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LOW TEMPERATURE INTERNAL FRICTION IN PURE IRON CHARGED WITH HYDROGEN OR DEUTERIUM

by

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Abstract - The search for the elusive hydrogen Snoek-peak in pure iron has been continued with specimens charged with either hydrogen or deuterium. The peaks observed are attributed to deformation produced during charging and can be classified as an α-type peak and a Snoek-Köster type peak. The detailed behaviour of these peaks during systematic outgassing of hydrogen or deuterium is described.

Introduction

At low temperatures, pure iron containing hydrogen gives rise to an internal friction spectrum which has been the cause of controversy. In the temperature range below 100 K, two peaks have been reported. The first, at 30 K (1 Hz), was reported in iron samples electrolytically charged with hydrogen (1). Keller attributed this peak to a Snoek mechanism involving isolated hydrogen interstitials and found a marked isotope shift with specimens charged with deuterium. Subsequently, a similar peak was observed by Gibala (2), Lord (3). The second peak, which occurs after tensile cold-work at ambient temperatures in uncharged specimens, was reported by Takita et al (4), and confirmed by Rivert et al (5) and Ritchie et al (6). This second peak is typical of the α-peaks in other b.c.c. metals and has been attributed to intrinsic dislocation mechanisms (e.g. double-kink generation (7)) but, a mechanism involving the interaction between hydrogen and dislocations can be envisaged also (8). Between 90 K and 120 K there is another peak, which requires the simultaneous presence of cold-work and hydrogen. This peak has been attributed to a Snoek-Köster mechanism (1) (2) (9). The same process also gives rise to a magnetic after-effect zone (10).

The purpose of this paper is to report : 1) an attempt to confirm the Snoek-peak and isotope shift, in iron of increased purity, and 2) a study of the effects of systematic hydrogen or deuterium outgassing on the α-peak and the Snoek-Köster peak.

Experimental techniques

The specimens used in this study were wires (0.6 mm in diameter, 10 cm in length) of ultra high purity (UHP) CEM-G Iron (11), preannealed at either 800°C or 850°C in various atmospheres (10^{-8} torr or purified hydrogen at a pressure of 1 bar). Charging with hydrogen (H) or deuterium (D) was carried out by electrolysis (H_2SO_4 or D_2SO_4 with CSe_2 as a poison) or by quenching in a pressure of 400 bars from 850°C to 20 K (7).

Internal friction (Q^{-1}) and elastic shear modulus changes (f^2) were simultaneously measured using an inverted torsion pendulum, operating at 0.5 Hz, with the specimen in a saturating axial magnetic field of 100 Oe. Magnetic after-effect measurements (MAE) were performed at 0.5 Hz with an apparatus described elsewhere (12).

Experimental results

(a) Attempted confirmation of the results of Heller (1) and Au and Birnbaum (13)

In a first publication (7) we repeated the experiments of Heller (1) and Au and Birnbaum (13) with UHP iron annealed in hydrogen at 400°C. We observed the HAE zones reported in (13) but reduced in magnitude by a factor of 10. We were unable to find the peak reported by Heller, but we did find a small a-peak in the same temperature range which was due to fresh dislocations induced by electrolytic charging.

In this study, we have repeated these experiments again but with specimens previously annealed at 800°C for 16 h in a vacuum of 10^{-8} torr. This annealing treatment leads to the complete absence of an a-peak after deformation at 300 K (6). These experiments confirmed our previous findings : after electrolytic charging with H, no low temperature internal friction peaks ($Q^{-1} > 2 \times 10^{-5}$) or HAE-zones ($\Delta r > 5 \times 10^{-5}$) were observed.

(b) Confirmation of the results of Takita and Sakamoto (9) at low frequencies

We have repeated the experiments of Takita and Sakamoto (9) with samples prerannealed in 1 bar of hydrogen at 400°C, then deformed 5 % in tension at RT and aged 1 h at 400 K to stabilize the a-peak (9). These samples were then charged in either H_2SO_4 or D_2SO_4 (+ CS_2) for 2 h, 0.1 A cm^{-2}. The internal friction spectra obtained after successive isochronal anneals are given in Fig. 1 and 2 (Each curve measured during an exponential rise in temperature was followed by a hold for 1/2 h in a primary vacuum). The evolution of the peak heights in Fig. 1 and 2, as a function of the annealing temperature, are detailed in Fig. 3.

