Journal of Alloys and Compounds, 211/212 (1994) 241–244
JALCOM 085

Thermal activation parameters and the annealing process of the hydrogen relaxation peak in an austenitic stainless steel

Li Guangyi
State Key Laboratory for Fatigue and Fracture of Materials, Institute of Metal Research, Academia Sinica, 110015 Shenyang (China)

Abstract

The hydrogen relaxation peak in 2179 austenitic stainless steel charged by high pressure gas has been studied. The thermal activation parameters of the peak were compared with those of H diffusion in the steel. The differences are discussed on the basis of an atom pair reorientation model. The annealing process of the peak was analyzed theoretically. A comparison of the experimental results with the theoretical analysis suggests that this peak is probably produced by a hydrogen–substitutional atom pair.

1. Introduction

The low temperature embrittlement of austenitic stainless steels is considered to be associated with H [1]. Internal-friction (IF) techniques have been applied to study the behaviour of H in the steels [2–4]. A hydrogen relaxation peak was observed in a series of the steels. However, some of the experimental results, *e.g.* the peak temperatures, are not quite consistent [2, 3]. Although the activation enthalpy of the peak in an austenitic stainless steel is approximately equal to that of H diffusion in the same steel, the diffusion coefficients converted from the relaxation times assuming reorientation of a single atom are much lower than those extrapolated from the high temperature diffusion data. As to the atomic mechanism responsible for the peak, different views have been given by different workers. Theoretically both H–H and H–substitutional atom pairs are possible.

Most of the previous work on the H peak in austenitic stainless steels used the electrolytic charging method with high current density and promoters. Because of the very low diffusivity of H in steels a large number of H atoms are concentrated in the surface layer of the specimen; the local concentration might be as high as a few tenths of the atomic ratio. Therefore it is likely that large numbers of dislocations, microcracks and other forms of damage are induced in the specimen, which in turn makes the IF spectra complex.

The aim of this work is to overcome the shortcomings of the electrolytic charging method. For this purpose a high pressure gas thermocharging method was adopted. Under an appropriate schedule, one is able to obtain a virgin specimen with a homogeneous distribution of H and perhaps without serious damage in it.

2. Specimens and experimental procedure

The specimens of dimension 1 mm × 1.6 mm × 90 mm were taken from a sheet of 2179 austenitic stainless steel with the following chemical composition: 20.3 wt.% Cr, 7.6 wt.% Ni, 9.3 wt.% Mn, 0.4 wt.% Si, 0.031 wt.% C, 0.26 wt.% N, 0.003 wt.% S, 0.027 wt.% P, less than 0.03 wt.% Al, 0.05 wt.% Ti, 0.08 wt.% Cu and balance Fe. The specimens were annealed at 1323 K for 1 h in a vacuum furnace, followed by water quenching. The residual H was found to be 3.9 wt.ppm.

H charging was performed in an autoclave at 10 MPa at 573 K for 2 weeks, followed by water cooling the autoclave. The H content in the charged specimen increased to 72 wt.ppm.

The IF measurements were carried out in a JN-1 vacuum inverted torsion pendulum, filled with He at 260 Pa and with heating at 0.5 K min^{-1}. Frequencies from 0.6 to 6 Hz were used. The maximum surface strain amplitude of the specimen was about 1×10^{-5}.

The specimens were annealed *in situ* in the pendulum with the following schedule: heating to the annealing temperature at 1.5 K min^{-1}, hold for 0.5 h and cooling to room temperature at 1.5 K min^{-1}. The annealing temperatures were increased in steps from 374 to 604 K.

SSDI 0925-8388(93)00085-D

3. Results and analysis

The IF of 2179 stainless steel as a function of temperature is shown in Fig. 1. Curve 0 is for an annealed specimen. Curve 1, for a charged specimen, shows a peak of height 3.7×10^{-4} at around 245 K (1.5 Hz), which is attributed to H. Note that there is a small peak at around the same temperature in curve 0, only about $(2\text{–}3)\times10^{-5}$ high, perhaps associated with residual H.

