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Effect of hydrogen on Young's modulus of AISI 1005 and 1070 steels

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Young's moduli of AISI 1005 and 1070 steels, in different metallurgical states, were measured before and after hydrogen charging by means of the classical resonant bar method. Different decreases in Young's modulus were found which could be correlated with the microstructural state of the steel. The maximum diminution of elastic modulus was observed for the martensitic structure of 1070 steel (−1.7%) and the minimum in 1005 steel in the normalized state (−0.4%). Moreover a linear relationship was established between the change of Young's modulus from the effect of hydrogen and the hydrogen embrittlement susceptibility of these steels.

1. Introduction

The effect of hydrogen on the elastic constants of iron has been the subject of several papers [1–3]. Basically they were intended to clarify the mechanisms of the hydrogen embrittlement of steels.

Due to the extremely low solubility of hydrogen in pure iron, Wriedt and Oriani [4] have studied the effect of hydrogen on Young's modulus of three other b.c.c. transition metals. They concluded that dissolved hydrogen increases the Young's modulus of polycrystalline vanadium, niobium and tantalum but these results did not allow them to infer anything about iron. Other authors [5, 6], working with single crystals, found different effects in the same metals. From the data of Fisher *et al.* [5], the Hill average of both Young's modulus, E, and shear modulus, G, can be computed. It can be seen that the effect of hydrogen on E and G is the same: both of them decrease in vanadium and tantalum while they increase in niobium with increasing hydrogen content.

Lunarska *et al.* [1] found that hydrogen decreases the shear modulus G of polycrystalline ultra-pure iron at low temperature. They reported that 1 at % H changes G by 8% at 100 K. No change in G was observed at room temperature due to the escape of hydrogen from the sample.

Bastien and Azou [2] have measured a decrease of 1.9% in Young's modulus in a steel (0.12% C) annealed for 6 h at 650 °C and charged with hydrogen in 10% HCl for 48 h.

More recently Zhang *et al.* [3] have investigated the influence of hydrogen on the apparent Young's modulus of polycrystalline high-purity iron. They found a decrease in the resonance frequency of hydrogen-charged specimens, measured with a Bordoni-type apparatus. It was attributed to a change in the internal stresses caused by hydrogen rather than a change of the interatomic cohesive force of the perfect crystals.

In previous work [7] different hydrogen embrittlement susceptibilities were reported for 1005 and 1070 AISI steels in different metallurgical states. This led us to question whether a connection might exist between hydrogen embrittlement susceptibility and the change of the Young's modulus of steel induced by hydrogen. To answer this question a series of experiments were performed in order to measure with a sensitive technique, the resonance frequency (Young's modulus) of those steels which exhibit different embrittlement behaviour (AISI 1005 and AISI 1070 steels), before and after charging with hydrogen.

2. Experimental procedure

2.1. Preparation of specimens

The materials used in this study were two commercial carbon steels, AISI 1005 and AISI 1070. Their chemical compositions are summarized in Table I.

After machining the samples to the required geometry for each test, they were heat-treated in order to obtain a variety of microstructures:

(i) AISI 1005 steel, normalized (N1): 1223 K for 15 min in vacuum, and then air-cooled.
(ii) AISI 1070 steel:

(a) Spheroidized (S): as received.
(b) Normalized (N2): 1113 K for 15 min in vacuum and then air-cooled.
(c) Quenched (Q): austenized in vacuum at 1113 K for 20 min and then water-quenched.
(d) Quenched and tempered (QT): quenched as above and then tempered at 723 K for 1 h.

The microstructure was examined by optical and scanning electron microscopy. Additional hardness tests were performed.

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TABLE I Chemical compositions of steels

	Composition (wt%)									
AISI	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Al
1005	0.05	0.31	0.03	0.007	0.015	0.02	0.03	0.01	0.02	0.002
1070	0.71	0.86	0.19	0.026	0.019	0.06	0.05	0.02	0.09	0.005

2.2. Frequency measurements

Measurements of the resonance frequency were conducted using the classical resonant bar method described by Rosinger *et al.* [8] (Fig. 1). Rectangular-section bars, 0.05 cm thick by 0.5 cm wide and 10 cm long, were cut from the original sheet with their long dimension parallel to the rolling direction. They were suspended horizontally by two threads at the nodal position of the first flexural mode. Acoustic excitation of vibration was used and the specimen response was detected by a non-contacting optical transducer. All the measurements were performed at room temperature.

