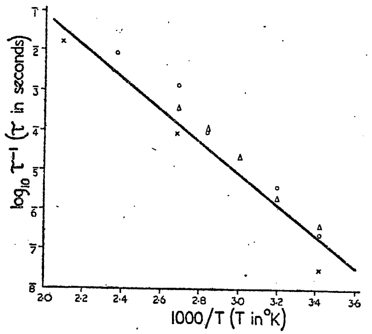

Figure 1. Dependence on temperature T of the rates τ^{-1} of strain aging and of quench aging.
(After Davenport and Bain.)

⊙ Davenport and Bain, stage aging
× Griffis. Kenyon and Burns, strain aging
Δ Davenport and Bain, quench aging

The results are plotted as triangles in figure 1, which shows a linear relation between the logarithm of the aging rate and the reciprocal of the absolute temperature, as required by equations (1) and (2), which lead to

$$\tau^{-1}=10{\cdot}4\,.\,10^{-4}x^{-2}e^{-9000/T}. \qquad \ldots\ldots(3)$$

The equation of the straight line drawn in the figure is

$$\tau^{-1}=4{\cdot}6\,.\,10^{6}e^{-9000/T}, \qquad \ldots\ldots(4)$$

corresponding to $x=1{\cdot}5\,.\,10^{-5}$ cm. The experimental points lie on a line very nearly parallel to this, and corresponding to a value of x of about 10^{-5} cm. The excellent agreement of the slopes justifies the belief that quench aging is caused by the diffusion of carbon, and the distance 10^{-5} cm. is of a reasonable order of agnitude.

§3. STRAIN AGING

If a low carbon steel is strained beyond the yield point, it becomes plastic, and only recovers a sharp yield point after an aging treatment. During this treatment its hardness steadily increases. The temperature dependence of this strain aging effect was studied by Muir (1900) and by Davenport and Bain (1935). Strain aging is distinguished from quench aging in various ways. It occurs only after straining, and it occurs both in freshly quenched specimens and in specimens which have been over-aged after quenching until the hardness has fallen below its initial value. At a given temperature the rate of strain aging is comparable with the rate of quench aging, but softening on over-aging occurs much more slowly after strain-aging than after quench-aging. The maximum hardness attained in quench aging decreases as the temperature rises; in strain aging the maximum hardness increases slightly with rising temperature. All of these observations are consistent with the view (which differs from that of Davenport and Bain) that strain aging is caused by the anchoring of dislocations by the diffusion of carbon from compressed to diluted regions in their neighbourhood.

Figure 1 shows that the activation energy for strain aging is almost exactly that for the diffusion of carbon, and that the distance through which the atoms diffuse is again of the order of 10^{-5} cm. The crosses represent the results of Griffis, Kenyon and Burns (quoted by Davenport and Bain) for the time after which "a certain arbitrarily chosen degree of susceptibility to stretcher straining may be regained after a cold working treatment of 1% reduction", as given below (table 2).

Table 2.

Temperature (° c.)	20	100	205
Time τ	1 year	3 hrs.	1 min.

The crosses are derived from the graphs given by Davenport and Bain, and represent the time taken to reach a Rockwell "B" hardness of 80 in a steel pre-aged and then cold-rolled to a hardness of 71, as given in table 3.

Table 3.

Temperature (° c.)	20	40	80	100	150
Time τ (minutes)	65 000	4 000	180	13	2

The observations of Muir are shown in figure 2, in which the dotted line shows the experimental dependence on temperature of the rate of recovery of the yield point, and the full line represents the time taken for carbon atoms to iffuse a distance of 2×10^{-6} cm. The method used to analyse the results is iven in the appendix.

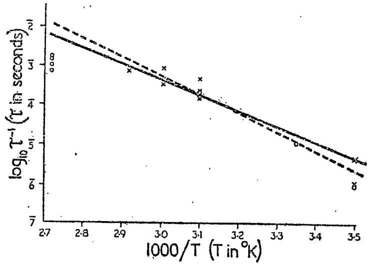

Figure 2. Dependence on temperature T of the rate τ^{-1} of recovery from overstrain.
(After Muir.)

× reliable points
○ doubtful points
---- regression of log τ^{-2} on T^{-2}
—— best fit line of slope corresponding to diffusion of carbon

To account for the relatively slow rate of softening after strain aging, we remark that quench aging sets up stresses and strains in the lattice, and that these impede the motion of dislocations through any part of the lattice. On over-aging, the elastic energy is reduced by changes in the shape of the particles of precipitate, or by recrystallization of the matrix, and the hardness falls. In strain aging the stresses already existing round dislocations are reduced by diffusion, thereby anchoring the dislocations to their own immediate parts of the lattice. The strain remains, but the stress is relieved, and there is no tendency for diffusion to alter the existing distribution of solute atoms. Softening can occur only by other processes.

