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TEM study on the formation of microcracks in connection with α′-martensite

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Hydrogen induced martensite phase transformation in austenite stainless steels have been extensively studied with respect to the relative stability of the austenite γ(f c c) phase, which in fact, is characterized by its tendency to transform to martensite on cooling or during deformation. The effect of hydrogen on the γ-phase stability is that hydrogen decreases the γ-phase stability and may induce transformation of the γ-phase to α'- or ϵ-martensite [1–6]. It has been shown that most steels that form α'-martensite are quite susceptible to hydrogen cracking; however this issue has become controversial due to the fact that embrittlement took place when no martensite has been formed [7].

No detailed transmission electron microscope (TEM) observation of the role of α' b c c martensite in connection with crack propagation through the cathodic polarization process is available at present.

The purpose of this study is to report the results of a TEM analysis on the existence of an α'-martensite in front of the crack tip, caused by cathodic polarization in the absence of an externally applied stress. The possibility that embrittlement of "unstable" stainless steel which forms α'-martensite may be controlled by an autocatalytic process is also discussed.

The studies were carried out on a 304L-type austenitic stainless steel. The steel was of commercial grade, with the composition shown in Table I and was received in the form of sheets 0.2 mm thick.

All of the samples used in these experiments were first solution annealed for 1 h at 1100° C and then water-quenched. Specimens suitable for electron microscopy were then prepared by electrolytic polishing at 65 V in a Tenupol polishing cell using 30 cm^3 perchloric acid, 300 cm^3 methanol and 520 cm^3 butanol solution at −18° C.

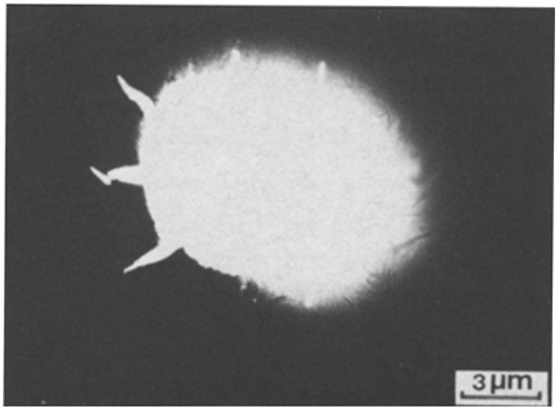

Figure 1 TEM micrograph in the "Mesh-Image" magnification showing cracks which were formed by cathodic charging in the thicker region of the specimen of 304L stainless steel.

After a TEM examination to ensure that no deformation structure had been induced during the thinning process, the specimens were cathodically charged with hydrogen and then were investigated again by TEM. The hydrogen charging was performed at room temperature in the absence of an external force in a 1 N H_2SO_4 solution with 0.25 g dm^{-3} l^{-1} of $NaAsO_2$ added as a hydrogen recombination poison. A platinum counter-electrode and a current density of 100 mA cm^{-2} were used. The charging time was 5 min. TEM analysis was carried out in a JEOL-200B electron microscope operating at 150 kV.

A TEM micrograph in the "Mesh-Image" magnification shows transgranular cracks in the

TABLE I Chemical composition of 304L stainless steel (wt %)

Cr	Ni	Mn	C	N	Mo	Si	Cu	Co	P	S
18.68	9.02	1.80	0.025	0.035	0.07	0.64	0.06	0.16	0.02	0.004

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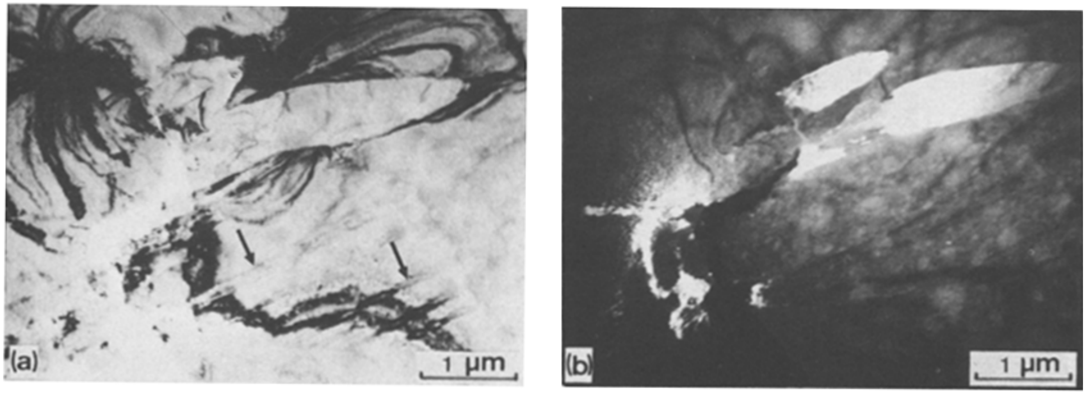

Figure 2 TEM micrograph of the 304L stainless steel which was cathodically charged with hydrogen (enlargement of the marked crack in Fig. 1) showing (a) bright field, and (b) dark field micrographs. Note the location of α'-martensite in front of the crack tip.

