

**"STUDY OF HYDROGEN INFLUENCE ON THE DISLOCATION MOBILITY IN 304 STAINLESS STEEL"**

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**Resumé** - Les effets de la déformation et du chargement en hydrogène sur le frottement intérieur basse fréquence de l'acier inoxydable type AISI 304 sont étudiés. Le résultat du vieillissement aux températures proches de 500K sur le frottement intérieur est présenté. Les relaxations observées sont discutées en termes des effets dus aux interactions entre dislocations et défauts ponctuels et à la mise en ordre, sous l'action d'une contrainte, de l'hydrogène associé à d'autres défauts ponctuels. On a obtenu les énergies d'activation des processus de relaxation.

**Abstract** - The effects of deformation and hydrogen charging on internal friction were investigated at 1 Hz for annealed Type AISI 304 stainless steel. The result of ageing for temperatures near 500K on internal friction is described. The observed relaxations are discussed in terms of effects due to dislocation-point defects interactions and stress induced ordering of hydrogen associated to other point defects. The activation energies for the relaxation processes have been obtained.

**1 - INTRODUCTION**

It is well known that hydrogen causes embrittlement in several metals and alloys [1], and among them are the austenitic steels [2]. For many proposed mechanisms [3] accounting for this embrittlement, hydrogen-dislocation interaction is thought to play an important role. Therefore it is quite essential to increase the knowledge of how hydrogen and dislocation interact with the crystal lattice to access the interaction among themselves. The aim of this work is to study these interactions and to determine relaxation parameters related to these processes. For this purpose, the most appropriate technique is internal friction (IF) in which relaxation peaks, obtained as a function of temperature, are unequivocally related to each relaxation process. Observation of a peak due to hydrogen itself is only possible provided its concentration is high enough to be detected by the IF technique and the lattice distortion created by hydrogen does not have the local crystalline symmetry.

Embrittlement in austenite is usually analysed using high pressure hydrogen gasification or cathodic charging. This last procedure was used for compatibility of results with the few previous analyses found in the literature [4-6] for 304 stainless steel (SS).

**2 - EXPERIMENTAL PROCEDURE**

**2.1.- Sample preparation.** Wire samples of 304 SS with 1.2 mm diameter (with the following composition in weight percent: 0.059 C, 17.8 Cr, 7.9 Ni, 0.022 P, 0.5 Si, 2.0 Mn, 0.38 Mo, Fe: balance) were encapsulated in a quartz tube under pressure of  $1.33 \times 10^{-1}$  Pa, heated at 1173K during 600 s and quenched in water. After this treatment the average grain size was 30  $\mu$ m.

**2.2.- Hydrogen charging.** Hydrogen charging was carried out at room temperature (RT) by the electrolytic charging method (platine anode) with a solution of 1N sulphuric acid poisoned with As<sub>2</sub>O<sub>3</sub> (100 mg/l). The current density and charging time were 500 A/m<sup>2</sup> and 3.6 Ks, respectively.

**2.3.- Plastic deformation.** After the procedure described in Section 2.1 some samples were deformed in tension at RT using an universal testing machine. The deformation rate,  $\dot{\epsilon}$ , was  $10^{-4}$  s<sup>-1</sup> and the plastic true strain was in the range of

0 to 8%.

2.4.- IF experimental technique. The IF and frequency measurements were carried out in an inverted torsion pendulum at a frequency of about 1 Hz and over temperatures ranging from 120 to 520 K. The free decay method was used for the measurements and the maximum surface strain amplitude was  $1.3 \times 10^{-5}$ . The heating rate was  $0.02^\circ \text{ s}^{-1}$ .

### 3 - RESULTS

3.1.- Samples subjected to thermo-mechanical treatments. Curve a in Fig. 1 shows the IF as a function of temperature obtained after the procedure described in Section 2.1 at 1.04 Hz (RT value). Curves b, c and d, in this figure were obtained

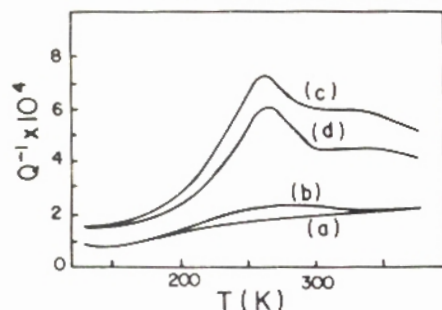


Fig.1- IF spectra of samples after a) annealing at 1173K and cold-work in tension at RT; b) 0.9%; c) 3.6% and d) 7.3%. Peak A at 263 K.