By means of changing the frequency an activation enthalpy H_i of 0.56_3 eV and a pre-exponential factor τ_0 of 3.37×10^{-13} s can be obtained.

In-situ annealing in the pendulum caused the peak to decrease in height gradually, but with no change in the peak temperature (see curves 2–4 in Fig. 1). Table 1 lists the peak heights in a charged specimen subjected to different annealing treatments. The average total diffusion distance of H in the specimen up to the current measurement of corresponding IF is also listed (see text below).

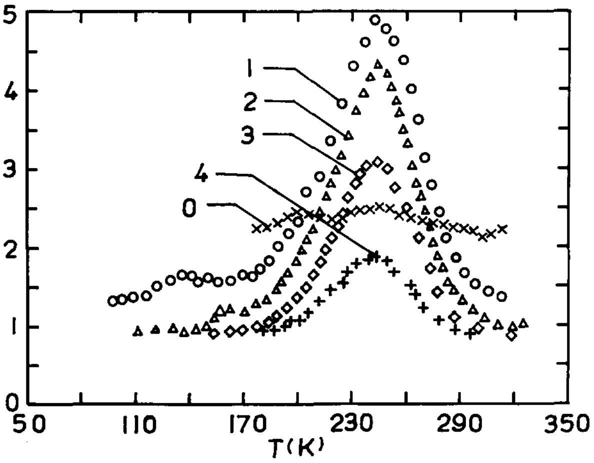

Fig. 1. IF in 2179 austenitic stainless steel: curve 0, annealed specimen; curve 1, charged specimen; curve 2, curve 1+374 K for 0.5 h; curve 3, curve 2+447 K for 0.5 h +500K for 0.5 h +549 K for 0.5 h; curve 4, curve 3+604 K for 0.5 h.

TABLE 1. The variation in the H peak height with annealing processes

Annealing temperature (K)	Peak height ($\times10^{-4}$)	$2(\int D\,dt)^{1/2}$ ($\times10^{-4}$ m)
288	3.7	0.066
374	3.4	0.32
447	3.1	0.71
500	2.5	1.29
549	2.0	2.42
604	1.1	4.31

4. Discussion

4.1. The thermal activation parameters

A permeability experiment on the steel used in this work showed that the activation enthalpy H_d of H diffusion is 0.51_8 eV and the pre-exponential factor D_0 of the diffusion coefficient, is 1.88×10^{-7} M^2 s^{-1} [5]. It can be seen that H_d is slightly lower than H_i. Using a model of a single octahedral interstitial jump in an f.c.c. lattice, the diffusion coefficient can be calculated from the relaxation time of the peak:

$$D_i = \frac{a^2}{6\tau_s} \tag{1}$$

where a, the lattice parameter, is 3.58×10^{-10} m.

The diffusion coefficients at the peak temperatures calculated using eqn. (1) are shown in Fig. 2 as open circles. Those taken from ref. 5 and their regression line are shown too. It is obvious that the apparent D_i is more than one order of magnitude lower than the value extrapolated from high temperature data. This difference exceeds the error generally estimated for the two methods. This difficulty has been pointed out previously for similar steels [4].

As a tentative explanation, we suppose that a single H atom does not cause any asymmetric distortion in the f.c.c. lattice, and therefore the observed H peak must be due to reorientation of an atom pair. In general the reorientation of an atom pair needs to overcome the binding enthalpy in addition to the enthalpy of diffusion of the single atom. However, the pre-exponential factors of the relaxation times for the two processes are about the same [6]. In the present case the pair is either H–H or H–substitutional atom. As a first approximation the binding enthalpy H_b can be