Immediately after charging, the a-peak is suppressed and a large Snoek-Köster (S-K) peak is evident. This increases in amplitude after an anneal at 270 K and then rapidly decreases and moves to lower temperatures. For both Fe-H and Fe-D samples the a-peak appears at the same stage (300 K) in the sequence. In contrast, as shown in Fig. 4, there is a systematic difference in the peak temperature of the S-K peaks for Fe-H and Fe-D. Within experimental error, the regenerated a-peaks in the Fe-H and Fe-D samples are at the same temperature.

A precursor peak (which we will label ß) is observed in the annealing range 240-300 K, just before the appearance of the a-peak. This ß-peak appears at very low temperatures, grows in amplitude and moves to higher temperatures until it is finally lost by the sudden appearance of a relatively large a-peak. A concomitant modulus defect is observed as shown in Fig. 3, where f^2 at 4 K is plotted as a function of the annealing temperature. These results can be attributed to either a peak below 4 K which decreases in height during annealing, or to an effect of H (or D) on the modulus at zero K.

(c) Amplitude Dependence

At strain amplitudes $\varepsilon \sim 2 \times 10^{-6}$ used in the experiments of Fig. 1 and 2, no significant amplitude dependence was observed at temperatures below the S-K peak. However, at amplitudes of $\sim 10^{-5}$ the addition of hydrogen has an effect which seems to confirm the existence of a ß-process at very low temperatures : for a specimen annealed at 800°C and carefully mounted in the pendulum there is no detectable a-peak but significant amplitude dependence associated with the background begins at 30 K. After a moderate hydrogenation (1 h in H_2SO_4 without CS_2), the amplitude dependence is already significant at 4 K even though no noticeable a-peak has been induced.

Discussion

Hydrogen Snoek-peak ? Our present experiments show that in UHP iron there is no peak which can be attributed to the reorientation of isolated hydrogen interstitials. As a final effort to check this point, we now wish again to [illegible] isolated hydrogen in the lattice of a room temperature charged sample by light

torsional cold-work at 4 K. Once again no hydrogen Snoek-peak was produced, but evidence that this procedure was successful was presented by a decrease in modulus at 4 K followed by an increase in several steps beginning at 18 K corresponding to the return of hydrogen to the dislocations. This type of procedure will be extended to more sensitive MAB measurements and reported in detail elsewhere.

Our negative results for the hydrogen Snoek-peak in UHP iron lead to two possible conclusions : i) the non-cubic lattice perturbation associated with isolated hydrogen interstitials in α-Fe is too small to be detected by relaxation measurements as in Nb, Ta and V (15) or, ii) insufficient hydrogen is isolated in the lattice after the charging techniques to lead to a detectable relaxation magnitude.

α-Peak : This peak gradually reappears in Fe-H or Fe-D specimens during annealing in the temperature range 300-400 K. In both cases, the peak temperature of the regenerated peak is 27.5 ± 0.5 K. This is strong evidence that diffusion does not play a major role in the mechanism, and the fact that the peak is still well developed in the temperature range where outgassing is normally assumed to be complete, leads us to reject the hypothesis that a Nasiguti-type interaction of dislocations with H or D is involved. At the present time, we believe that the major contribution to this composite peak is an intrinsic dislocation mechanism (6).

The γ-peak (~ 300 K), which is attributed to an intrinsic dislocation mechanism involving screw dislocations (5)(6) reappears immediately during the anneal at 300 K before the α-peak is significantly developed. This is confirmatory evidence that non-screw dislocations which give rise to the α-peak strongly interact with H (or D), while the screw dislocations giving rise to the γ-peak have a much weaker interaction.

Snoek-Köster peak - The result (Fig. 4) which shows a systematically increased peak temperature for the Fe-D peak (8-10 K) compared with the Fe-H peak is very satisfying result for a Schoeck mechanism (14), which involves interstitial diffusion. However, the quantitative interpretation of this isotope shift is difficult because of the extreme structure sensitivity of the S-K peak. The initial increase in the peak height (Fig. 3) in the annealing range 240-300 K is attributed to vibration conditioning which leads to a correlated distribution of H (or D) pairs or clusters on the dislocations. Our interpretation in terms of pairs or clusters is consistent with the experimental results since it would be difficult to justify a Schoeck mechanism associated with single hydrogen interstitials, in the absence of an observable Snoek peak.