The fact that the maximum hardness achieved on strain aging after complete quench aging increases with rising temperature is probably to be explained as follows. After complete quench aging the matrix is just saturated with carbon, and at higher temperatures there is more carbon in solution and available to relieve stress round dislocations. At higher temperatures the "Debye-Hückel atmosphere" of carbon atoms is less firmly bound to the dislocation, but, if we assume that the mean binding energy in the atmosphere is less than the heat of formation of cementite, the increase in the number of carbon atoms in solution is still the predominnat factor.

The discussion of strain aging given here is in some ways similar to the discussion by Konobeevski (1943) of analogous effects in substitutional solid solutions. A brief treatment has also been given by Dijkstra (1947), who considers in addition the influence of nitrogen.

§4. DELAYED YIELD AND BLUE BRITTLENESS

If a specimen is loaded in a tensile test at room temperature by a constant static load slightly less than that at which yield would occur under a slowly increasing load, it does not immediately yield. After a period which is characteristically two or three minutes (but may be as little as a few seconds or as much as several hours) the specimen begins suddenly to deform. Our picture of the process is that dislocations are anchored by carbon atoms which relieve the stress around them in their original positions. The external stress moves the dislocation slightly, and the changed stress field leads to a redistribution of the carbon atoms among the neighbouring interstitial sites. Snoek has shown that the relaxation time for the relief of shear stress by the movement of carbon atoms from (100) to (001) faces is about 10 seconds at room temperature. After a time of this order the anchoring of the dislocations is weakened. A dislocation suddenly breaks free from its atmosphere, and travels through the crystal too fast for an atmosphere to form round it. This fast-moving dislocation multiplies, probably according to the mechanism proposed by Frank (1948), and yield occurs.

At higher temperatures the carbon atoms are more mobile, and even a moving dislocation is surrounded by an incomplete atmosphere of carbon atoms which exert a viscous drag on it. Since the drag is the smaller the faster the dislocation moves, the break-away of a dislocation from its atmosphere is a catastrophic process. The higher the temperature and the more mobile the carbon atoms, the larger is the stress which must be applied before the dislocation breaks away. This is the phenomenon of blue brittleness, in which the mechanical strength of iron containing carbon shows a maximum around 300° c. in slow tests. Data on blue brittleness have been summarized by Kenyon and Burns (1939). In impact tests the material is only protected from brittle fracture and a low impact value if plastic flow occurs very rapidly. Such rapid flow is most impeded, and the impact figure shows a minimum, at still higher temperatures around 500° c., where the carbon atoms are still more mobile.

At very high temperatures blue brittleness again disappears. Each dislocation is accompanied by its atmosphere, but the carbon atoms are so mobile that their presence does not appreciably retard the movement of the dislocation.

It is known that the temperature at which blue brittleness occurs is higher for impact tests than for normal tensile tests, and it is reasonable to suppose that a similar effect will occur at lower temperatures in very slow tests. Dr. Cottrell has pointed out that such slow tests have been made on mild steel rods by Edwards, Phillips and Liu (1943). They find that at moderate rates of loading the yield point increases as the rate of loading increases, while at very slow rates below about 0·06 tons/in^2/hour the yield point is a decreasing function of the rate of loading. We can examine the possibility that this increased strength at very low rates of loading represents the room temperature analogue of blue brittleness. The effect of Edwards, Phillips and Liu was observed at a temperature of about 15° c. and a rate of loading R of about 0·06 tons/in^2/hour, while in normal tensile tests with a rate of loading of, say, 20 tons/in^2 in 2 minutes the strength begins to rise at a temperature of about 150° c. If we assume that the processes are the same, but occur at rates of loading given by a law of the form

$$R = R_0 e^{-B/T}, \qquad \ldots\ldots(5)$$

we find $B = 8300$, in reasonable agreement with the value 9000 which according to (2) represents the temperature dependence of the rate of diffusion of carbon in iron. Since, for tests at normal rates of loading, the increase in strength is only beginning at 150° c., and the maximum is reached at about 275° c., this explanation would imply that the maximum yield point at room temperature is attained only at rates of loading very much less than the lowest used by Edwards, Phillips and Liu.

It is, however, possible that the effect observed at room temperature is of an entirely different nature. The model with which we have worked, based on the ideas of Orowan and Mott, is one of dislocations trapped in imperfections of the iron lattice, and further stabilized in these traps by an atmosphere of carbon atoms. We have considered a dislocation breaking away from the shallowest of these traps and leaving behind its stable atmosphere. If the applied stress is small, this dislocation, once it has broken away, reaches a limited maximum speed, and creep occurs without sudden yield. If the applied stress is large, no limit to the speed of the free dislocation is set by the carbon atmosphere, it multiplies, and there is a sudden yield. Suppose now that a small stress is applied for a sufficiently long time. The dislocations in the shallowest traps migrate with their equilibrium atmospheres into deeper traps. Let the stress now increase to a value at which dislocations in the shallowest traps could escape in a reasonable time both from their traps and from their atmospheres, leading to the possibility of yield. Now, the shallowest traps are all empty, and dislocations can only escape from the deeper traps if they carry their carbon atmospheres with them. Such dislocations cannot escape from their atmospheres under the applied stress, and sudden yield cannot occur.