thicker region of the charged specimen and is shown in Fig. 1. The bright field electron micrograph of the marked crack in Fig. 1 is shown in Fig. 2a. The selected area diffraction (SAD) pattern at the crack tip is represented in Fig. 3a and its schematic diagram is given in Fig. 3b. These findings have revealed Debye ring reflections from a fine-grained bcc α'-martensite and a fcc γ-matrix. The existence of hcp ϵ-martensite, which was also formed by the cathodic polarization process, is indicated by the arrows in Fig. 2a. The dark field technique in the 200 α'-bcc ring intensities shows that this phase is located in front of the crack tip (Fig. 2b). The bcc phase and the surrounding α'–γ interface showed a completely fine-grained polycrystalline structure while the SAD pattern taken at about 0.5 μm from the α'–γ interface showed single crystal fcc γ-phase

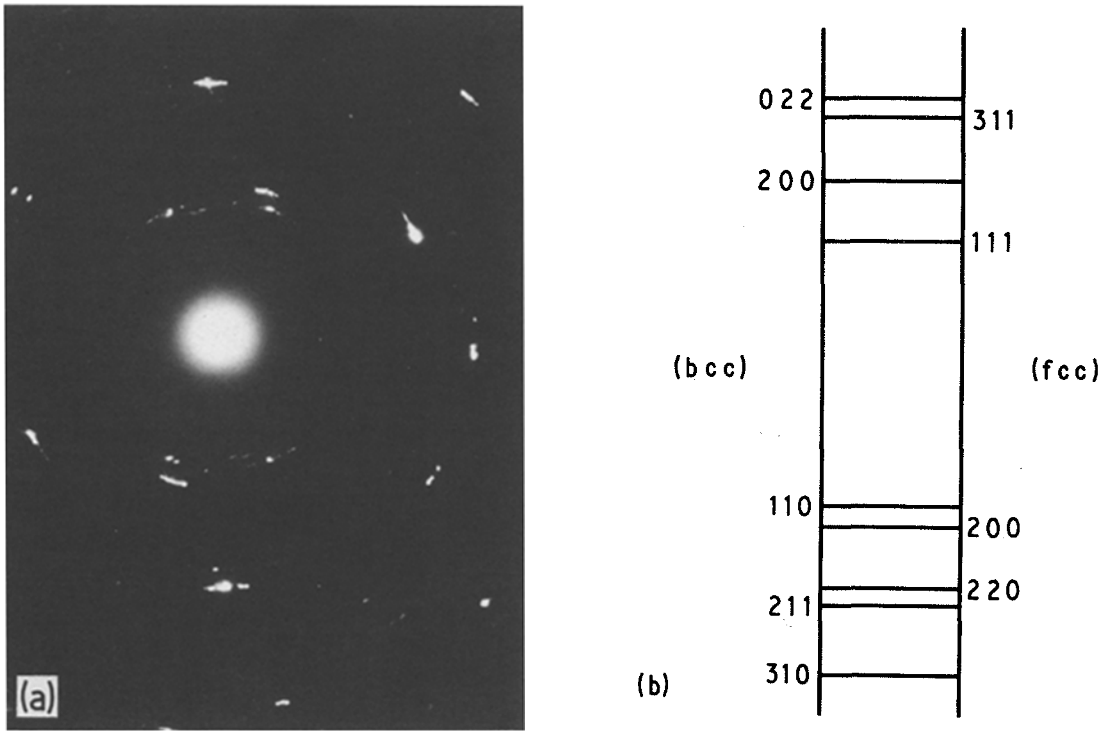

Figure 3 (a) Electron diffraction pattern, taken at the crack tip of the marked crack in Fig. 1. (b) Schematic diagram of electron diffraction pattern shown in (a).

indicating that the formation of the polycrystalline structure for the γ-phase was highly localized to that area. Further charging to the same specimen in the above conditions, and re-examination by TEM studies have revealed crack propagation through the martensite phase in front of the crack tip. Thus it can be concluded that hydrogen, which ingresses the austenite matrix, in the thicker region of the specimen of "unstable" steel that forms α'-martensite, can have the form of an autocatalytic process. Crack initiation occurs through triaxial stresses caused by hydrogen penetration and evidently followed by the formation of α' b c c martensite when hydrogen egresses the specimen. The existence of the b c c phase in front of the crack tip escalates hydrogen entry and crack propagation through the embrittled martensite phase which in turn aids martensite formation.

References

1. M. L. HOLZWORTH, *Corrosion* **25** (1969), 107.
2. M. L. HOLZWORTH and M. R. LOUTHAN, *ibid.* **24** (1968) 110.
3. D. ELIEZER, "Hydrogen Effects in Metals" edited by I. M. Bernstein and A. W. Thompson (The Metallurgical Society of AIME, New York, 1981) p. 565.
4. E. MINKOVITZ and D. ELIEZER, *J. Mater. Sci.* **16** (1981), 2507.
5. E. MINKOVITZ, M. TALIANKER and D. ELIEZER, *ibid.* **16** (1981) 3506.
6. N. NARITA and H. K. BIRNBAUM, *Scripta Metall.* **14** (1980), 1355.
7. C. L. BRIANT, "Hydrogen Effects in Metals" edited by I. M. Bernstein and A. W. Thompson (The Metallurgical Society of AIME, New York, 1981) p. 527.

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