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Enhancement of hydrogen solubility in α-iron by coherent precipitates

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Abstract

Hydrogen solubility of some internal nitrided Fe–Ti and Fe–V alloys were studied. The alloys were subjected to internal nitriding by a plasma treatment, and strong lattice distortion was introduced by precipitation of internal nitrides. Hydrogen solubilities of the internal nitrided alloys were measured by an electrochemical method, and it was found that hydrogen solubility of internal nitrided alloys increased more than 10 times larger than non-nitrided materials. The increase in solubility was thought to be attributed to the large lattice distortion and its magnitude was fairly well in proportion to initial concentration of the nitride-forming element (Ti or V).

Keywords: Hydrogen solubility; Nitrided alloys; Lattice distortion

1. Introduction

Recently, it has been reported that hydrogenation characteristics of alloys were strongly influenced by their physical or mechanical properties as well as by the alloy chemical compositions. For example, lattice distortion and phase structures of alloys sometimes strongly affect their storage capacities and cycle lives [1,2].

Unlike the case of controlling chemical properties, the physical or mechanical properties are difficult to control and evaluate. Lattice distortion can be introduced into the materials by plastic deformation followed by some appropriate heat treatments, however, its amount is not so easily controlled.

Some kinds of coherent precipitates are known to introduce a larger amount of lattice distortion than plastic deformation, and the lattice distortion can be controlled to some extent by changing the amount of precipitates. In the present work, we have attempted to introduce a tetragonal distortion into α-iron by dispersing small and coherent nitride precipitates (VN and TiN) in the iron matrix, and studied the influence of the lattice distortion caused by the precipitates on hydrogen solubility of the iron matrix.

2. Experimental details

Alloy ingots of about 20 g were prepared by arc melting in the water-cooled crucible under an argon atmosphere using high-purity metals. The chemical compositions of the alloys prepared (before nitriding treatment) are $Fe_{99.5}Ti_{0.5}$, $Fe_{99}Ti_1$, $Fe_{99}V_1$, $Fe_{97}V_3$ and $Fe_{95}V_5$. In order to achieve uniformity in chemical composition, the alloy ingots were remelted several times.

The ingots were then cold-rolled and made into plates 200 μm thick. After being annealed in vacuum at 1173 K for 3 hours, the plates were cut into smaller plates, the areas of which were about 5 mm × 30 mm.

The alloy plates were subjected to plasma-nitriding process at 823 K for 12 hours. The plasma-nitriding conditions are listed in Table 1. As has been reported [3–6], a kind of internal nitrided layer, where only the solute element forms small and coherent nitride precipitates in the α-iron matrix, is formed by nitriding of such dilute iron alloys. Takada et al. [7] reported that the thickness of the internal nitrided layer increase in proportion to $\sqrt{t}$. The nitriding time employed in the present work is sufficiently long to grow the internal nitrided layer throughout the specimen.

The electrochemical hydrogenation of the internal nitrided alloys were carried out in an open cell, using about

Table 1
Plasma nitriding condition

Nitriding temperature	823 K
Total pressure	1 torr
Gas composition	$H_2 : N_2 = 3 : 1$
Sample current density	0.5 mA
Glow-voltage	400 V

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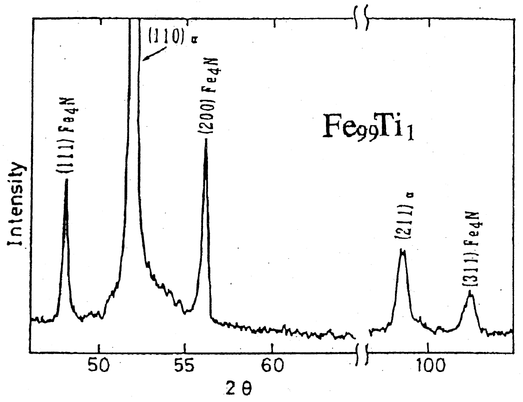

Fig. 1. X-ray diffraction profiles of the internal nitrided layers of $Fe_{99}V_1$ alloy.

