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Internal stresses in austenitic steels cathodically charged with hydrogen

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Hydrogen cathodic charging of austenitic stainless steels has been manifested by a reduction of the ductility under dynamic tensile stresses and by the appearance of nonductile fracture surfaces. The electrolytic charging process provides a huge hydrogen fugacity, and thus large amounts of hydrogen may be driven into the specimen. This process leads to the development of internal stresses, phase transition to α' and ϵ martensite, and intensive intergranular and transgranular cracking [1–6].

The purpose of this study is to find the reasons for the development of internal stresses as a result of cathodic charging of stainless steel and to correlate between the surface cracking and internal stresses.

The studies were carried out on a type 316 austenitic stainless steel. The samples were obtained in the form of 0.1 mm thick sheets and were solution annealed. The grain size, as measured by ASTM E-112 method, was of the 10.5 number ASTM, corresponding to the mean grain size of 9.4 μm. The samples were cathodically charged for 24 h at room temperature in an 1 N H_2SO_4 solution with 0.25 g per litre of $NaAsO_2$ added as a hydrogen recombination poison. A platinum counter-electrode and a current density of $50\,\mathrm{mA\,cm^{-2}}$ were used.

A conventional Philips diffractometer equipped with step-motor, programmer, and teletype printer was used for the X-ray diffraction study. The choice of the X-ray wavelength is of special importance. In diffraction with reflection (Bragg–Brentano) geometry, we actually obtain information only from the thin surface layer of the flat sample. The intensity I_t of rays scattered by the surface layer of thickness t is equal to [7]:

$$I_t/I_\infty = 1 - \exp\,[-2\mu t/(\sin\theta)] \qquad (1)$$

where I_∞ is the intensity of rays scattered by the infinitely thick sample, μ is the linear absorption coefficient of the material and θ is the Bragg angle. The thickness $t_{0\cdot 95}$, representing 95% of the total intensity of scattered rays, may be easily calculated from Equation 1 for various diffraction peaks and radiations. For 1 1 1 austenite peak and radiations Cu$K\alpha$, Co$K\alpha$, Cr$K\alpha$, and Mo$K\alpha$ we get values of $t_{0.95}$ equal to 2.6, 6.2, 8.7 and 8.7 μm, respectively. As was investigated in this work, the cracks after severe cathodic charging propagate inside the material to a depth approximately equal to the grain size (8 to 10 μm). Our purpose is to characterize the layer of this thickness. It is evident that the Cu$K\alpha$ radiation is inappropriate. Among the three remaining radiations, Co$K\alpha$ radiation reveals the fortunate combination of high intensity, angular resolution, and satisfactory depth of penetration. This radiation, therefore, was used in the present study.

The diffraction pattern of the stainless steel sample taken immediately after charging reveals the usual features of cathodic charging [1], i.e. shifting of austenite peaks up to the lower diffraction angles and the appearance of martensitic phases α' (bcc) and ϵ (hcp). The peak shift is the result of lattice expansion due to the interstitial intrusion of hydrogen. In our case centroid of 1 1 1 austenite peak is displaced by 1.15° of 2θ angle. This displacement to the linear lattice expansion is approximately 2%.

The second and no less interesting characteristic of the γ-phase, that has not attracted too much attention until now, is peak broadening. As taken immediately after charging, the diffraction peaks of austenite are much broader than the corresponding peaks in the uncharged sample (Fig. 1). In the uniform solid solution, the intensity of the diffraction peaks decreases due to local lattice distortion, but the peaks themselves remain sharp. The reason for peak broadening in our

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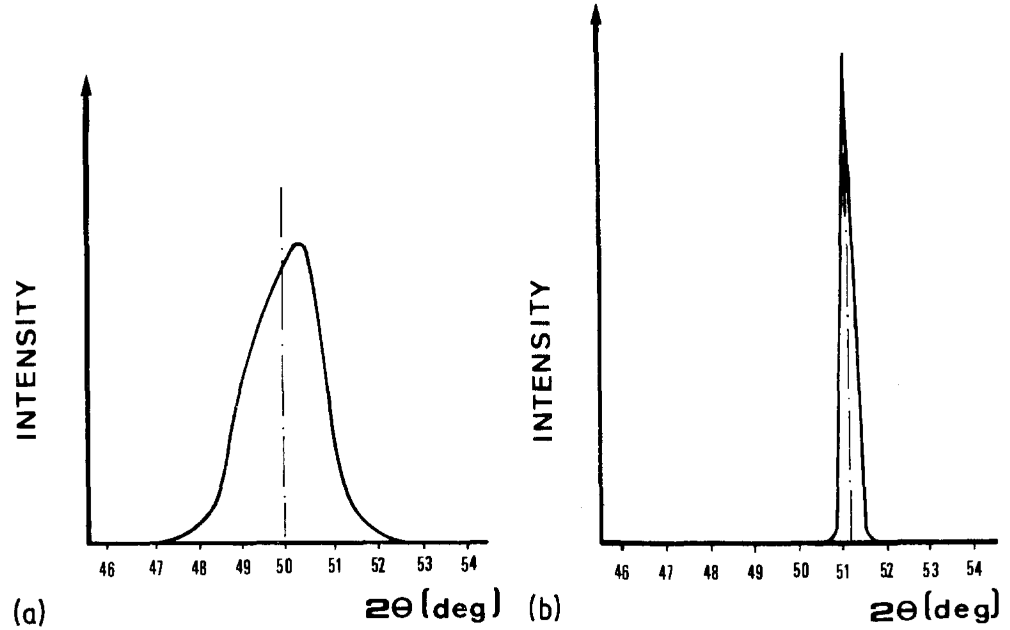