These two mechanisms should be distinguishable experimentally. On the former, the yield point depends only on the rate of strain in the tensile test, and is not affected by prolonged loading below the yield point before the test. On the second mechanism, such prolonged loading would increase the yield strength in a subsequent tensile test conducted at a normal rate.

§5. CONCLUSION

In this preliminary account it has been possible only to indicate the expected mechanical effects of carbon in iron, and to suggest identifications of these predicted effects with known mechanical properties. Clearly the theory requires further development, and it is hoped that it will also lead to further experiment.

A promising field would be the study of the mechanical properties of iron containing a concentration of carbon less than that required to saturate the iron at the rtesting temperature.

APPENDIX

Analysis of Muir's Results

A specimen of iron was caused to yield at a load of 27 tons/in^2, and then tested after annealing for various times at various temperatures. The extension during the yield work-hardened the specimen, so that after recovery its yield point had been raised to 53 tons/in^2. Testing below this new yield point did not produce appreciable changes either in the work-hardening or in the recovery. Passing the yield point again put the specimen in the overstrained plastic state.

By interpolating in Muir's diagram No. VIII it is possible to find the extension under a load of 27 tons/in^2 after the different annealing treatments. The results are shown in the table

Test number	Extension E (10^{-3} inch)	Duration t of anneal (minutes)	Temperature of anneal (° c.)	$\log_{10} \tau^{-1}$ (τ in seconds)
1	Yield			
2	1019	30	13	—
3	962	5	50	$\bar{4}\cdot664$
4	903	15	50	$\bar{4}\cdot375$
5	890	1020	13	$\bar{6}\cdot029$
6	860	15	50	$\bar{4}\cdot356$
7	828	5	95	$\bar{3}\cdot170$?
8	820	4320	13	$\bar{7}\cdot993$?
9	954	Yield in	Test 8	—
10	933	240	13	$\bar{6}\cdot677$
11	900	15	50	$\bar{4}\cdot178$
12	830	15	70	$\bar{4}\cdot861$
13	820	5	95	$\bar{3}\cdot001$?
14	934	Yield in	Test 13	—
15	832	15	60	$\bar{4}\cdot921$
16	818	10	95	$\bar{4}\cdot865$?
17	818	Specimen	turned down	—
18	948	Yield in	Test 17	—
19	910	5	60	$\bar{4}\cdot669$
20	859	15	60	$\bar{4}\cdot537$
21	821	960	15	$\bar{5}\cdot052$?
22	840	15	60	—
23	813	10	95	$\bar{3}\cdot222$?

To reduce these observations to a common basis, we assume that the extension E which has been increased by yield returns with increasing time t to an equilibrium value E_0 according to a law of the form

$$E_2 - E_0 = (E_1 - E_0)e^{(t_1 - t_2)/\tau}, \qquad \ldots\ldots(3)$$

where the relaxation time τ is a function of the temperature of annealing. In fact, the law of recovery is probably not of this simple exponential form, but it is necessary to assume some specific law in order to derive a time of relaxation which can be used to estimate the rate of recovery between two successive tests. We assume that $E_0 = 810$ units, and regard as doubtful the estimates of τ derived from tests 6 and 7, 7 and 8, 12 and 13, 15 and 16, and 20–23, in which the final value of $E - E_0$ is very sensitive to the assumed value of E_0. We are compelled to reject the recovery between tests 21 and 22, during which the plasticity apparently increased. The resulting estimates of τ are given in the table. The rate of relaxation τ^{-1} clearly increases rapidly with increasing temperature T, and we attempt to express its dependence on T by a law of the form

$$\tau^{-1} = \tau_0^{-1} e^{-\theta/T} \qquad \ldots\ldots(4)$$

by plotting $\log \tau^{-1}$ against $1/T$, as in figure 2. The regression of $\log_{10}\tau^{-1}$ on $1/T$, determined by applying the method of least squares to the ten points on the figure which are considered reasonably accurate, is given by

$$\log_{10}\tau^{-1} = 10{\cdot}896 - (4718 \pm 2392)/T, \qquad \ldots\ldots(5)$$

corresponding to

$$\tau^{-1} = 7{\cdot}87 \times 10^{10} e^{-(10900 \pm 5500)/T}. \qquad \ldots\ldots(6)$$

The limits ± 2392 and ± 5500 are standard errors. The regression (5) is shown by the dotted line in figure 2.

The estimated value $\theta = 10\,900$ in (6) agrees with the coefficient 9000 in expression (2) for the diffusion of carbon in α-iron sufficiently closely to justify the belief that the recovery of the yield point in α-iron is a process the rate of which is determined by the migration of interstitial carbon atoms.

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