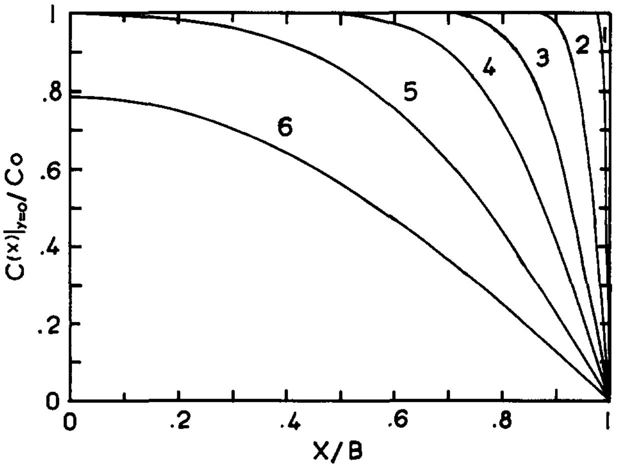

Fig. 2. Theoretical curves of H distribution in the IF specimen for various annealing temperatures: curve 1, 288 K; curve 2, 374 K; curve 3, 447 K; curve 4, 500 K; curve 5, 549 K; curve 6, 604 K.

taken as $H_b = H_i - H_d$. So the relaxation time τ_p of the pair is related to the relaxation time τ_s of the single atom by the equation

$$\tau_p = \tau_s \exp\left(\frac{H_b}{kT}\right) \tag{2}$$

If eqns. (1) and (2) are combined, a new conversion expression can be obtained:

$$D_i = \frac{a^2}{6\tau_p \exp(-H_b/kT)} \tag{3}$$

A rough estimate shows that the diffusion coefficient at the peak temperature calculated by eqn. (3) is about ten times that by eqn. (1). The calculated D_i values using eqn. (3) are also shown in Fig. 3 as crosses. It can be seen that they approach the extrapolated line more closely.

Trapping effects will result in a lower diffusivity in the low temperature region. This means that the extrapolation line in Fig. 3 would curve downward as the temperature decreases. If this is the case, the difference between the diffusion coefficients obtained from the two kinds of method would be further reduced.

4.2. Annealing process of the H peak

An ion probe analysis demonstrated that the H distribution in a 2179 austenitic stainless steel specimen 5 mm thick, charged in the same way as used in this work, is very homogeneous [7]. Therefore it is reasonable to consider the H distribution in the virgin IF specimens used in this work, *i.e.* just after charging, to be also homogeneous. Outgassing on annealing will give rise to variations in the H distribution in the specimens.

Considering the IF specimen as an infinitely long bar with rectangular section ($2a \times 2b$), H diffusion in it will be two dimensional and the concentration will be determined by

$$\frac{\partial C_H}{\partial t} = D\, \nabla^2 C_H \tag{4}$$

with the initial conditions

$$C_H(x, y, 0) = C_0 \tag{5}$$

where C_0 is the initial concentration of H in the specimen, and the boundary conditions

$$C_H(\pm b, y, t) = C_H(x, \pm a, t) = 0 \qquad t > 0 \tag{6}$$

The solution of the equation is

$$C_H = C_0 \Phi 1 \Phi 2 \tag{7}$$

where $\Phi 1$ and $\Phi 2$ are Gaussian error functions with different geometric parameters, which are functions of coordinates, diffusion coefficient and time. The H concentration of a definite point in the specimen depends only on a composite variable, $2(Dt)^{1/2}$, referred to as the average diffusion distance, which can be calculated according to the thermal history of the specimen including heating, cooling and isothermal hold stages. In the present case the average diffusion distance can be estimated by $2(\int D\, dt)^{1/2}$, with the results listed in Table 1. Figure 2 shows the H concentrations, normalized by C_0, along the x axis at $y = 0$ in a specimen subjected to different annealing treatments.

Since the shear stress in a rectangular section bar suffering twist deformation is non-homogeneous, the elastic strain energy of an elementary volume will depend on its position in the bar. However, the H peak height in an elementary volume is related to the local H concentration. The peak height is proportional to C_H for the H–substitutional atom model but to C_H^2 for the H–H pair model. Therefore the apparent IF of the specimen must be calculated through an integral operation.

Theoretically calculated annealing laws of the H peak are shown in Fig. 4, where Q_a^{-1} is the apparent H peak height in the specimen and Q_0^{-1} is the peak height for the virgin state. Curve 1 is for H–substitutional atom pairs, and curve 2 for H–H pairs. Obviously, the H peak will decay more quickly with annealing if the H–H pair mechanism operates. The experimental results taken from Table 1 are also plotted in Fig. 4, from which it can be concluded that the H peak in 2179 steel charged by the above gas method is probably produced by the H–substitutional atom pair mechanism.