Figure 1 Diffraction peak 111 of austenite; (a) immediately after charging, (b) before charging.

case seems to be the formation of nonuniform solid solution of hydrogen in the austenite matrix. Indeed, both processes of hydrogen penetration during charging and hydrogen release during ageing are diffusion controlled, and large concentration gradients in the thin surface layer comparable with the depth of X-ray penetration are expected. The solid confirmation is found in the recent work of Atrens *et al.* [8]. Immediately after removing the sample from the charging cell, hydrogen concentration increases from zero on the surface up to a maximal value within the layer of 5 to 10 μm. Actually, the hydrogen concentration is nonuniform within a single grain. The nonuniform concentration of hydrogen results in nonuniform expansion of the material. The latter inevitably leads to the development of the internal stresses.

The situation is very similar to the nonuniform heating of the body where thermal stresses appear due to nonuniform expansion or contraction. The well developed theory of thermal stresses [9] is quite applicable in our case of nonuniform concentrations of the solid solution.

The following models may be regarded in order to estimate the magnitude of the stresses:

(a) One-grain model. As was shown elsewhere [8], intergrannular diffusion of hydrogen is much faster than transgranular diffusion. For the first approximation, a grain may be regarded as a sphere with hydrogen concentration increasing from the surface of the sphere to the centre during charging and in opposite direction during ageing.

(b) The multigrain model. This model takes into account the interaction between grains. The sample is represented by the two-dimensional sheet of similar rectangular grains (Fig. 2a). Distribution of hydrogen concentration is periodical (Fig. 2b). The maximum of the concentration corresponds either to the grain boundary (charging process) or to the centre of the grains (ageing process).

The radial stresses caused by nonuniform expansion of the sphere is given by [9]:

$$\sigma_r = \frac{2KE}{1-\nu}\left(\frac{1}{b^3}\int_0^b Cr^2\,\mathrm{d}r - \frac{1}{r^3}\int_0^r Cr^2\,\mathrm{d}r\right) \quad (2)$$

where E is Young's modulus, ν is Poisson's ratio, b is the radius of spherical grain, $K = \mathrm{d}\epsilon/\mathrm{d}C$, the equivalent of the linear expansion coefficient (K = constant if the Vegard's law is valid), ϵ is the relative deformation of the lattice, $C = C(r) - C_c$, where $C(r)$ is the concentration at the distance r from the centre, and C_c is the concentration at the centre of the sphere.

The whole formulation of σ_x and σ_y stresses in the multigrain model is also given in [9], but they are too cumbersome to be implemented here. The qualitative distribution of stresses is given in (Fig. 2c).

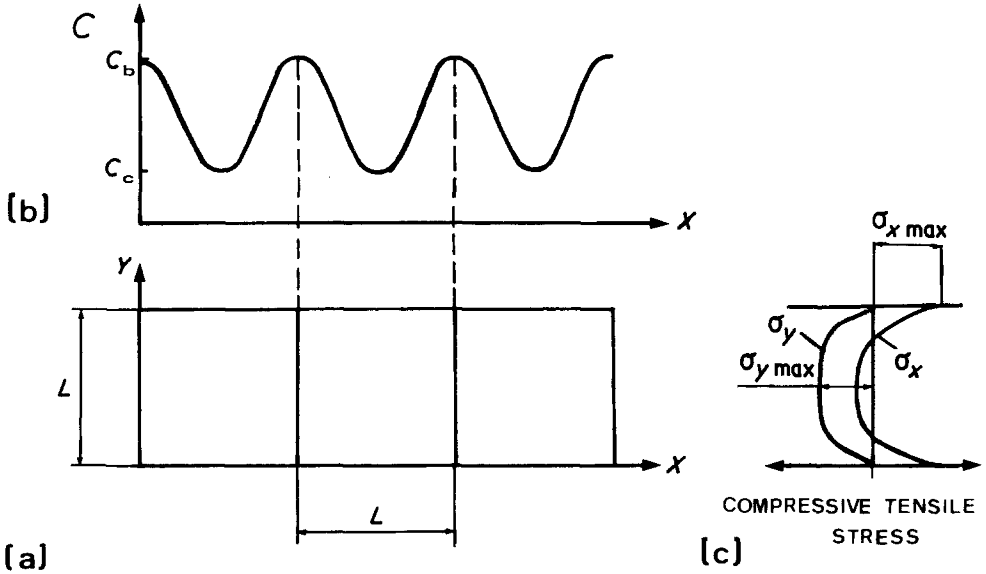

Figure 2 Multi-grain model. (a) Geometrical model, (b) distribution of hydrogen concentration, and (c) distribution of stresses along grain boundary.