At least ten specimens of each material were tested for resonance frequency. Specimens were identified in such a way that the frequency variation after charging refers to the same specimen.

The general equation that relates Young's modulus and the first flexural resonant frequency is given by [8]

$$E = \frac{48\pi^2 f^2 L^4 \rho}{4.7300\, e^2}$$

where f is the resonant frequency, L is the specimen length, ρ is the density and e is the specimen thickness. The specimen dimensions and density changes induced by hydrogen can be calculated from data on the relative change of the iron lattice parameter $\Delta a/a$. Taking the value for the partial molar volume of hydrogen $V_H = 2.0\ \mathrm{cm^3\,mol^{-1}}$ given by Hirth [9], a concentration of hydrogen of 15 p.p.m. (the highest in our samples) gives $\Delta L/L = \Delta e/e = 3 \times 10^{-5}$ and $\Delta\rho/\rho = 10^{-4}$. That is, the frequency variations due to changes in dimensions and density after charging were not expected to be greater than 0.002%. Then changes in resonance frequency greater than the frequency error (0.04%) can be attributed to the presence of hydrogen.

Hydrogen was introduced into the specimens at room temperature by cathodic galvanostatic charge in a 1 N H_2SO_4 solution with a current density of $-5\ \mathrm{mA\,cm^{-2}}$ during 24 h. Pt was used as anode. These charge conditions were chosen to prevent formation of internal cracks and blisters.

Immediately after charging the specimens were coated with a thin layer of copper by dipping in a Cu_2SO_4 solution to prevent any hydrogen loss. In order to confirm the efficacy of this procedure the hydrogen content of the specimens was measured by means of a Leco Hydrogen Determinator, 5 min and 24 h after copper coating. The hydrogen content was determined in the 1005 and 1070 steels, both in the normalized state.

Eight out of the ten specimens of each series were charged with hydrogen and two of them were left as blanks. All the specimens were coated with copper.

3. Results

No cracking was visible under SEM examination of the charged specimens. Therefore the Young's modulus losses observed in hydrogen-charged specimens should correspond to hydrogen at the lattice imperfections (weak and strong traps).

Figs 2–5 show the microstructure of spheroidized, normalized, quenched, and quenched and tempered AISI 1070 steels. Results of hydrogen analysis of charged and copper-coated specimens are reported in

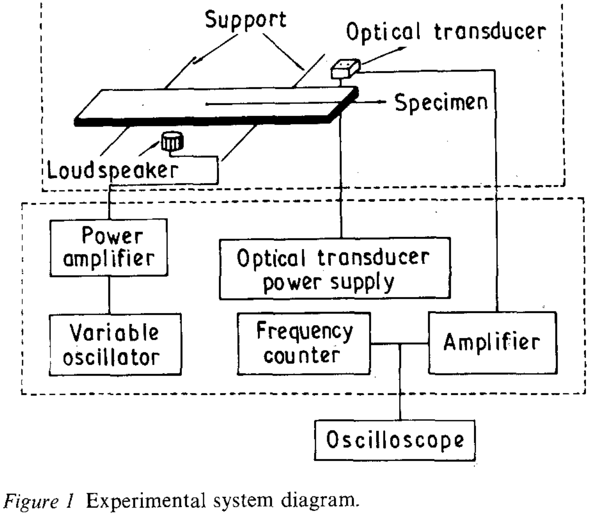

Figure 1 Experimental system diagram.

