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THE EFFECT OF HYDROGEN CHARGING ON THE DISLOCATION RELAXATION IN IRON

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Abstract.— Dislocation internal friction observations in iron are reported with "in situ" hydrogen charging to study its influence on the kink pair formation in screw dislocations (γ peak) and its possible relation to earlier observed softening effects. Also some substructures in the hydrogen cold-work peak are revealed.

1. Introduction.— Hydrogen charging (HC) gives rise to a remarkable softening effect of high purity iron /1-6/. This softening phenomenon has been observed either by tensile test experiments during electrolytic charging /1,2/, or by tensile tests carried out at low temperature following electrolytic charging at room temperature and rapid cooling /3/. There are good reasons to believe that this softening is a result of enhanced mobility of screw dislocations /1-6/. It should be possible to test this idea by monitoring the γ-peak during HC since this peak is widely accepted to be due to the kink pair generation process on screw dislocations /e.g. 7/. Internal friction (IF) experiments carried out on deformed and hydrogen doped iron /8/ so far did not retain high enough hydrogen concentrations in the γ-peak range.

Another point of interest is a sometimes observed substructure in the hydrogen cold-work peak /9/.

2. Experimental.— The specimens used in this study are similar with those used in the tensile experiments in /1/. They are produced from Johnson-Matthey iron by UHV zone melting followed by hydrogen treatments. The residual resistance ratio is ranging from 2500 to 4000. The specimens are 1 mm diameter × 30 mm long bamboo-structured polycrystals.

To obtain a well defined γ-peak, most of the samples are deformed in a standard way, i.e. in tension by 2% at room temperature and 1% at 77 K. They are further deformed in torsion in the pendulum at various temperatures.

The apparatus is an inverted torsion pendulum equipped with an electrolytic cell around the specimen to allow HC during measurements. IF and modulus were measured between 90 K and 400 K with surface strain amplitudes of 4 to 7×10⁻⁶. Electrolytic HC, however, was only possible between about 170 K and 330 K.

Sulphuric acid diluted with ethanol containing 10 mg/l NaAsO₂ was used mainly as a charging electrolyte. The charging current density was 21 A/m² to 210 A/m².

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3. Results.- 3.1. As deformed state. Figure 1 shows the IF measured after low temperature torsional deformation in the pendulum. The peak temperature $T_p$ shifts to higher temperature after the first heating up to 300 K, but then $T_p$ stays fairly constant. The peak height decreases slowly by successive annealing.

Because of the similarity in the peak temperature with other reports /e.g. 7,10/ this peak is concluded to be the so-called $\gamma$-peak and it is assumed that this peak corresponds to the kink pair generation on screw dislocations.

3.2. After charging experiments. Figure 2 shows the annealing behaviour of H doped, deformed iron. Immediately after the cooling a broad peak is seen centered at about 150 K with a height of $5.6 \times 10^{-3}$. In the 2nd run the main peak splits up into 3 components: one at 142 K, the second at 160 K, and the last at 170 K. By further annealing (curve 3) the central 160 K peak grows remarkably and the peaks on both sides remain as shoulders. After annealing at 230 K the 170 K peak has grown to be the largest peak at the expense of the 160 K peak. The broad peak in curve 5 - probably two peaks - reduces gradually with annealing and the higher temperature component anneals out more quickly.

Since the $\gamma$-peak was not measured just before HC prior to this series, direct comparison of the peak height between the hydrogen charged state and the one without H is difficult. It can be said, however, that the peak height after HC is larger than the height which is normally obtained by similar deformation conditions without hydrogen. The annealing of the $\gamma$-peak is rather fast as compared with the peak without hydrogen (cf. figure 1), but this is not always true. The peak-temperature shift with annealing is also increased by hydrogen.

3.3. In-situ HC experiments. In figure 3 curve 1 shows the $\gamma$-peak height immediately before HC. Curve 2 was measured during HC with a current density of 210 A/m$^2$ during cooling down. A large peak with a height of $1.02 \times 10^{-2}$ is seen at 217 K. The irregularity at the low temperature side of this peak is probably due to a change in the electro-chemical reaction at the surface of the specimen. Curve 3 is the heating run following immediately curve 2. The peak has been shifted to a lower temperature and has also split into 2 peaks, one at 180 K and the other at 200 K. Curve 4 was measured after curve 3 with the electrolyte out and rapid cooling from 270 K. The peak is shifted to about 150 K with a shoulder at about 180 K. In this curve the $\gamma$-peak is again well defined with similar height as curve 1. From this figure it may be said, that the $\gamma$-peak height is not changed appreciably by HC. It should be noted for the later discussion that during HC at 300 K, prior to curve 2, the IF value never exceeded $4.8 \times 10^{-3}$.