Role of H or D in the internal friction spectrum - Our results suggest the following interpretation. After cathodic charging with H or D the existing dislocation structure is rendered immobile at low temperature by strong pinning. If excess hydrogen exists in the lattice, it does not lead to an observable relaxation (impurity concentration is too low to giving rise to a measurable Impurity-Hydrogen peak). At 120 K, H (or D) pairs or small clusters on the non-screw dislocations can be dragged giving rise to an S-K peak. Vibration conditioning and annealing in the temperature range 210 K to 270 K leads to two important effects : i) the height of the S-K peak is slightly increased, and ii) the population of dislocations is sufficiently freed from H (or D) to allow motion of geometrical kinks at ~ 4 K, which in turn gives rise to the precursor β-peak and a slight amplitude dependence.

300-400 K annealings allows H (or D) to gradually escape from the dislocations and migrate to the surface. During this outgassing, the S-K peak gradually disappears and when the free lengths of non-screw dislocations become long enough, the α-peak attributed to double-kink generation on these lengths reappears.

Above 400 K, the specimen is completely purged of hydrogen leaving a fully developed α-peak which does not diminish until the annealing temperature reaches

the range where major changes in the dislocation structure occur.

Conclusions

We conclude that using the conventional forms of hydrogen charging, a Snoek-peak cannot be produced in UHP iron. The α-peak contains a major component which is due to the generation of double-kinks on non-screw dislocations. The S-K peak is due to non-screw dislocation dragging pairs or small clusters of H (or D) atoms.

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Figure Captions

Fig. 1 and 2 : Internal friction spectra during successive warm ups of UHP iron charged with H_2SO_4 and D_2SO_4 (for clarity, the spectra are displaced on the Q^{-1} axis ; on the left is indicated the temperature of the previous annealing).

Fig. 3 : Evolution of the amplitude of the α, β, γ and S-K peak during annealing. The evolution of f^2 measured at 4 K is also shown (no significant difference is observed between hydrogenated and deuterated samples).

Fig. 4 : Evolution of the S-K peak temperature with height of the peak (a difference of 8-10 K appears between hydrogenated and deuterated samples).

