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Journal of Alloys and Compounds 293–295 (1999) 356–360

Journal of ALLOYS AND COMPOUNDS

Hydrogen surface effects in ferritic stainless steels

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Abstract

The surface microstructure of ferritic chromium stainless steels subjected to hydrogen charging was investigated. Mono- and polycrystalline samples after severe cathodic hydrogen charging were examined using optical, scanning and transmission electron microscopy. The H-induced multiple twinning effect was observed, which manifested itself in the formation of grain oriented needles with a pronounced surface relief, similar to those appearing in the quasi-martensitic transformation. This was accompanied by a heavy increase in the dislocation density and microhardness, intensification of microcrack formation, a strong refinement of the ferrite grains and a radiation-like damage to the structure of the surface layer several microns thick. These results indicate that the surface zone is much more saturated with hydrogen, which is ''implanted'' into the steel during cathodic charging, than the bulk.

Keywords: Ferritic stainless steels; Hydrogen; Surface effects; Microstructure; Radiation-like damage

1. Introduction

Ferritic stainless steels undergo embrittlement when subjected to hydrogen charging in aqueous solutions, but the mechanism of ductility loss has not yet been explained satisfactorily [1–3]. In our earlier studies, we observed a strong grain refinement and the formation of needle-shaped microtwins in the surface layer of H-charged ferritic stainless steels [4–7]. These needles were grain oriented and showed a pronounced surface relief indicating a transformation associated with a volume change. The H-induced needles and martensitic plates have many common features, such as the shape, surface relief, microtwin structure with the presence of a midrib and an increased dislocation density [6]. The observed strong H-induced microstructural changes in ferritic chromium steels cannot only be attributed to the effect of hydrogen present in the form of a solid solution, since the solubility of hydrogen in bcc ferrite is very poor. To find a complete explanation, further investigations into this effect are necessary. The present study was aimed at investigating more thoroughly the H-induced microstructural changes that take place in ferritic stainless steels.

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2. Materials and experimental procedure

Single crystal specimens of [111], [110] and [100] orientations were prepared from ferritic stainless steel containing 16.0% Cr (laboratory melt) and polycrystalline specimens were prepared from two commercial ferritic stainless steels containing 17.0% Cr (OH17T) and 19.3% Cr (00H19T). After cutting, the specimens were first mechanically polished and then electropolished. Hydrogen was introduced by cathodic charging at 0.1 A/cm^2 at room temperature for 15 min to 2 h using a platinum anode in a 1 N H_2SO_4 solution with 1 mg of SeO_2 per 1 dm^3 as a hydrogen recombination poison. TEM specimens were prepared by preliminary electrolytic thinning without perforation, then cathodically charged and thinned from one side by electrochemical polishing until perforation. The H-charged surface was left unaffected by the preparation procedure so that the H-induced microstructural changes in the sample surface zones could be examined. The microstructure examinations were performed using optical, scanning and transmission electron microscopes (JEOL JEM 100B).

The microhardness of the hydrogen-charged samples, gradually polished, was measured in such a way as to obtain results through the depth of the sample.