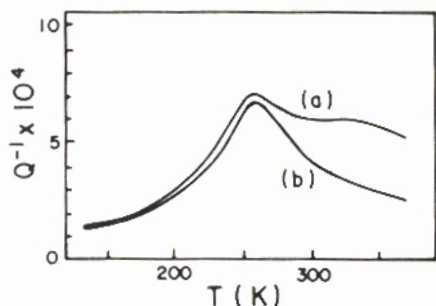


Fig.2- IF spectra of a sample annealed at 1173K and 3.6% cold-worked in tension at RT (a), and then annealed at 523 K (b).

after mechanical tests with true strains of 0.9, 3.6 and 7.3%, at 1.15, 1.08 and 1.07 Hz, respectively. Curve b shows a small broad peak at 263 K named A. The height of peak A increases with deformation, which also develops the high temperature part of the peak (Fig. 1, curves c and d). In order to study the influence of ageing treatments on IF, some measurements were performed following linear annealings until 523 K. Curve a in Fig. 2 shows the IF against temperature obtained after RT tensile deformation (3.6%) and curve b, after linear annealing at 523 K. From this figure it was concluded that annealing causes the following effects: a) a small variation of the IF background at low temperatures, b) a reasonable decrease of the IF at the higher temperature side of the peak, and c) almost no influence on the peak height. Curves a, b and c, in Fig.3 show the IF as a function of temperature obtained after

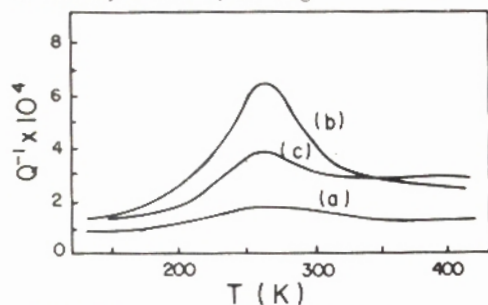


Fig.3- IF spectra of samples annealed at 1173K, cold-worked in tension at RT [a) 0.9%, b) 3.6% and c) 7.3%], and annealed again at 523 K.

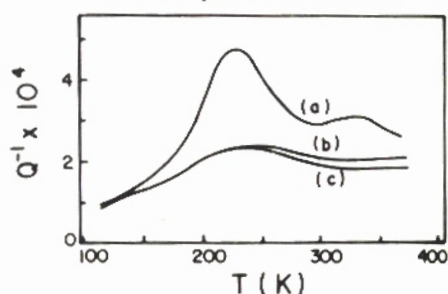


Fig.4- IF spectra of a sample annealed at 1173K and hydrogen charged: a) after charging, and then annealed at b) 373K and c) 473K. H-peak at 228K.

linear annealings at 523 K for three samples plastically deformed 0.9, 3.6 and 7.3%, respectively.

3.2.- Hydrogen charged samples. Curve a in Fig. 4 shows the IF as a function of temperature obtained with a specimen subjected to hydrogen charging, as described

in Section 2.2. This curve shows a peak at 228 K assigned H-peak. This peak has been related to the one observed at 300 K by Asano et al. [4,5] and Igata et al. [6]. In order to observe the evolution of the IF spectrum with ageing treatments, measurements of IF as a function of temperature were performed after linear annealings at 373 K and 473 K, as shown in curves b and c of Fig. 4. It is observed that the first annealing decreased the peak height by about 60%, while the last annealing affects very little the precedent spectrum.

#### 4 - DISCUSSION

There is not a great amount of work done using the IF technique to study the behaviour of 304 SS. Recently, S. Asano et al. [4,5] and Igata et al. [6,7] studied the influence of thermo-mechanical and hydrogen charging treatments in 304 SS using this technique. Asano's group has given special attention to the 310 SS in order to avoid problems of instability of 304 SS concerning phase transformations induced by these treatments.

4.1.- Peak A. The comparison between the IF spectra of the RT deformed samples permitted to associate peak A to the peaks located at 320 K (550 Hz) and at 328 K (1000 Hz) showed by Asano et al. [5] and Igata et al. [6], respectively. Fig. 5 presents the measured frequency curve as a function of the peak temperature. The value obtained by Igata's group for their P<sub>3</sub> peak was not considered because its IF

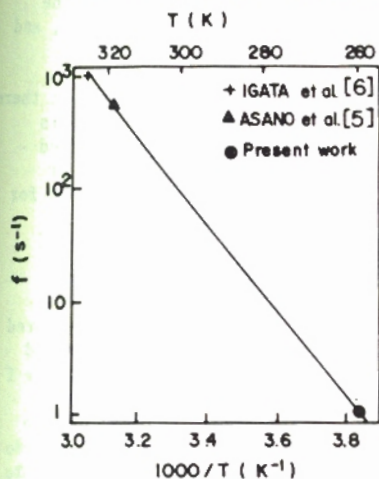


Fig.5- Arrhenius plot for peak A.