Now we have to evaluate the distribution function $C(r)$ (or $C(x)$ in the second model) and the constant K in order to estimate the magnitude of the stresses. With regard to a spherical grain, Fick's laws lead to the following distribution of concentration:

$$[C_b - C(r)]/[C_b - C_c] = 1 - (r/b)^2 \quad (3)$$

where C_b and C_c are the hydrogen concentrations on the surface of the sphere and at its centre, respectively. The periodical distribution $C(x)$ in the second model may be represented by the simple cosine function (Fig. 2b):

$$C(x) = (C_b + C_c)/2 + [(C_b - C_c)/2] \cos 2\pi X/L \quad (4)$$

where L is the grain size. If ϵ_b and ϵ_c are the relative deformations of the lattice for the solid solutions with concentrations C_b and C_c, then

$$K = (\epsilon_b - \epsilon_c)/(C_b - C_c) = \Delta\epsilon/\Delta C \quad (5)$$

The quantity $\Delta\epsilon$ is determined by the diffraction peak width.

$$\Delta\epsilon = \Delta d/d = -(Ctg\theta\ \Delta 2\theta)/2 \quad (6)$$

where d is the mean interplanar distance, $\Delta 2\theta$ is the width of the diffraction peak. In order to estimate the maximum deformations and stresses we have to measure the width $\Delta 2\theta$ at the foot of the peak rather than at the half heights.

The 111 austenite peak was chosen as a master peak. Overlapping of a very weak 002 peak of hcp (ϵ) martensite does not interfere with our estimation. The width at the foot of the 111 austenite peak is $\Delta 2\theta \simeq 3°$ and $\Delta\epsilon = 5.4 \times 10^{-2}$ according to Equation 6. From Equations 2, 3, 5 and 6, using $E = 2 \times 10^{11}$ Pa and $\nu = 0.3$, we obtain the tensile stress in the centre of the sphere (the first model) $\sigma_r = 6 \times 10^9$ Pa. The similar value of tensile stress on the grain boundaries $\sigma_x = 5.2 \times 10^9$ Pa was obtained for the second model. The estimated internal stresses are much greater than the ultimate tensile strength of the 316 stainless steel (5×10^8 Pa).

The above estimation of the internal stresses was based on the Hook's law and may be regarded as an approximation. Nevertheless, the order of magnitude of these stresses confirm their significance.

These stresses induce two phenomena well known in the process of cathodic charging of stainless steel [1–3, 5]:

(a) Formation of intergranular and transgranular cracks.

(b) Stress-induced phase transition of austenite to α' and ϵ-martensites.

The estimation of the internal stresses performed in this work, though not precise, allows to explain, at least qualitatively, some major phenomena accompanied by the cathodic charging. The more precise estimation of the internal stresses should be based on the real distribution of hydrogen in the material. The latter may be obtained by the analysis of the diffraction peak profile, which is now in progress.

References

1. M. L. HOLZWORTH and M. R. LOUTHAN, *Corrosion* **24** (1968) 110.
2. C. L. BRIANT, *Met. Trans.* **10A** (1979) 181.
3. H. OKADA, Y. HOSOI and S. ABE, *Corrosion* **26** (1970) 183.
4. A. W. THOMPSON, *Mater. Sci. Eng.* **14** (1974) 253.
5. D. ELIEZER, "Hydrogen Effects in Metals", edited by A. W. Thompson and I. M. Bernstein (The Metallurgical Society of AIME, New York, 1981) p. 565.
6. E. MINKOVITZ and D. ELIEZER, *J. Mater. Sci.* **16** (1981) 2507.
7. H. P. KLUG and L. E. ALEXANDER, "X-ray Diffraction Procedures" (John Wiley, New York, 1974) p. 360.
8. A. ATRENS, J. J. BELLINA, N. F. FIORE and R. J. COYLE, in "Proceedings of the Symposium on the Metals Physics of Stainless Steels", Denver, Colorado, 1978 (TMS-AIME) p. 54.
9. S. P. TIMOSHENKO and J. N. GOODIER, "Theory of Elasticity" (McGraw-Hill, New York, 1970) p. 433.

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