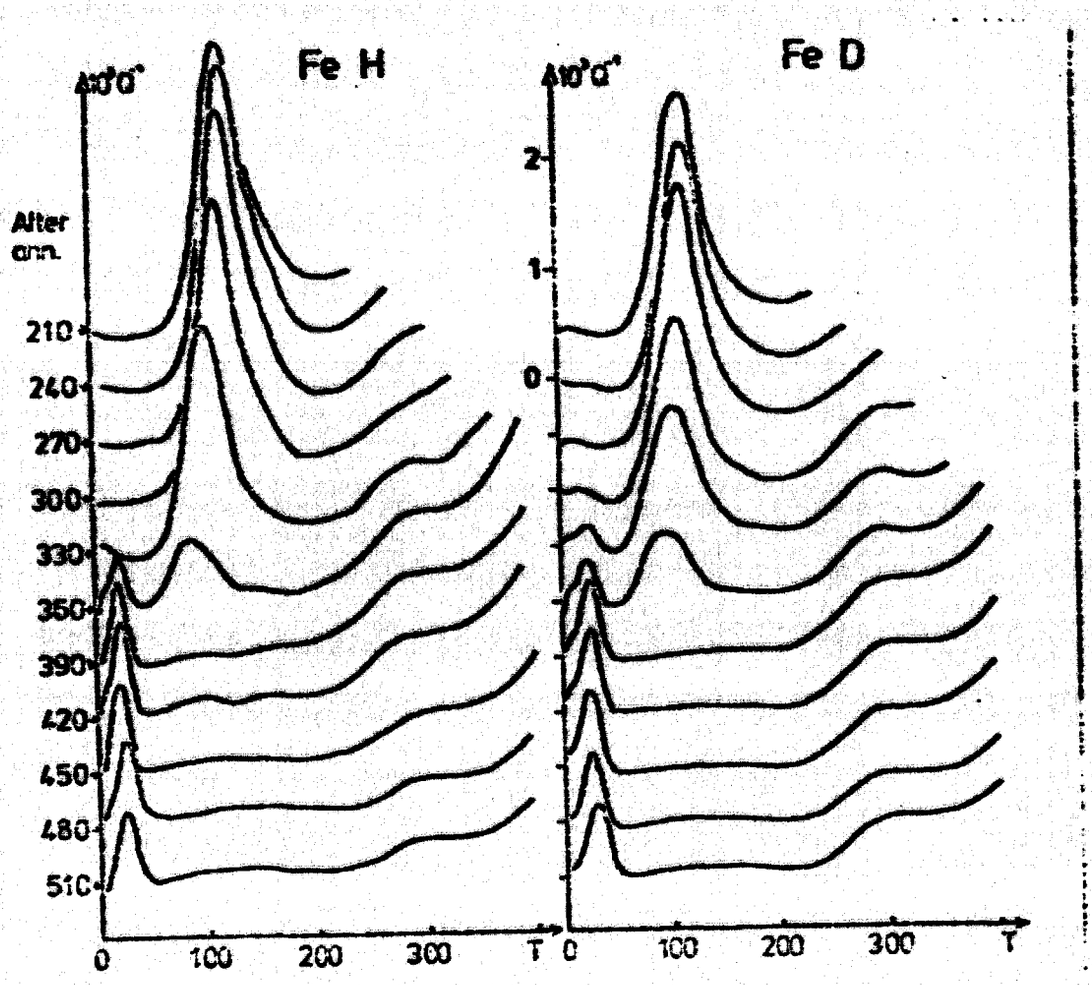

Fig. 1

Fig. 2

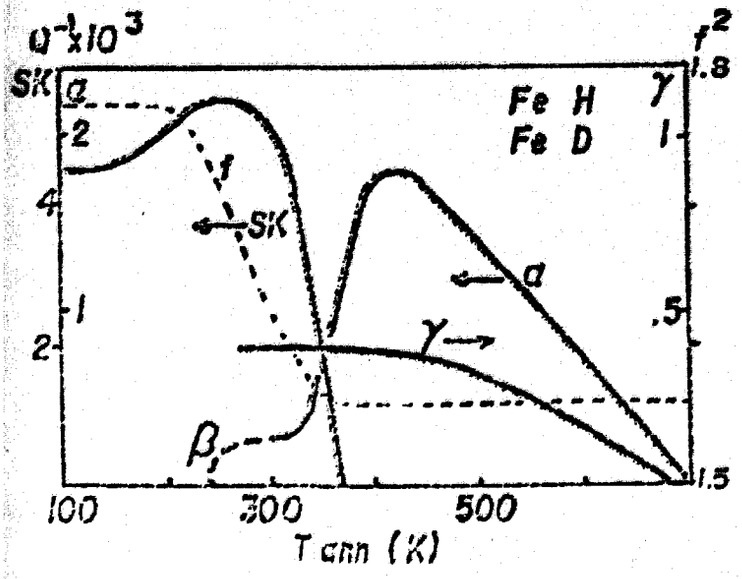

Fig. 3

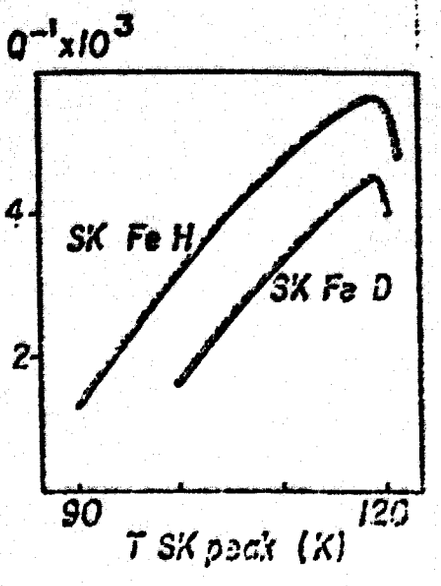

Fig. 4