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PII: S0925-8388(99)00401-6

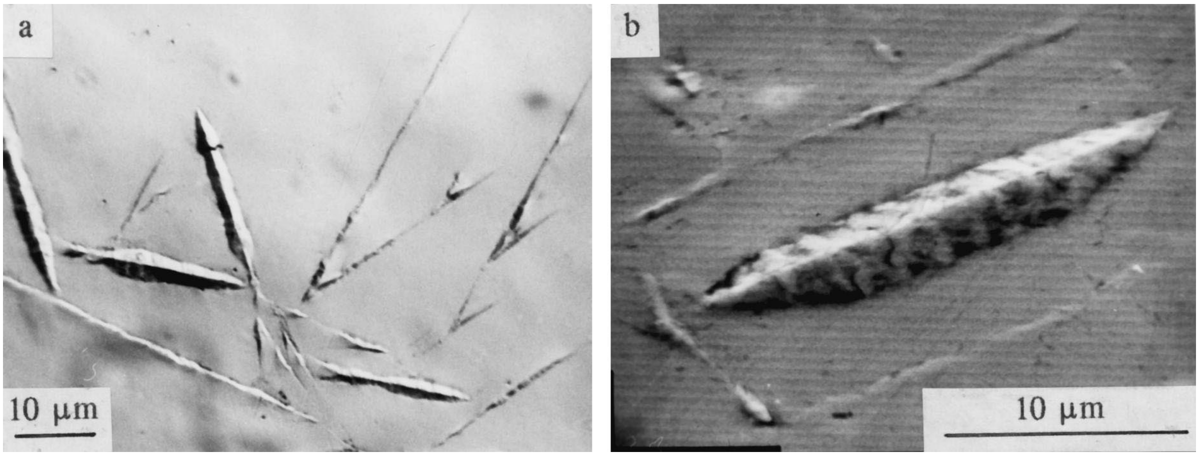

Fig. 1. Hydrogen-induced twins in the form of needles and deformation bands forming the surface relief of a ferritic steel single crystal (16% Cr). (a) Matrix orientation [111], magn. 1000×; (b) matrix orientation [100], magn. 3200×.

3. Results and discussion

Fig. 1a shows the H-induced twins, in the form of needles visible on the surface of a single crystal specimen of the [111] orientation, and the deformation bands. Both the needles and the bands show a pronounced surface relief. Fig. 1b is obtained for a higher magnification of a single needle with microcracks and a characteristic midrib formed in a [100] oriented specimen. The pattern formed by the deformation bands on the surface of this specimen differs from that in Fig. 1a. Electrochemical etching of the H-charged polycrystalline specimens revealed many defects present in the surface layer, which manifested themselves by numerous pits visible on the surface. The pits either formed rows along the twinned needles or were distributed randomly between them (Fig. 2a). Figs. 2b,c show a cross-section of a hydrogen-charged specimen, mounted in a resin and then electrolytically etched. Hydrogen-induced blisters can be seen along the grain boundaries and the surface attack at the specimen edge. For comparison, Fig. 2d shows an uncharged specimen prepared in the same way. It is worth noticing that the edge of this specimen remains smooth after etching. This fact indicates that the hydrogen-charged surface zone is much more susceptible to etching than the bulk of the material. The heavily defected surface zone of the hydrogen-affected ferritic steel can be removed by electropolishing.

Fig. 3a shows the dislocations present in the ferritic steel before H-charging. Their density is approximately 9×10^{16} cm^{-3}. In the same steel the density of twins is nearly 1.6×10^{16} cm^{-3} (Fig. 3b) after H-charging. The fact that the orders of magnitude of the two densities are similar suggests that the dislocations may be the heterogeneous nucleation sites of H-induced needle twins.

In monocrystalline hydrogen-charged 16% Cr ferritic steel, several morphologically different forms of twins were observed. There are symmetrical double-twins with a midrib and microtwins, triple twins showing an ideal twin orientation relationship with the matrix, multiple microtwins, and twin lamellae with a short range strain field concentrated in the vicinity of the twin boundary [8]. The multiple twinning effect was detected on the {112} planes in the [110] orientation of the matrix. Symmetrical double-twins with a midrib, microtwins and microcracks (Fig. 3b) are typical for the materials under study. The hydrogen embrittlement due to the many microcracks visible in Fig. 3b as the white lines that run along the midrib and within the twin segments (composed of microtwins) is evident.

The hydrogen charging introduced a localized disorder into the original crystalline structure of the surface zone. This is manifested by the significant strain–stress contrast visible in the dark field micrograph, with a matrix operated reflection, in the form of many small oval and curved contours of the extinction lines seen on both sides of the dark needle (Fig. 3c). Probably, the energy of the H atoms evolved ''in statu nascendi'' is far above the thermal energy of the formation of the interstitial solution.

The irradiation-like effect observed in the surface zone (whose microstructure is similar to that formed due to irradiation [9]) of hydrogen-charged 19% Cr steel can be seen in the area free of twins in the ferritic matrix. A cellular dislocation structure (similar to the structure of the displacement cascade occurring in irradiated steel) and regular voids associated with very fine hydrogen-induced precipitates are shown in Fig. 3d. This is the most striking result of the present study. The density of the voids is near to 2.9×10^{16} cm^{-3} and the dislocation density within the same area is approximately 2.4×10^{18} cm^{-3}. This means that the hydrogen charging increases the dislocation density by two orders of magnitude, which should affect the mechanical properties, such as, for example, the hardness of the surface zone. And, indeed, the microhardness measurements made from the surface of H-charged samples through their depth have shown that, in the surface zone, the hardness is increased (Fig. 4) with respect to that in the bulk.

