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BEHAVIOUR OF Fe-Ni-C ALLOY DOPED WITH HYDROGEN IN THE γ PHASE

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Abstract.— The purpose of this paper is to compare the internal friction behaviour of Fe-Ni-C hydrogenated specimens and of hydrogen free specimens when reheating from 77 to 300 K the recently quenched structure. Cathodic hydrogen charging was done in the austenitic phase at high temperatures with a recently developed method using molten salts. A new peak (called $\textcircled{H}$ peak) appears at about 150 K (in the 1 Hz frequency range) in hydrogenated specimens.

1. Introduction.— The influence of carbon content and time related parameters on the internal friction behaviour (between room temperature and 77 K) of Fe-Ni-C alloys with subzero M_s temperature has already been studied in the 100 Hz frequency range (Carrard and co-workers, 1977) and in the 1 Hz frequency range (Prioul and Carrard, 1979). Eventhough some aspects are still discussed (Prioul and Carrard, 1981) the physical interpretation of the internal friction behaviour observed in the (77-300) K temperature range can now be considered as well established.

From this knowledge we focussed our attention on the internal friction behaviour of hydrogen charged Fe-Ni-C alloys (in the γ phase), in order to have a better understanding of the effect of hydrogen from both technical and academic points of view.

Internal friction behaviour of Fe-Ni and Fe-Ni-C alloys doped with hydrogen have never been studied as far as we know. Nevertheless several papers have been published using other experimental methods. Thus, from room temperature electrochemical experiments Beck and co-workers (1971) have determined that the diffusion coefficient D falls from about $10^{-4} \text{ cm}^2/\text{s}$ for pure iron to about $10^{-10} \text{ cm}^2/\text{s}$ for Fe-40% Ni (in weight). Those values resemble closely the results of Dresler and Froberg (1973) for a Fe-30% Ni ($5.10^{-9} \text{ cm}^2/\text{s}$ at 58°C) and the values given in the litterature for Ni (Combette and Azou, 1970). The solubility c rises by about 10^3 between pure iron and Fe-40% Ni (Beck and co-workers, 1971), then remains constant up to pure nickel. Between 0 and 30-40% Ni the dominant factor which controls the value of D and c is the fall of the mole fraction of the α (b.c.c.) phase in the alloy counterbalanced by the rise of the γ (f.c.c.) phase.

Since it is more soluble in austenite than in martensite hydrogen is also expected to increase the thermodynamic stability of austenite. According to Maulik and Burke (1975) no significant effect on the M_s temperature of Fe-Ni alloy is observed after room temperature cathodic charging even in the presence of poison (NaAsO_2). This result does not agree with observations of Ramachandran and Dasarathy (1961) in Fe-C base steels and with the results of Abdelhadi (1976) on Fe-Ni-C alloys. On the other hand, cathodic charging (below the M_d temperature) of an austenitic structure can produce large amounts of α martensite in Fe-Ni (Maulik and Burke, 1975) and in Fe-Ni-C alloys (Abdelhadi, 1976). The phase transformation occurring during cathodic hydrogen charging at room temperature is probably "strain induced". In that case the strain is induced by the deformation resulting from the introduction of the gas under conditions of high surface supersaturation and low diffusivity.

This brief review of current knowledge about the effect of hydrogen on the behaviour of Fe-Ni and Fe-Ni-C alloys shows the complexity of the phenomena when hydrogen is present. Also it appears that hydrogen charging must be carried out at temperatures as high as possible, but avoiding such phenomena as graphitisation (Carrard and co-workers, 1973) and decarburisation.

We shall present this study in two parts. In the first part we shall present methods and results connected with hydrogen charging. The second part is concerned with a qualitative analysis of hydrogen effects on internal friction behaviour.

2. Material. - Two Fe-Ni-C alloys were used for this study. The treatment of the specimens was the same as the one described by Prioul and Carrard (1981) and leads to an entirely γ structure at room temperature. The alloys used for hydrogen charging, abbreviated to A (0.34% C ; 27.21% Ni ; 0.53% Mn ; 0.38% Si ; 0.020% P in weight) and for internal friction experiments, abbreviated to B (0.41% C ; 24.20% Ni ; 0.27% Mn ; 0.33% Si ; 0.011% P) have a M_s temperature close to 215 and 225 K for both the A and B alloys.