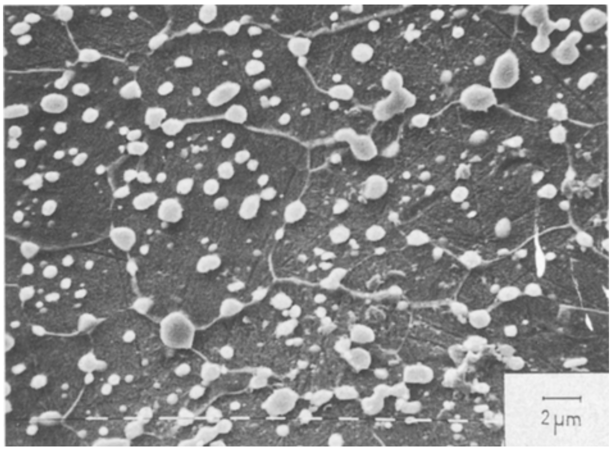

Figure 2 Scanning electron micrograph showing typical spheroidal structure of pearlite in 1070 steel.

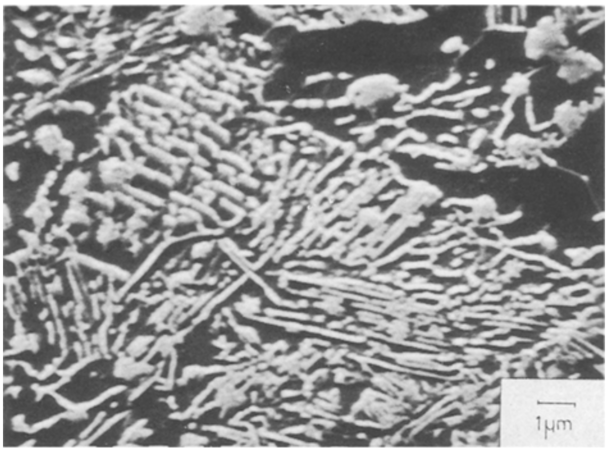

Figure 3 SEM photomicrograph showing the typical lamellar pearlite of 1070 steel.

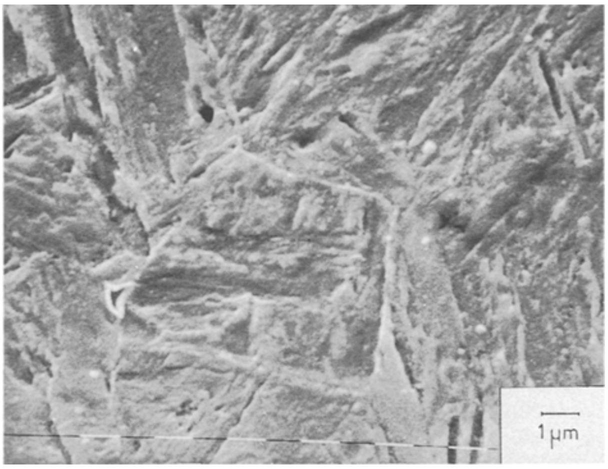

Figure 4 SEM picture of the martensitic microstructure of 1070 steel.

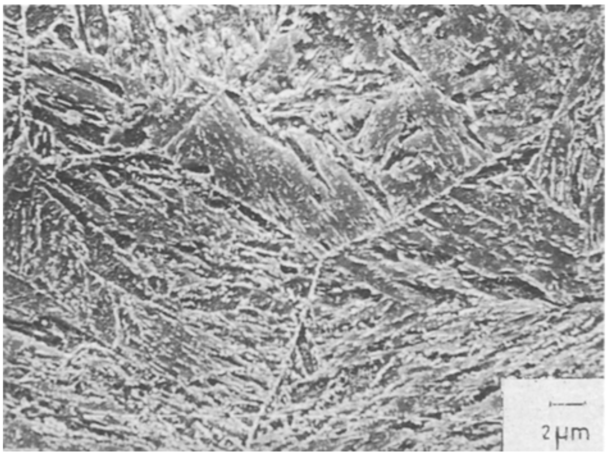

Figure 5 SEM micrograph showing typical tempered martensite of 1070 steel.