100 mg of internal nitrided alloy electrode (plate), 6 M KOH electrolyte, Hg/HgO reference electrode and $Ni(OH)_2$/NiOOH counter electrode. The electrochemical hydrogen storage capacities were measured by discharging at constant current densities after full charging at 10 mA for 12 hours followed by resting for 3 hours. Charge/discharge currents were controlled by use of a conventional galvanostat (Hokuto Denkoh, HA-151). The lattice structures were determined by X-ray diffraction with Co–Kα radiation.

3. Results and discussion

3.1. Internal nitrided layer

Fig. 1 and 2 show the x-ray diffraction profiles of the internal nitrided $Fe_{99}Ti_1$ and $Fe_{95}V_5$ alloys, respectively. The (110) reflection of the iron matrix is broadened and the peak positions are shifted to the left hand side. For the vanadium containing alloy, the (110) peak tended to split into two peaks. These facts suggest that the iron matrix of the internal nitrided layer is partially compressed and partially expanded, and on the whole, the iron matrix is distorted into a tetragonal structure. The lattice spacing of the (110) plane in the internal nitrided layer for each specimen is calculated from the diffraction angles by using the Bragg's relationship, and the values are summarized in Table 2 together with their lattice distortion, ϵ. The magnitude of ϵ increased almost proportionally with increasing the initial concentrations of the nitride-forming elements.

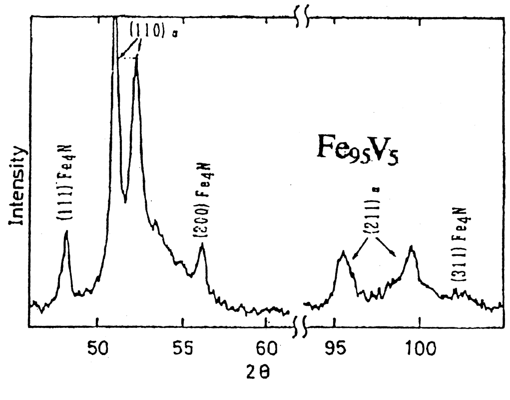

Fig. 2. X-ray diffraction profiles of the internal nitrided layers of $Fe_{95}V_5$ alloy.

Table 2
The spacings of 110 lattice plane and its distortion[a]

Alloy	$d_{110-\mathrm{IN}}$	ϵ (%)
α-iron	2.0266	–
$Fe_{99.5}Ti_{0.5}$	2.0302	0.178
$Fe_{99}Ti_1$	2.0422	0.276
$Fe_{99}V_1$	2.0368	0.503
$Fe_{97}V_3$	2.0514	1.224
$Fe_{95}V_5$	2.0776	2.517

[a] $\epsilon = d_{100-\mathrm{IN}} - d_{100-\alpha}$; where $d_{100-\mathrm{IN}}$ = (100) spacing of nitrided alloy; $d_{100-\alpha}$ = (100) spacing of pure iron.

It has been reported that titanium nitride (TiN) had precipitated coherently in the iron matrix [3,4], having a Baker-Nutting's (B–N) relationship with the matrix. In such a case, the nitride particles are too small to generate strong reflection peaks in the XRD profile. In the present work, no peaks from alloy nitride (VN or TiN) were found in the XRD profile for each specimen. This suggests that the size of nitride precipitates obtained in the present work is very small and the precipitates are well coherent with the iron matrix.

3.2. Discharge capacities

The internal nitrided alloy electrodes could be electrochemically hydrogenated and were rechargeable. Fig. 3 shows discharge curves of the nitrided and non-nitrided $Fe_{95}V_5$ alloy electrodes. The internal nitrided $Fe_{95}V_5$ alloy

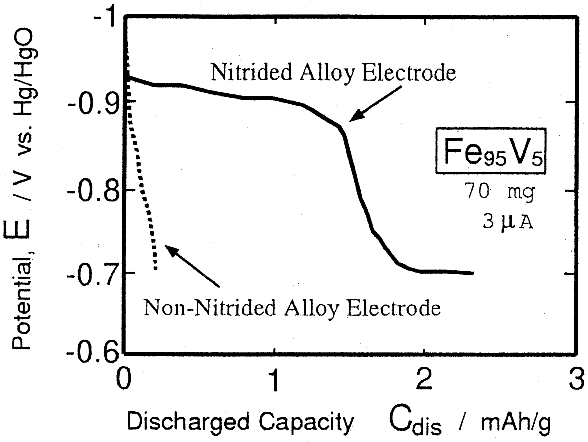

Fig. 3. Discharge curves of nitrided and non-nitrided $Fe_{95}V_5$ alloy electrodes.