3. Hydrogen charging. - In order to avoid hydrogen induced phase transformation and microcracking as pointed out in the first part of this paper, hydrogen charging was conducted at temperatures above room temperature. We used a new method described by Chene (1977) which consists of cathodic hydrogenation in hot molten salts. The electrolyte is a eutectic mixture of $\text{NaHSO}_4\text{-H}_2\text{O}$ (57%) and KHSO_4 (43%) which can be used between 398 and 523 K. The bath temperature is thermostatically

controlled by a separate circuit of oil. The electrolytic cell is closed and steam is condensed in the upper part in order to avoid and over-rapid dehydration of the molten salts solution. The hydrogen charging is done at a constant potential by using a two-electrode system. The potential of the sample is measured with reference to an Ag/Ag^+ electrode situated near the sample. The current necessary to hold this potential at a constant value is controlled by an electronic potentiostat through an auxiliary electrode (a cylinder of Pt netting being placed round the sample). Under these conditions the anodic and cathodic reactions are equivalent to the electrolysis of the water in the bath.

Different electrochemical conditions were tested (charging potentials from -2 000 to -800mV of duration between 1 and 30 h, the temperature of the bath being in the (400-500) K range). A detailed study of the results obtained will be published subsequently. Nevertheless it is important to notice that after hydrogen charging under these conditions :

- no phase transformation was detected by metallographic examination ;
- the M_s temperature was lowered ;
- an average gases content in the sample of 5 to 15 ppm (in weight) was measured in the γ state by desorption (1.4×10^{-3} Pascal, 1 000 K). Mass-spectrometry of the desorbed gases revealed that these gases are mainly hydrogen ;
- outgasing the α' structure (after quenching the γ structure at 77 K) reveals a lower hydrogen content than outgasing the γ structure.

4. Internal friction behaviour. - Internal friction and frequency measurements were performed on an automatic inverted torsion pendulum manufactured at the laboratory and recently connected to a micro-computer (Prioul and co-workers, 1981). We used cylindrical specimens (diameter 3 mm, useful length 50mm) anchored by two threaded heads (diameter 6mm, length 15mm). After an in-situ quenching to 77 K (cooling rate 1.5K/min) and a maintenance for one hour at 77 K, the measurements were performed during reheating (heating rate 1.5K/min). The strain amplitude during measurements was less than $\epsilon_0 = 5 \times 10^{-6}$ and unless otherwise specified test frequency was 1.5 Hz. Hydrogen charging of alloy B used for internal friction experiments, was made under the following conditions : potential -1 000mV, temperature 405K, duration 16h. After such impregnation the hydrogen content was about 10 ppm. The samples doped with hydrogen were held for about half an hour at room temperature after charging, in order to set up the experiment.

In fig.1 we illustrate the effect of hydrogen on internal friction Q^{-1} and relative frequency $(F-F_0)/F_0$ evolutions. These are plotted versus temperature during the heating of the samples from the 77K recently quenched state up to 300K. F_0 equals $F(77K)$ measured at the beginning of each experiment.

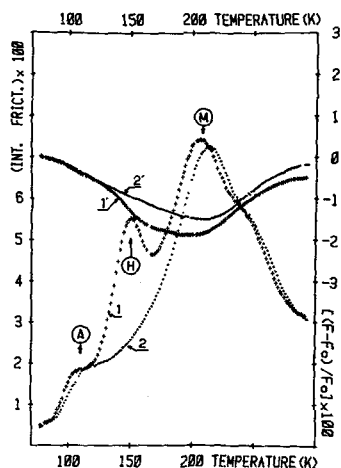


Fig.1: Internal friction and relative frequency versus temperature for continuous heating from 77 to 300K curves 1,1' corresponding to hydrogenated specimen curves 2,2' corresponding to hydrogen free specimen.

A comparison between hydrogen charged specimens (curves 1,1')¹ and hydrogen free specimens² (curves 2,2') shows that :

- a new internal friction peak (called (H) peak) appears at 150K for a 1.4 Hz test frequency in hydrogen charged specimens. A frequency anomaly is associated with this peak.
- the main maximum (M) is shifted from 215 to about 205K in the case of the hydrogen charged specimen. The amplitude of this maximum remains constant.
- all the internal friction curve is shifted towards lower temperatures.

The effect of hydrogen on the (A) anomaly will not be discussed in this study. This anomaly has been correlated to a reheat transformation in a previous paper (Prioul and co-workers, 1979).

A first heating of a hydrogenated specimen (Fig.2, curves 1,1') was stopped at 170K and the specimen was cooled down to 77K. A second heating of the same specimen (curves 2,2') indicates that both the (H) peak and the correlated frequency anomaly are still present; only peak height is reduced. A third heating of the same hydrogenated specimen,

(1) in this paper curves 1,2,...are assigned to internal friction evolutions, whereas curves 1',2',...are assigned to frequency evolutions. (2) for detailed studies of (A) anomaly and (M) maximum see respectively Prioul and Carrard (1979) and Prioul and Carrard (1981).

after maintenance at room temperature for 16h, produced an internal friction curve showing no significant effect due to the initial charging of the γ phase (curves 3,3').