TABLE II Mean values of hydrogen analyses of 1005 and 1070 steels in the normalized state

Steel	Ageing time in air	C_H (p.p.m.)
1005	5 min	5.4 ± 0.3
	24 h	5.0 ± 0.3
1070	5 min	11.3 ± 0.4
	24 h	11.0 ± 0.4

TABLE III Resonant frequency variation (Δf), hydrogen embrittlement susceptibility (RA_{LOSS}) and Vickers microhardness (H_V) of steels; $RA_{LOSS} = 100\ (RA_0 - RA_H)\ /RA_0$, where RA_0 and RA_H represent the reduction of area of the uncharged and charged specimens, respectively

Sample	$\Delta f = \frac{f_H - f_0}{f_0} \times 100$	RA_{LOSS} [7]	H_V
N1	-0.2 ± 0.04	3	83
S	-0.3 ± 0.04	10	220
N2	-0.4 ± 0.04	22	245
QT	-0.6 ± 0.04	44	344
Q	-0.85 ± 0.04	–	732

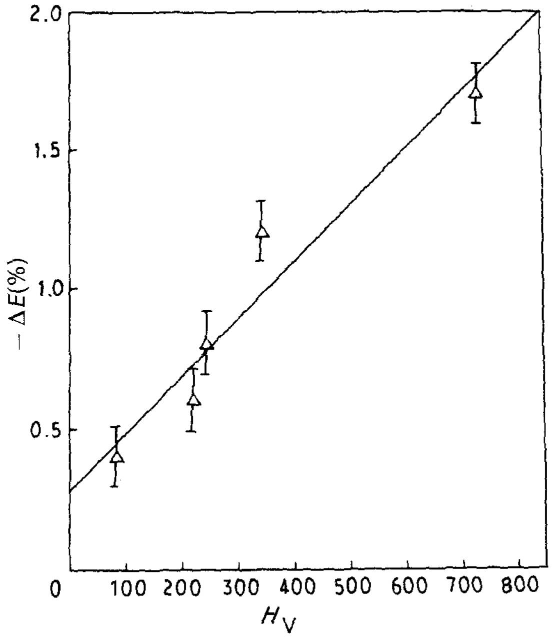

Figure 6 Diminution of Young's modulus ($-\Delta E$) versus Vickers microhardness (H_V) of 1005 and 1070 steels.

Table II. These results indicate that the layer of copper certainly prevents any hydrogen loss before and during testing.

No variation in resonant frequency in the two samples left as blanks was detected. Δf calculated from the resonance frequency change after charging with hydrogen is the average for the eight samples of each series. Δf values are given in Table III.

The curves of hydrogen embrittlement susceptibility of steels (RA_{LOSS}) and Vickers microhardness H_V versus reduction of Young's modulus caused by hydrogen ($-\Delta E = -2\Delta f$) are shown in Figs 6 and 7, respectively.

Hydrogen decreased the Young's modulus ($-\Delta E$) of 1070 and 1005 steels. The maximum $-\Delta E$ is obtained when 1070 steel has a martensitic structure (Fig. 4) and it decreases with heat treatment.

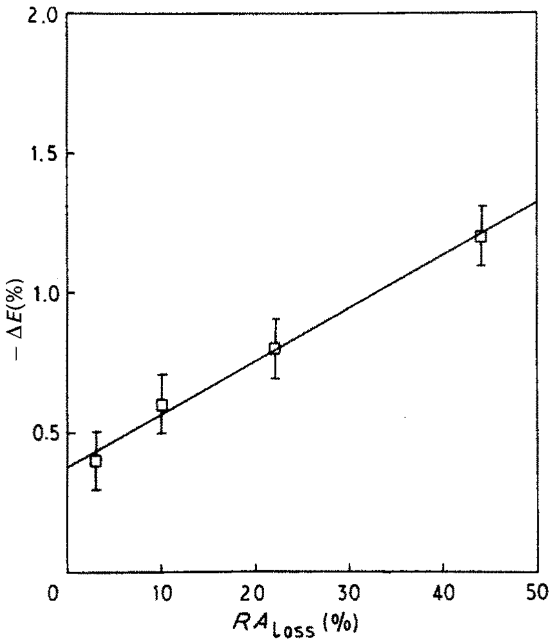

Figure 7 Reduction of Young's modulus ($-\Delta E$) versus hydrogen embrittlement susceptibility ($RA_{\rm Loss}$) of 1005 and 1070 steels.