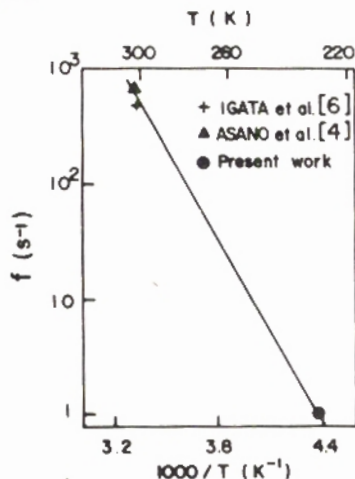


Fig.6- Arrhenius plot for the H-peak.

spectrum is very complex. The activation energy value for this process obtained by them was 0.60 eV while a value of 0.75 eV was estimated from Fig. 5.

4.2.- H-peak. The data points obtained from IF and testing frequency spectra are plotted in Fig. 6, as a function of the measured temperatures, for the 304 SS samples subjected to hydrogen charging treatments. The peak temperatures and frequencies of Fig. 6 correspond to the H-peak of Fig. 4 and to those peaks obtained by Asano et al. [4,5] and Igata et al. [6]. The activation energy was evaluated to be approximately 0.52 eV.

#### 4.3.- Comparison between FCC and BCC structures.

4.3.1.- Dislocation mobility. The screw dislocation mobility in the BCC lattice at low temperatures is rather lower than the mobility of 71° dislocations, which is comparable to the mobility of the screw and 60° dislocations in the FCC structure. This fact implies some differences among the IF spectra concerning the Bordoni relaxation; the two peaks overlapping in the FCC structure [8] but not in the BCC one (Funk and Schultz, to be published). If it is admitted that in 304 SS dislocations behave like the ones in the FCC metals, it should be concluded that peak A is not a Bordoni-type peak. Two facts support this conclusion: a) the observed background increase at low temperatures with the deformation amount in the previous [5-7] and present works (Fig. 1), and b) the behaviour concerning the N and

C influence observed by Igata et al. [7] for their  $P_3$  peak, which was associated to the unpinning of dislocations from defect complexes. At present, it is difficult to precise the mechanism responsible for peak A, but it is believed that IF measurements made as a function of vibration amplitude after the linear annealing at 523 K would confirm Igata's hypothesis.

4.3.2.- H diffusivity and solubility in 304 SS. The hydrogen diffusion energy in  $\alpha$ -Fe at RT and lower temperatures is about 70 meV [9]. Despite the fact that hydrogen occupies tetrahedral interstices [10] and should therefore give rise to a Snoek-type relaxation, this effect has not been observed in  $\alpha$ -Fe [9]. In 304 SS the diffusion energy near RT is 0.51 eV [11]. The relaxation due to hydrogen in this structure may be observed only if hydrogen were associated to atoms or vacancies, forming a pair or a defect complex, since the octahedral interstice has the lattice symmetry. The value of 0.52 eV obtained from Fig. 6 for the activation energy of the process suggests that hydrogen is indeed associated, and the observed relaxation is of the Snoek-type.

The 304 SS has a higher H solubility than the  $\alpha$ -Fe, which is  $<1$  at ppm below RT [9]. This difference is due mainly to the ability of octahedral interstices of the FCC lattice to accommodate hydrogen atoms without lattice distortions, which is not the case for the BCC lattice, in which hydrogen causes severe distortions. Perhaps for this reason the hydrogen Snoek peak was not observed in  $\alpha$ -Fe while a cold work peak (CWP) appears in deformed and hydrogen charged samples [9]. On the other hand, the hydrogen charging treatment in 304 SS originates a peak (Fig.4), and the combination of this treatment with deformation seems to create independent relaxations [5,6]. The distinct behaviour of peaks A and H (Figs. 2 and 4, respectively) towards linear annealing supports this fact. This should mean that there is no CWP in this case, and that possibly hydrogen-dislocation interaction occurs only when the hydrogen solubility limit is surpassed. It should also be mentioned that the H-peak may occur due to the stress-induced ordering of H-H pairs [4] or H-Ni pairs in austenitic stainless steels, since H has more affinity for Ni than for Fe or Cr [12]. Additional credit to this last hypothesis may be inferred by observing Fig. 1 of reference 4, in which the H-peak height increases with the Ni content.

## 5 - CONCLUSION

The IF of 304 SS subjected to plastic deformation and hydrogen charging was measured at about 1 Hz in the temperature range between 120 and 523 K. An IF peak was found at 260 K after plastic deformation. Its characteristics are summarized as follows: (1) it is resistant to linear annealing at 523 K and (2) its activation energy is about 0.75 eV. In order to determine the relaxation mechanism it is interesting to verify the IF behaviour as a function of amplitude. After hydrogen charging an IF peak was observed at 228 K. The linear annealing at 473 K decreases the peak height but does not eliminate it. Its activation energy was found to be about 0.52 eV, which is close to the hydrogen diffusion energy in 304 SS. This fact suggests a Snoek-type mechanism with hydrogen associated to other atomic species, forming pairs or defect complexes.

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