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HYDROGEN INDUCED MARTENSITIC TRANSFORMATION AND TWIN FORMATION IN STAINLESS STEELS

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Abstract - Hydrogen charging induces the formation of an hcp phase, ε and α'-martensites in a metastable austenitic stainless steel, and the formation of microtwins and a braid-like dislocation structure in a ferritic stainless steel. Microcracks are initiated along α' lath boundaries and ε/α' boundaries in the former, and inside of microtwins in the latter.

I. INTRODUCTION

It has been reported that hydrogen charging to metastable austenitic stainless steels induces martensitic transformations(1-8). Holtzworth et al.(1) found ε- and α'-martensite and an unidentified fcc phase in a hydrogen charged 304L stainless steel. The fcc phase is considered to be a hydride(6). Kamachi et al.(5) has reported that rain cloud like ε' is formed after generation of a large number of dislocations and stacking faults, and that it decomposes into ε and α' during prolonged charging time. However, little is known about the initial stage of the formation of the fcc phase and ε'. Ferritic stainless steels lose ductility in hydrogen atmosphere, although no transformation occurs in them. The mechanism of ductility loss has not been known yet. In the present study, attempts have been made to clarify the initial stage of microstructural changes which are induced by hydrogen charging in thin foils of an austenitic and a ferritic stainless steels.

II. EXPERIMENTAL PROCEDURES

The steels used were a low C austenitic stainless steel (0.02%C, 18.1%C, 8.1%Ni) and a low C ferritic stainless steel (0.004%C, 19.1%Cr), which were solution treated for 30 min at 1100°C and quenched into water. Thin foil specimens, which were prepared by electrolytic thinning using an electrolyte composed of glacial acetic acid and 10% perchloric acid, were cathodically charged with hydrogen in a solution of 1N-H2SO4 containing 250mg/l of Na3AsO3 with a current density of 0.25 A/cm² at 20°C. A part of this foils were ion-polished prior to hydrogen charging in order to remove surface films. Observations of microstructures were carried out within 10 min after hydrogen charging. In situ observations of the structural changes during heating were also carried out. The electron microscope used was HU-1000D operated at 1 million volt.

III. RESULTS AND DISCUSSION

1. Hydrogen-induced Transformations in a Low Carbon 18%Cr-8%Ni Steel

The microstructure of the steel before hydrogen charging is shown in Photo. 1, where only a few unextended dislocations are observed. Hydrogen charging for 1 sec induces remarkable change in the microstructure. Small plates resembling stacking faults are formed mainly near the foil edge (Photo.2(a)). Majority of them lie on a (111)γ plane. On the other hand, in thicker parts of a foil, small triangular platelets having edges parallel to <110>γ directions are formed. They also lie on a (111)γ plane and tend to grow into stacking fault-like plates (Photo.2(b)).
All of the diffraction patterns obtained from the stacking fault-like and the triangular phase can be indexed as a hcp phase having lattice constants slightly larger than those of c-martensite. The diffraction pattern shown in Photo.2(c) contains reflections from planes belonging to [110], and [011] hcp zones. The orientation relationship between γ and the hcp phase seems to be close to the Shoji-Nishiyama's relationship(9). Elongated intensity distribution of the reciprocal lattice points of the hcp phase as well as local distortion of the foil may allow reflections from the planes belonging to the [011] zone, which is 11.4° apart from [0223] that should be parallel to [110], when the Shoji-Nishiyama's relationship is exactly obeyed.

Heterogeneous distribution of the triangular hcp platelets suggests that preferential nucleation may occur at defective parts of thin oxide films which may have been formed during electrolytic thinning, since ion polishing of foil surfaces prior to hydrogen charging brings about quite homogeneous distribution of the platelets. A few stacking faults that are occasionally observed may be formed by dissociation of dislocations due to decrease in stacking fault energy by hydrogen absorption. Thus, there may be no direct relation between development of stacking faults and the formation of the hcp phase. The hcp phase is stable at room temperature and they are retained even after aging for more than 400 h.

Photo.3 shows dense formation of the hcp phase in a nearly (001) oriented γ matrix after hydrogen charging for 3 sec. The relatively weak (200) and (200) spots of γ are surrounded by 4 spots of the hcp phase. They can be indexed as (1101) and (1102) belonging to [1011] and [2021] zones of the hcp phase, which are about 8° and 10°, respectively, apart from [4043] that should be parallel to [001]γ. The hcp platelets have strain fields around them. Within accuracy of electron diffraction, the lattice constants of the hcp phase (a=2.60Å, c=4.25Å) seem to be larger than those of c-martensite (a=2.53Å, c=4.13Å). However, it is not clear whether it is a hcp hydride or hydrogen containing c-martensite.
With increasing charging time, the hcp platelets extend along (111)$_{\gamma}$ planes and overlap each other. As the result, details of microstructure are lost as shown in Photo.4(a). Diffraction pattern includes a slightly distorted net belonging to [110] zone of the hcp phase and a pair of spots (indicated by arrows) which are considered as (200) reflections of a fcc phase with $a=3.75\text{Å}$. This implies the presence of a fcc hydride(1) or $\gamma$ phase which is expanded by hydrogen. Both of the hcp and the expanded fcc phase are stable, and they persist up to 500°C during heating in the electron microscope. When the foil is heated at 600°C, the hcp phase disappears leaving a large number of dislocations, and a diffraction pattern of [110] zone of normal $\gamma$ (unexpanded) is obtained (Photo.4(b)).