In figure 4 IF values are plotted against time during HC with the temperature being kept constant. Curve 2 was measured at 272 K, which corresponds to the valley between the $\gamma$-peak and the cold-work peak. By applying a HC current of 42 A/m$^2$, the IF increases and then saturates to about $4.2 \times 10^{-3}$, by switching off the current, the IF recovers to roughly the same level as before HC. A current of 21 A/m$^2$ makes the saturation value to $3.2 \times 10^{-3}$ and by further increase of the current, the IF increases.
again and saturates roughly to the same level as before. Thus this behaviour is rather reversible. Curve 1 was measured at 304 K, which is approximately at the top of the γ-peak. It is seen by applying a HC current, that the IF increases remarkably with time up to \(8 \times 10^{-3}\). The IF decreases rapidly on switching off the current and the IF level after this is smaller than before, i.e. the γ-peak has decreased in height. This on-off cycle of the current is not reversible at this peak temperature, i.e. the IF value sometimes decreases gradually without switching off the current. The reason for this is not well understood at present, but the structural change, which is suggested by the decrease of the γ-peak, is probably at least partly one reason and the change in the electro-chemical reaction due to build up of contamination at the surface is the other. It is interesting to note here that the zero point shift or "self twist" becomes very large when the IF is larger than about \(6 \times 10^{-3}\) at the γ-peak temperature. The quantity of this twist was not measured with time, the total amount of the twist during this run in figure 4 amounts to \(7 \times 10^{-4}\) shear strain at the surface. When the IF decreases gradually without switching off the current, this self twist also recovers during the decrease of IF and at the end the zero point recovered roughly to the original point.

Because of the rather unstable nature of the high IF value at the γ-peak temperature, the attempt to measure the IF as a function of temperature in such a condition was not quite successful. In figure 5 such an attempt is shown. Curve 1 shows the γ-peak prior to the HC. HC was started at 300 K and when the IF value saturated at about \(6 \times 10^{-3}\), the specimen was started to cool while measurement continued (curve 2). Since the temperature was changing during free decay oscillation, the scatter is rather large. In the following heating run (curve 3) a large peak appears at 210 K with a large shoulder at about 170 K and another small shoulder at about 250 K. The IF value in the γ-peak temperature range has remarkably decreased probably due to the above mentioned causes. It is seen in curve 5, the back measurement after stopping the HC, that the γ-peak has really become smaller and broader. It should also be noted here that the HC current density, in this experiment, may not always be a reliable parameter to estimate the hydrogen concentration in the specimens.

4. Discussion.- 4.1. The γ-peak. From the study mentioned above the effect of HC on the γ-peak may be summarized as follows: The peak shift due to hydrogen is not remarkable, although the shifting rate with annealing is larger with hydrogen than without hydrogen. No definite conclusion on the peak height is drawn, but there is a strong indication that the peak height is enhanced by hydrogen as seen from figure 4.

From the thermal activation analysis of the data shown in /1/ and /3/ the activation energy of the macroscopic deformation decreases by 0.5 eV at 100 MPa and by 0.3 eV at 70 MPa, respectively, by HC when softening takes place. This difference, however, decreases rapidly with decreasing stress and at the very small stress levels employed in the IF experiment the difference may be extrapolated to a negligible small value. Thus the very small, if any, peak shift by hydrogen may be readily
understandable. From the viewpoint of the mechanism in which the mobility of screw dislocations is enhanced by hydrogen, this small difference in the activation energy is the result of the stress sensitive nature of the screw dislocation cores in b.c.c. metals. It is quite likely that the core structure change by external stress is augmented by the presence of hydrogen, and thus results in the enhanced mobility. The large self twist is the result of screw dislocation motion relieving the internal stress, this has become possible by hydrogen.

Another possibility would be the possible precipitation of hydride during HC. It is known in Va metal-hydrogen systems that a large self twist takes place during hydride precipitation /11/. In this idea the softening is a result of the punched out edge dislocation motion by the hydride precipitation. The difficulty in this idea, however, is firstly that it is difficult to explain the orientation dependence of the flow stress during HC, and secondly that there has been no observation of hydride in iron.

4.2. The cold-work peak. The appearance and the annealing behaviour of the cold-work peak are quite similar, though not for the details, with the magnetic after effect measurements using the same material /12/ and also with the IF measurements in which hydrogen was doped by the gas discharge method /13/. The peak shown by curve 3 in figure 3, for example, may be the same as the 180 K peak of ref. /12/, and also as ref. /13/. The growth of the peak shown in figure 2 with annealing is considered the result of a redistribution of hydrogen atoms among trapping sites with different binding energies around dislocations. Then it should be assumed that there is a rather high energy barrier between the deepest trapping sites and the next nearest-and-deepest sites. The 170 K peak in curve 4 is then considered due to hydrogen trapped in the deepest sites.

5. References.
/6/ A. Kimura, H. Matsui, and H. Kimura, ibid
/12/ H. Matsui and H. Walz, in preparation
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Fig. 1: IF of iron deformed in the standard way followed by a torsional deformation at 90 K by ±0.65% including elastic strain. Frequency 2 Hz.

Fig. 2: Annealing behaviour of iron deformed in the standard way followed by a torsional deformation at 100 K by ±0.65%, then charged with hydrogen at 270 K with a current density of 64 A/m². Rapid cooling after charging (20 min to 90 K). Different curves correspond to successive runs.
Fig. 3:
1. Twisted at 200 K and annealed at 329 K.
2. measured during hydrogen charging with 210 A/m².
3. after 2., measured upwards.
4. after 3., charging being finished and rapidly cooled.

Fig. 4:
IF at constant temperature during hydrogen charging,
curve 1: T = 304 K
curve 2: T = 272 K

Fig. 5:
1. before hydrogen charging.
2. measurement during rapid cooling during hydrogen charging.
3. after 2., measured upwards.
4. same as 3. but with high current density.
5. back measurement, after charging being finished, rapidly cooled down.