The above conclusion draws some support from the small peak in the annealed specimen shown in Fig. 1. On comparison with the charged specimen, it can be seen that the ratio of the H concentrations is similar to the ratio of the H peak heights for the two specimens as expected from the H–substitutional atom model.

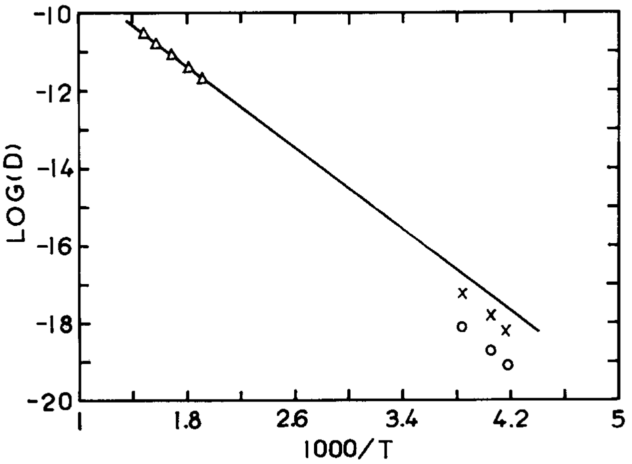

Fig. 3. Diffusion coefficients of H in 2179 steel: △, data from diffusion experiment [5]; ○, data from IF experiment using eqn. (1); ×, data from IF experiment using eqn. (3).

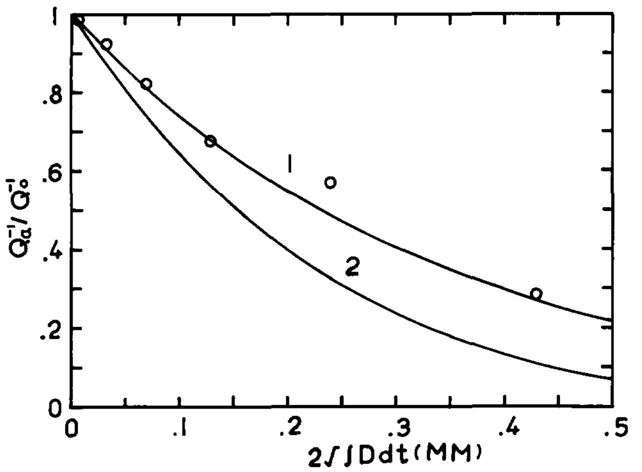

Fig. 4. Decay laws of the H peak in the specimen: curve 1, H–substitutional atom pair model; curve 2, H–H pair model; ○, experimental data.

5. Conclusions

(1) A relaxation peak has been observed in 2179 stainless steel, charged with H in a high pressure gas autoclave.

(2) The thermal activation parameters of the peak are different from those of H diffusion, with a slightly higher activation enthalpy and a much lower converted diffusion coefficient assuming single-atom reorientation. The results can be explained by reorientation of atom pairs in the steel.

(3) The annealing process of the peak is controlled by two-dimensional diffusion. Theoretical annealing curves for the H–H pair and H–substitutional atom pair models have been obtained. A comparison of the experimental results with the theoretical analysis indicates that the H peak in the steel is probably due to the H–substitutional atom pair model.

References

1 A.J. West and M.R. Louthan, *Metall. Trans. A, 13* (1982) 2049.

2 J.A. Peterson, R. Gibala and A.R. Troiano, *J. Iron Steel Inst., 207* (1969) 86.

3 S. Asano, M. Shibata and R. Tsunoda, *Scr. Metall., 14* (1980) 377.

4 A. Zielinski, *Acta Metall. Mater., 38* (1990) 2573.

5 Sun Xiukui and Xu Jian, *J. Chin. Soc. Corros. Prot., 7* (1987) 274.

6 R. Gibala and C.A. Wert, *Acta Metall., 14* (1966) 1095.

7 Ma Luming, Li Yiyi, Liu Shuwang and Chen Lian, *Acta Metall. (Chin.) B, 24* (1988) 274.