Photo.3 Dense formation of the hcp precipitates after 3 sec charging

Photo.4 (a) Hcp phase including an fcc phase with expanded lattice constants (15 sec charging), and (b) dislocations left after heating at 600°C in the electron microscope

Photo.5 (a) $\epsilon$-martensite formed in the hcp phase (after 30 sec charging), and (b) large plate-like $\epsilon$-martensite (after 60 sec charging)
After charging for 30 sec, ε-martensite appears in regions where many hcp platelets are already formed (Photo.5(a)). Diffraction pattern indicates that the newly formed ε-martensite (solid line) has a normal (unexpanded) hcp structure. Occasionally large plate-like ε-martensite is formed as can be seen in Photo.5(b).

Two types of α' martensite crystals are observed after hydrogen charging for more than 30 sec. Majority of them have lath-like morphology as shown in Photo.6(a). This type of α' is observed in regions where many hcp plates are formed, and it will be of strain-induced type. Another type of α' has a lenticular shape, and is formed in large plate-like ε-martensite (Photo.6(b)). It will be of stress-assisted type.

When charging time exceeds 100 sec, microcracks are initiated along α' lath boundaries and ε/α' boundaries (Photo.7). As the formation of α' proceeds, solubility of hydrogen in a thin foil will be decreases and excess hydrogen will segregate to these boundaries to form cracks. Hosoya et al.(10) have reported that straight cracks are propagated along large plate-like ε-martensite in thin foils of a 0.08%C-18%Cr-8%Ni steel. However, since the steel used in the present study transforms to α' more easily because of its very low carbon content, plate-like ε will be devided into finer blocks by α'. This will result in occurrence of a large number of small microcracks instead of a long straight cracks.

2. Hydrogen Induced Twin Formation in a Low C-19%Cr Steel

Hydrogen charging to thin foils of the ferritic stainless steel brings about generation of a large number of fairly straight dislocations and peculiar braid-like structures as shown in Photo.8(a). Dislocations seem to be of screw type since their directions are usually parallel to the projections of <111>ε directions on the foil plane. The braids look like to be arrays of precipitates along straight lines at an initial stage of formation (Photo.8(b)). In this case the plane of the foil is (111) and the braids A, B, C, and D are parallel to [121], [112], [211], and [541], respectively. Thus, they might seem to lie on {321} planes or to be parallel to
<211> directions. However, these braids are not necessarily straight, but they usually change their directions as they grow. Trace analysis of the straight parts of braids in 10 differently oriented grains (more than 50 areas) has failed to determine definite crystallographic directions or planes on which they might lie. Ion polishing of foil surfaces prior to hydrogen charging does not bring about any appreciable change in the morphology of braids.

A diffraction pattern taken from the central part of Photo.8(c) includes three sets of twin-related \{110\}_\alpha spots, and the dark field images obtained from twin spots (indicated by the arrows) demonstrate the presence of microtwins along braids, particularly at intersections of two braids (Photos.8(d),(e)). Thus, it is likely that hydrogen charging may facilitate local formation of microtwins probably due to decrease in stacking fault energy, although detailed mechanism and preferential sites of such microtwin formation has not been known. Formation of microtwins will increase local strain, and punched out dislocations will be tangled to form braids.

As the charging time is increased, the size of microtwins and the width of braids become larger. In addition, many microcracks are formed in microtwins as shown in Photo.9(a). The plane of these microcracks is usually parallel to \{110\}. Further hydrogen charging results in high density of dislocations all over the foil.

Photo. 8 (a),(b) and (c) Braid-like structures induced by hydrogen charging for 5 sec, (d) and (e) dark field images showing microtwins, and (f) diffraction pattern obtained from (c)
Thus, the microstructure resembling that observed in heavily cold worked materials is obtained (Photo.9(b)). It contains many microcracks which are generated inside of microtwins and are propagated mainly along \{110\}_1 planes. Crack formation around grain boundary carbides is also observed. Thus, it is likely that ductility loss in ferritic stainless steels due to hydrogen charging may be caused by formation of microcracks in hydrogen-induced microtwins.

IV. CONCLUSIONS

Microstructural changes induced by hydrogen charging in thin foils of an austenitic and a ferritic stainless steel have been observed using a 1 MeV HVEM. The main results will be summarized as follows;

(1) In a low C-18%Cr-8%Ni steel, a short time hydrogen charging brings about the formation of small platelets of a hcp phase, which has lattice constants slightly larger than those of \(\varepsilon\)-martensite. As the charging time is increased they grow on \{111\}_h planes with an orientation relationship with the matrix which is the same as or very close to the Shoji-Nishiyama’s relationship. Further charging leads to the formation of \(\varepsilon\)- and \(\alpha’\)-martensite in regions where a large number of the hcp plates are formed. Occasionally lenticular \(\alpha’\)-martensite is formed in large plate-like \(\varepsilon\). Hydrogen charging for longer than 100 sec results in initiation of microcracks at \(\alpha’\) lath boundaries and \(\varepsilon/\alpha’\) boundaries.

(2) In a low C-19%Cr steel, hydrogen charging brings about the formation of microtwins and braid-like structures which may be formed by tangling of dislocations punched out from microtwins. The braids are neither parallel to any definite directions nor they lie on any definite planes. Further hydrogen charging results in the growth of microtwins, inside of which microcracks are formed, and they are propagated mainly along \{110\}_1.

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(1) Holtzworth, M.L. and M.R. Louthan, Jr., Corrosion, 24(1968), 110.