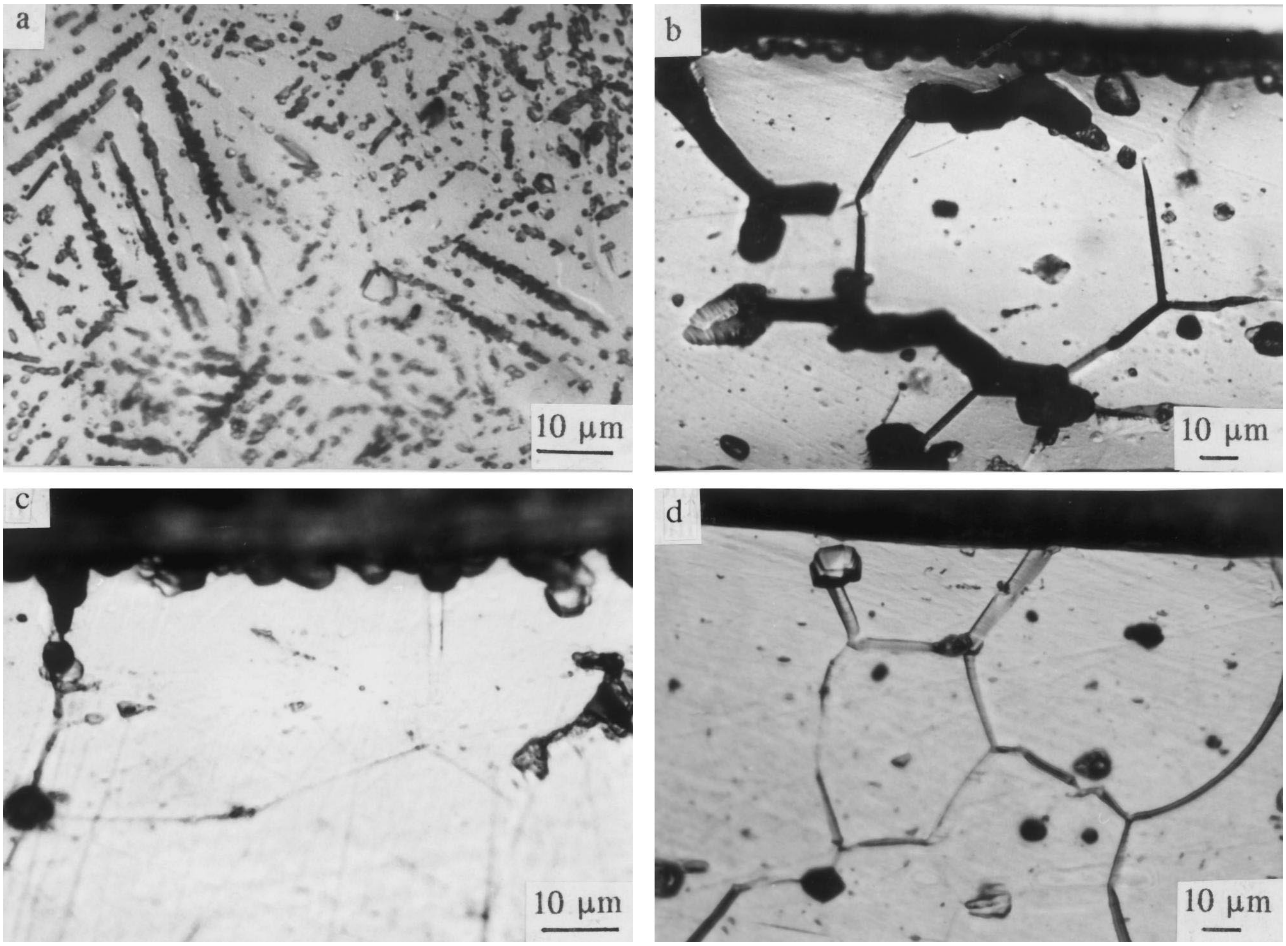

Fig. 2. Polycrystalline specimens of ferritic steel (19% Cr). (a) Hydrogen-charged and electrochemically etched surface of the sample, magn.1000×. (b) Hydrogen-charged, cross-sectioned sample, mounted in a resin and electrochemically etched, magn. 500×. (c) As in (b), magn. 1000×. Notice a strong attack at the edge. (d) A cross-section of an uncharged specimen, mounted in a resin and electrochemically etched, magn. 500×. Notice the smooth edge of the sample.

