TEM investigation of hydrogen induced ϵ-hcp-martensite in 316L-type stainless steel

The austenitic stainless steels are known to transform to α'(bcc)- and ϵ-(hcp)-martensite during plastic deformation at temperatures below the critical M_D temperature [1, 2]. The relative stability of the austenitic γ-(fcc)-phase 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 [3–7]. It is not known, however, whether this martensitic transformation is a cause or a result of the hydrogen embrittlement.

The purpose of this communication is to report our results of a transmission electron microscopy (TEM) study of hydrogen-induced ϵ-martensite in 316L-type stainless steel, in the absence of any externally applied stresses.

The studies were carried out on a 316L-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.

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 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 1 h. TEM analysis was carried out in a JEOL-200B electron microscope operating at 150 kV.

The bright-field electron micrograph of the charged specimen is shown in Fig. 1a. Thin plates of hydrogen induced ϵ-(hcp)-martensite are clearly seen. These plates appear in a heavily faulted region, as shown in Fig. 2.

Fig. 1b represents a dark-field electron micrograph of the ϵ-martensitic plates, taken from reflection of ϵ-martensite. The selected-area diffraction pattern is shown in Fig. 3a and its schematic diagram is given in Fig. 3b. Using the electron

TABLE I Chemical composition of 316L-type stainless steel in wt%

Cr	Ni	Mn	C	N	Mo	Si	Cu	Co	P	S
17.65	11.10	1.80	0.026	0.061	2.08	0.50	0.21	0.35	0.03	0.009

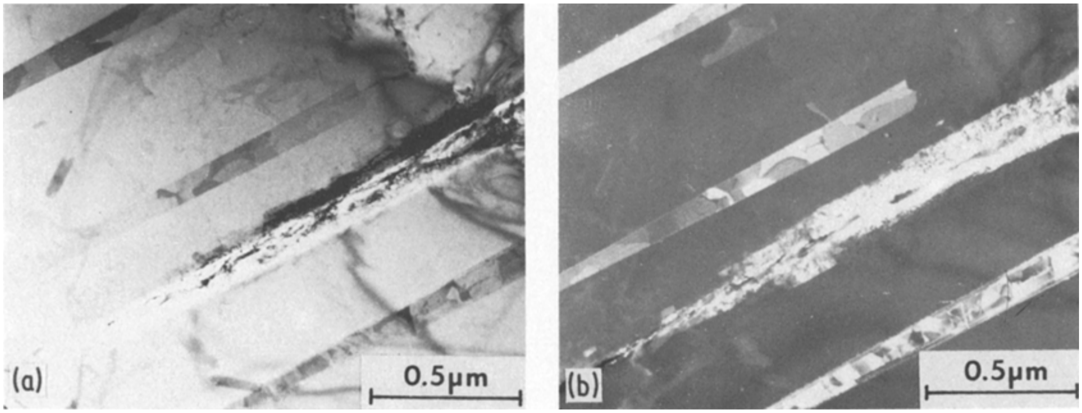

Figure 1 TEM micrographs of the 316L specimen, which was cathodically charged with hydrogen. The plates of ϵ-martensite can be seen. (a) Bright-field and (b) dark-field, taken in the ϵ-reflection.

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diffraction pattern shown in Fig. 3, the superimposed stereographic projection of ϵ-plates and γ-matrix was constructed (Fig. 3c). The zones of γ-reflections and ϵ-reflections are represented by solid arcs. The analysis of this projection leads to the following orientation relationships between ϵ-martensite and the γ-matrix

$$(1\,1\,1)_\gamma \parallel (0002)_\epsilon$$

$$[01\bar{1}]_\gamma \parallel [11\bar{2}0]_\epsilon.$$

This result demonstrates the appearance of hydrogen-induced ϵ-phase in 316L-type steel. It is consistent with other results previously reported for strain-induced ϵ-phase in 310 and 304 steels [8–10].

No evidence of the appearance of α'-martensitic phase after hydrogen charging was found by electron microscopy. However, it has been shown by us [6] that hydrogen-induced cracking takes place after hydrogen charging.

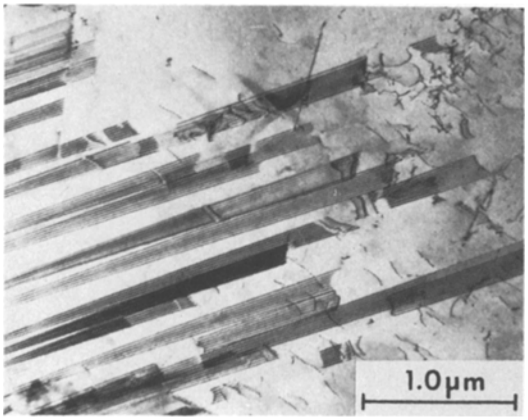


Figure 2 Bright-field electron micrograph of the same specimen as in Fig. 1, which shows a heavily faulted region caused by hydrogen charging.