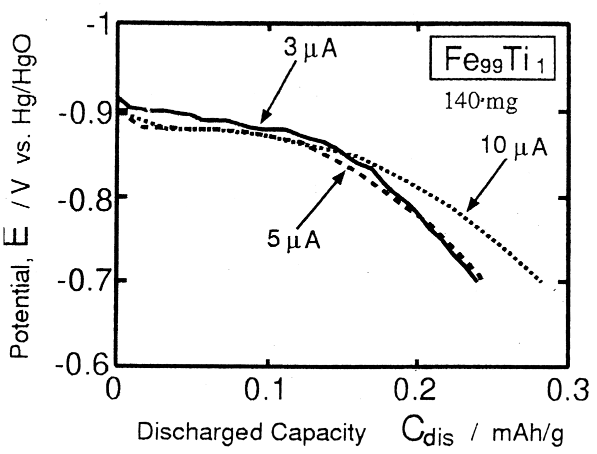

Fig. 4. Discharge curves of nitrided $Fe_{99}V_1$ alloy electrodes. Discharge currents; 3, 5, and 10 μA / alloy 140 mg.

had a discharge capacity about 2.33 mAh/g (4×10^{-3} in H/M), which was more than one order greater than that of non-nitrided alloy electrode. Fig. 4 shows the discharge curves of internal nitrided $Fe_{99}Ti_1$ alloy electrode with varying discharge currents between 2.5 μA and 10 μA for the alloy electrode of 140 mg. This shows that the discharge overpotential is not so large and the discharge capacities of the alloy electrode do not so strongly depend on the discharge current densities under such discharge current densities. The discharge capacities of nitrided alloy electrodes are summarized in Fig. 5. They increased with increasing initial concentration of the nitride forming element (Ti or V).

Considering the lattice structure, hydrogen atoms can hardly occupy the sites in the nitride precipitates, because the size of interstitial sites in the nitride (NaCl type) are too small to accommodate hydrogen atoms. Therefore, the hydrogen atoms must be dissolved into the iron matrix. Jack et al. [8] reported that the iron lattice distorted by coherent precipitates can dissolve more nitrogen atoms than precipitate-free iron lattice. The "excess" nitrogen atoms are thought to be trapped at the surface of precipitates in the iron matrix, because the iron lattice just at the surface of the coherent precipitates is expanded by the lattice misfit and the nitrogen atoms can be trapped more stably in the expanded interstitial sites than in distortion-free interstices. Therefore, hydrogen atoms are thought to be trapped around the nitride precipitates, because hydrogen atoms also occupy the interstitial sites.

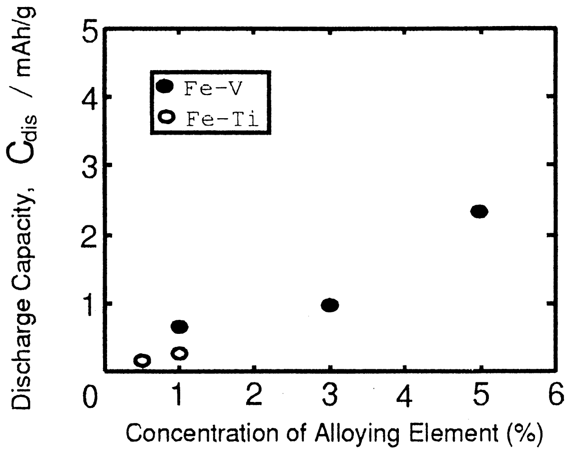

Fig. 5. Concentration of alloying element vs. discharge capacity.

4. Conclusion

Based on the study of the electrochemical hydrogen-storage capacities of internal nitrided iron alloys, the following results were obtained:

1. The hydrogen solubility of α-iron is strongly increased by the existence of small and coherent nitride precipitates.
2. The amount of increase in hydrogen solubility is almost proportional to initial concentration of the nitride forming elements.

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