It is difficult to explain the observed unusually strong structural changes in ferritic stainless steels taking into account only hydrogen in solid solution in the bcc lattice of the α-phase, because hydrogen solubility in ferrite is very low.

The observed effects require a higher hydrogen concentration than that in the solid solution. Such conditions can be attained only on the charged surface. It is quite probable that the surface zone is much more saturated with hydrogen, which is ''implanted'' into the steel during cathodic charging, and indeed the needle precipitates and other microstructural changes do form at the surface only and not in the bulk. The higher concentration of hydrogen inside the needles makes their volume larger which thus results in a surface relief and plastic accommodation of the surrounding material. Some volume change of the needles is perhaps also the reason of the microcrack formation inside them. Microcracks can grow during hydrogen desorption from the material. Desorption of hydrogen starts immediately when charging is stopped and runs very fast because of the very high diffusion coefficient of hydrogen in the bcc lattice of ferrite. As a result of hydrogen desorption the needles shrink and microcracks appear inside them. Microcracks formation also infers an embrittlement of the hydrogen-charged materials.

4. Conclusions

Surface effects induced by cathodic hydrogen charging into ferritic stainless steels have been examined using optical, scanning and transmission electron microscopes.

The main results are as follows:

- Hydrogen charging brings about the formation of grain oriented needle-shaped twins in the surface layer with a pronounced surface relief inferring a transition connected with volume change, similarly as in the quasi-martensitic transformation.
- Inside the needles many microcracks are formed indicating that hydrogen entry makes these steels embrittled.