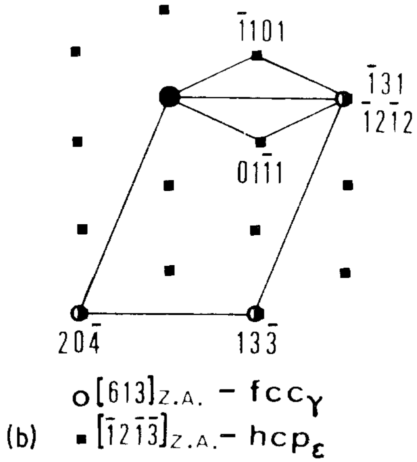
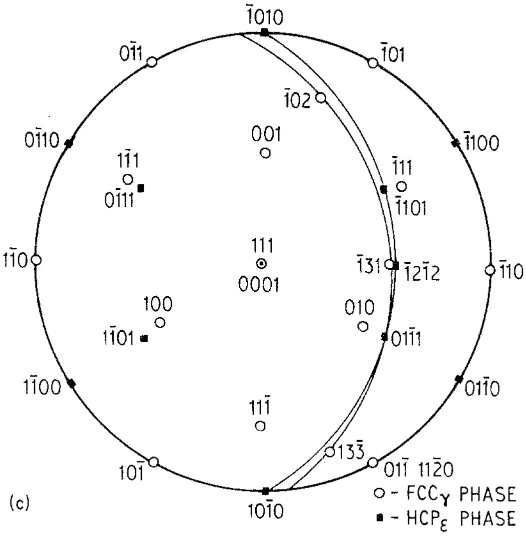


Figure 3 (a) Electron diffraction pattern taken from the area shown in Fig. 1; (b) schematic diagram of electron diffraction pattern shown in (a) and (c) superimposed stereographic projection of γ-austenite/ϵ-martensite. The γ/ϵ orientation relationships are: $(1\,1\,1)_\gamma \parallel (0\,0\,0\,2)_\epsilon$ and $[0\,1\,\bar{1}]_\gamma \parallel [1\,1\,\bar{2}\,0]_\epsilon$.



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Self-diffusion of Sn and Te in $Pb_{0.8}Sn_{0.2}Te$ at a temperature of 600° C

$Pb_{1-x}Sn_xTe$ is a material of considerable interest for use in tunable laser diodes [1] and despite much work on material and device preparation very little information is available on self- and impurity-diffusion, although such data are important in the control of material and device parameters. Simirskii *et al.* [2] have described the results of radio-tracer Sn self-diffusion measurements (using Sn 113) in single-crystal samples with $x = 0.1$ and 0.2 at temperatures between 600 and 750° C, measured as a function of non-stoichiometry on the Te-rich side. A sealed silica ampoule arrangement requiring three separate temperature zones was used. However, according to Brebrick [3] a two-zone system is sufficient to define the degree of non-stoichiometry with the sample in the high-temperature zone and the temperature of the cooler zone used to control the non-stoichiometry. We have used such a two-zone system to measure the self-diffusivities of Sn 113 and Te 127 m in $Pb_{0.8}Sn_{0.2}Te$ at 600° C, over a range of Te partial pressures.

The diffusion samples were obtained from a single-crystal boule grown by a vapour-phase vertical Bridgman technique [1]. Samples with masses of approximately 1.5×10^{-4} kg and thicknesses of about 1 mm were used. Dislocation densities were typically about 10^8 m^{-2}. All samples were annealed for 10 days at 600° C in sealed silica ampoules with excess $Pb_{0.8}Sn_{0.2}Te$ prior to the self-diffusion experiments. Sample composition was confirmed by an electron beam microprobe. The principal faces of the samples were made parallel by lapping followed by a chemical polish using 4 vol% Br–HBr. All the radio-tracer diffusion experiments were carried out in sealed silica ampoules which had been acid etched (HF/HNO_3 etch) and vacuum baked at 1100° C prior to being loaded and sealed-off. The internal volume of the ampoule was approximately 6×10^{-6} m^3. The diffusion source for each of the Sn 113 diffusions was 10^{-3} kg of granular $Pb_{0.8}Sn_{0.2}Te$ containing 1.2 MBq Sn 113. The Sn 113 source was held at the same temperature as the diffusion sample (600° C). The Te partial pressure, P_{Te_2}, was controlled by adding approximately 10^{-5} kg Te to the ampoule and varying the temperature (< 600° C) of the tip of the ampoule remote from the sample and source. In the Te 127 m diffusions the same procedures were followed except that 13.3 kPa of argon was admitted to the ampoule before it was sealed-off and the diffusion source was now also provided by the Te pellet used to control P_{Te_2}: the ampoule therefore contained only the diffusion sample and Te pellet (about 3 MBq Te 127 m). The argon pressure was needed to avoid surface deterioration of the sample during the diffusion anneal. For all the experiments the anneal period was 36 h. Radio-tracer diffusion profiles were obtained by standard radio-assay methods. All the profiles

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