In Fig.2 a comparison between curves 4,4' and curves 1,1' (for temperatures below 170K) and between curves 4,4' and curves 2,2' (for temperatures above 170K), obtained from two different specimens, shows consistent results for both internal friction and frequency curves. Nevertheless (H) peak height and low temperature behaviour are different (see curves 1 and 4). These differences are probably related to the room temperature maintenance after hydrogen charging (30 min for curves 1,1' and 24h for curves 4,4').

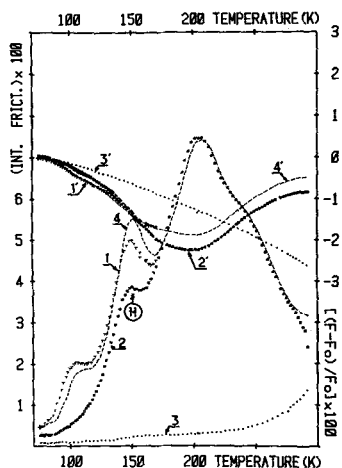


Fig.2: Behaviour of hydrogenated specimens
curves 4,4' typical evolution of the internal friction and the relative frequency
curves 1,1' first heating stopped at 170K
curves 2,2' second heating of the same specimen
curves 3,3' third heating of the same specimen after a 16h room temperature maintenance.

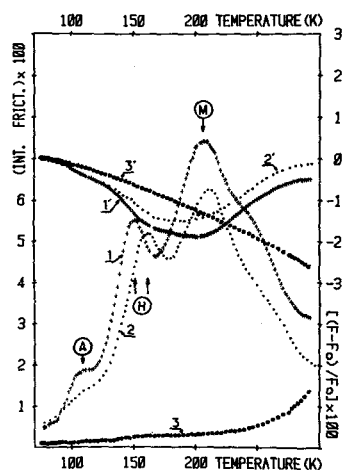


Fig.3: Influence of the test frequency on the behaviour of hydrogenated specimens
1.4 Hz - curves 1,1' first heating
 - curves 3,3' second heating
6.8 Hz - curves 2,2' first heating.

The (H) peak temperature is shifted from 150K to 160K but (H) peak height is unaffected (Fig.3) when the frequency used in the test is changed from 1.4 Hz (curves 1,1') to 6.8 Hz (curves 2,2').

5. Discussion of the internal friction results. - From these preliminary internal friction results, obtained after hydrogen charging of Fe-Ni-C alloys, the (H) peak (which appears at 150K for a 1.4 Hz test frequency) seems to be correlated with a relaxation phenomenon (see

modulus anomaly, reversibility, frequency shift). The structural state of the sample (high density of mobile dislocations and presence of hydrogen) and the temperature of the (H) peak (150K for a 1.4 Hz test frequency) lead us to propose that the mechanism at the origin of the (H) peak could be a hydrogen-dislocation interaction in the α' phase. Experiments are currently being made at higher frequencies in order to identify the characteristics of the observed (H) peak. Nevertheless a quantitative analysis of the phenomenon must be conducted carefully because dislocations seems to be at the origin of both (H) peak (this paper) and background noise (Prioul and Carrard, 1981).

Both the explanation put forward to explain the (M) maximum in a hydrogen free sample (Prioul and Carrard, 1981) and the shift towards lower temperatures of this (M) maximum due to hydrogen charging (see Fig. 1) point to a second effect within this structure, related to the presence of hydrogen. This presence of hydrogen seems to modify the interaction between carbon and dislocations and thus increasing the apparent carbon mobility.

6. Conclusion.— Results obtained after high temperature cathodic hydrogen charging in molten salts, of γ Fe-Ni-C structures have shown that :

- this hydrogen charging method is an appropriate method in the case of γ structures.
- the quantity of hydrogen desorbed after quenching at 77K is lower in comparison with that desorbed in the γ phase;
- hydrogen is responsible of a new internal friction peak ((H) peak) which appears when reheating the recently quench structure. This (H) peak is situated at about 150K for a 1.4 Hz test frequency. The main characteristics of this peak indicate that it is probably a relaxation peak associated with hydrogen-dislocation interaction;
- hydrogen seems to modify the interaction between carbon and dislocations in the sense of an apparent increase in carbon mobility.

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