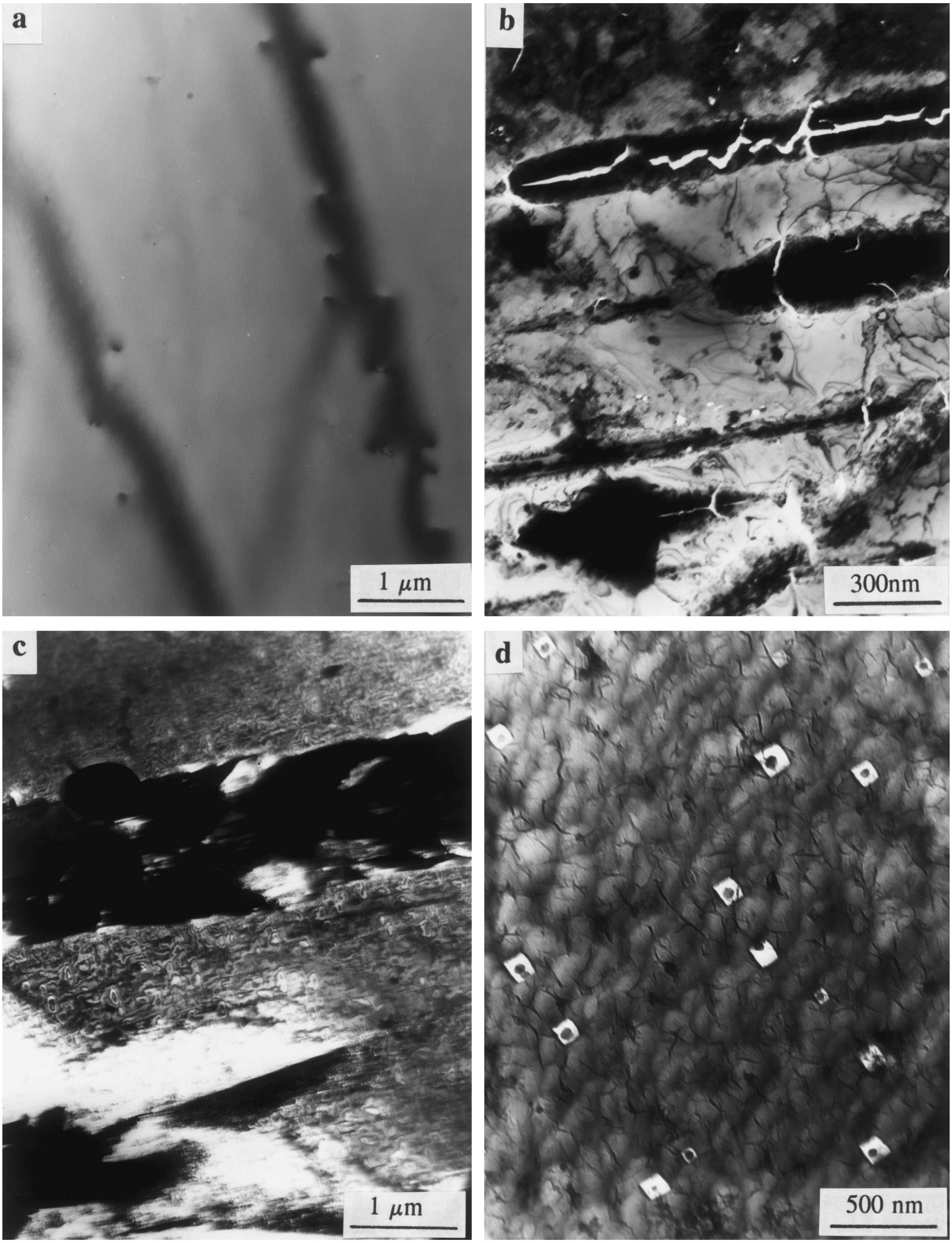

Fig. 3. (a) Dislocations in a [110] orientation single crystal of 16% Cr stainless steel before hydrogen charging. (b) Regular array of double twins (with microcracks) and twin lamella with a high density of dislocations in the vicinity of the twin interface in a hydrogen-charged single crystal of the [110] orientation. (c) Dark field TEM micrograph, with a matrix operated reflection, of a hydrogen-charged [110] orientation single crystal. Significant strain–stress contrast is visible in the extinction contours on both sides of the dark twin needle. (d) TEM microstructure of hydrogen-charged 19% Cr ferritic steel. Note the irradiation-like effects on the surface: cellular dislocation structure and voids associated with precipitates.

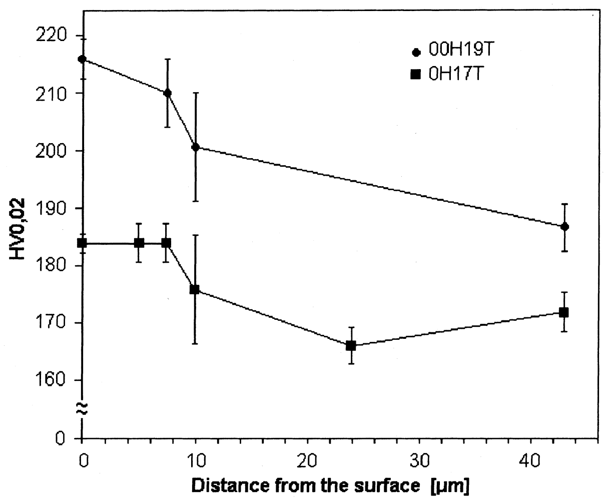

Fig. 4. Change of microhardness from the surface of the hydrogen-charged specimens of two ferritic stainless steels through their depth.

- The needle precipitates are built of rows of microtwins divided by a midrib similar to those of martensite.
- Strong ferrite grain refinement in the surface layer of hydrogen-charged specimens was observed.
- The microstructure changes are accompanied by a substantial increase in the dislocation density and microhardness.
- In the surface zone an irradiation-like effect is observed, which is manifested by regular voids associated with very fine hydrogen-induced precipitates, by a cellular dislocation structure (which is similar to the displacement cascade occurring in irradiated steel) and by significant strain–stress contrast in the form of many small oval and curved contours of the extinction lines.
- These results indicate that the surface zone is much more saturated (or even ''implanted'') with hydrogen during cathodic charging than the bulk.

Acknowledgements

This work was supported by the Committee for Scientific Research, Poland, under grant No. 3P407 034 05. The authors would like to thank Mr S. Jezierski for the very precise preparation of the difficult TEM samples.

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