The decrease of Young's modulus after cathodic charging with hydrogen is a minimum for 1005 low-carbon steel in the normalized condition.

In the 1070 steel the spheroidal cementite structure (Fig. 2) has a lower $-\Delta E$ than the lamellar structure (Fig. 3). This fact is consistent with the hardness and hydrogen embrittlement sensitivity of steels. In other words, there exists a linear relationship between the change of Young's modulus from the effect of hydrogen and the hydrogen embrittlement sensitivity of the steel.

4. Discussion

The solubility of hydrogen in the iron lattice at room temperature is extremely low (approximately four hydrogen atoms per 10^8 iron atoms [10]), so most of the hydrogen is trapped at lattice imperfections such as dislocations, microtwins etc. The local hydrogen concentrations in these sites are 10^4 times the equilibrium values. Consequently the lattice defects promote heterogeneous hydrogen accumulation in the microstructure of steel [11].

The trapping of hydrogen at lattice defects has been confirmed by tritium autoradiography [12, 13], the hydrogen microprint technique [14] and permeation measurements [15, 16]. An enhancement of hydrogen concentration over the lattice concentration was always found.

The martensitic structure of 1070 steel (Q) is composed of a mixture of lath and plate martensite (Fig. 4). The substructure consists of a high density of dislocations and very fine microtwins (high density of lattice defects) [17, 18]. Therefore a high level of microstresses exists. In the other words a large number of hydrogen traps exist in this microstructure.

This heterogeneous distribution of traps promotes hydrogen concentration centres in the martensite structure, giving rise to important changes in the properties of this microstructure [19, 20]. For this reason the martensitic structure of 1070 steel displayed the maximum diminution of Young's modulus and, in agreement with earlier observations, the greatest hydrogen embrittlement susceptibility [20].

In the case of spheroidal cementite (S) (Fig. 2), fine lamellar pearlite (N2) (Fig. 3) or tempered martensite (QT) (Fig. 5), the lattice defects (dislocations, microtwins etc.) are widely separated and the internal stresses are decreased. This means that the number of hydrogen traps decreases, leading to a decrease in both the reduction of Young's modulus and the hydrogen embrittlement susceptibility of 1070 steel.

A decrease in the carbon content (1005 steel) decreases the reduction of Young's modulus ($-\Delta E$) of hydrogen-charged steel. This behaviour of Young's modulus in the annealed structure is due to the fact that a decrease of the carbon content of steel produces a decrease of the relative amount of cementite, thus reducing the interface area between cementite and ferrite which acts as a trapping site for hydrogen atoms. This means that a diminution of hydrogen-rich sites leads to a decrease in the reduction of Young's modulus and hydrogen embrittlement susceptibility of steel. These facts clearly show that the process is controlled by the trapping of hydrogen in lattice imperfections of the microstructure.

It is well known that the elastic modulus of metals is proportional to the second derivative of the cohesive energy [21]. The direct relationship between the Young's modulus losses caused by hydrogen and the hydrogen embrittlement susceptibility of steels leads us to think that hydrogen segregation at the lattice imperfections (traps) would reduce the cohesive energy of the iron lattice according to the decohesion mechanism suggested by Troiano [22] and expanded by Oriani [23].

5. Conclusions

The analysis of our results leads to the following conclusions:

1. Hydrogen decreases the Young's modulus of 1070 and 1005 steels.
2. A correlation exists between the microstructural state of steel and the Young's modulus losses caused by hydrogen. The maximum diminution of Young's modulus is obtained in the martensitic structure of 1070 steel (-1.7%) and the minimum in 1005 steel in the normalized state (-0.4%).
3. Hydrogen segregation at lattice defects could be the cause of the decrease of the cohesive energy of the iron lattice.

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