

Heat Treatment for the Stabilization of Hydrogen and Vacancies in Electrodeposited Ni-Fe Alloy Films

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In an effort to realize the long-term stability of the magnetostrictive property of electrodeposited Ni-Fe alloy films, heat treatments needed for eliminating the possible effect of hydrogen and hydrogen-induced vacancies have been investigated, mainly by use of thermal desorption spectroscopy. While metal-atom vacancies begin to move only above ~500 K, hydrogen atoms can undergo slow motion and concomitant changes of state at room temperature, and are therefore believed to be a major cause of the long-term drift of the magnetism. Hydrogen atoms dissolved on regular interstitial sites can be completely removed by high-frequency pulse heating to 668 K, and those trapped by vacancies with relatively low binding energies by additional heat treatments to 453 K for over 1 h. This combination of heat treatments was found to reduce substantially the change of state of hydrogen during subsequent aging tests (383 K for 400 h), and proved to be effective for ensuring the long-term stability of magnetostrictive Ni-Fe film sensors. [doi:10.2320/matertrans.MRA2008199]

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1. Introduction

A number of methods have been adopted for the dynamical detection of loads/torques acting on structural components of high rigidity. However, these methods depend invariably on some device to amplify the loads/torques by introducing a section of reduced rigidity in the structure. Although this is usually deemed indispensable for making the loads/torques measurable in the form of amplified strains or macroscopic displacements, it is certainly more desirable to have some technique that allows measurements of the loads/torques directly without sacrificing the rigidity of the structure.

We have been investigating this problem for the last years, and found that a sufficient sensitivity for measuring loads/torques could be achieved by using a magnetostrictive sensor composed of electrodeposited Ni-Fe alloy films. By detecting impedance changes caused by strains in the films, such a sensor could measure the loads/torques acting on the substrate material with sensitivities equivalent to other existing methods. It turned out, however, that such sensors, as deposited, undergo gradual changes in their performance at room temperature, and therefore require some treatment for assuring their long-term stability.

In this paper, we attempt to identify and eliminate the origin of this temporal variation, by focusing attention on the behaviors of hydrogen and hydrogen-induced vacancies introduced in the course of electrodeposition.

When hydrogen is dissolved in metals, the thermal equilibrium concentration of metal-atom vacancies increases dramatically.¹⁻³⁾ This phenomenon, called superabundant vacancy (SAV) formation, occurs because the formation energy of a vacancy is reduced by trapping hydrogen atoms. The most stable structure of metal-hydrogen alloys thus

becomes a defect structure containing a large number of vacancy-hydrogen clusters.¹⁻⁸⁾

Effects of SAV formation are twofold: First, the enhancement of vacancy concentration leads to the enhancement of metal-atom diffusion. The diffusivity of metal atoms can be increased by many orders of magnitude (in some cases by some tens of orders of magnitude).⁹⁻¹⁵⁾ Second, hydrogen and vacancies well in excess of their thermal equilibrium concentration in ordinary states can exist in the form of vacancy-hydrogen clusters.

Up to now, most experiments on SAV formation have been performed by observing the process of their introduction at high temperatures and high hydrogen pressures. However, there are limited cases where SAVs were observed in electrodeposited metals, Cu, Ni,¹⁶⁾ Cr¹⁷⁾ and Ni-Fe alloys.¹⁸⁾ In electrodeposition, hydrogen atoms and vacancies are deposited simultaneously with metal atoms. The excess voltage during electrodeposition allows to accommodate a large amount of hydrogen and vacancy-hydrogen clusters in metals. On removal of the excess voltage, however, most of these hydrogen atoms are desorbed, leaving only those trapped by vacancies. Some of these vacancy-hydrogen clusters are very stable. In the case of electrolytic Cu and Ni, for example, vacancy-hydrogen clusters of concentration $\sim 10^{-4}$ were found to be retained after more than 10 years at room temperature.¹⁶⁾ In the case of Ni-Fe alloys, hydrogen atoms weakly trapped by vacancies were desorbed gradually over several days at room temperature, whereas those deeply trapped by vacancies and voids remained stable.¹⁸⁾

These observations suggest strongly that hydrogen and/or vacancy-hydrogen clusters should be a primary cause of the temporal variation of the magnetostrictive properties of the film. As hydrogen atoms and vacancies are the sources of lattice distortion, it may well be anticipated that any changes of their state, including their number and distribution, should affect the magnetostrictive properties.

This paper describes how we characterized the behaviors of hydrogen and vacancies in electrodeposited Ni-Fe films,

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and subsequently, how we succeeded in devising a stabilization heat treatment for controlling their state of existence, effective for the practical use of the films as a load/torque sensor.

The paper is organized as follows: Starting with a brief description of the characterization of electrodeposited films, including their composition and structure, we elucidate the temporal variation of the state of hydrogen after electrodeposition, examine its underlying mechanism of gradual detrapping from hydrogen-induced vacancies, and finally describe a recipe of heat treatments we devised for eliminating the effect of hydrogen on magnetostrictive properties of the film.

This paper is based on our two previous papers published in the Journal of Japan Institute of Metals (in Japanese).^{18,19)}

2. Thermal Desorption Spectroscopy (TDS) of Electrodeposited Films

2.1 Specimens

Specimens were Ni₆₄Fe₃₆ alloy films electrodeposited on a carburized chromium-molybdenum steel shaft of 20 mm in diameter, and peeled off subsequently. They were prepared by rapid electrodeposition at a high current density using Watt's bath to which ferrous sulfate had been added. The conditions of electrodeposition are given in Table 1. A vigorous stirring of the bath allowed the formation of a film, 40 μm thick, in 4 min with excellent uniformity and reproducibility. The cathode current efficiency was 89–90%. Determination of the nickel concentration by titration using an ethylenediaminetetraacetic acid (EDTA) standard solution showed a variation of less than 1 at% (63–64 at%) between the specimens.

Figure 1 shows the results of mass spectrometry of gases (H₂⁺ and CO⁺) thermally desorbed from the specimen. A major component was H₂⁺, released at 400–700 K and above 1200 K. CO⁺ was desorbed at 1070–1100 K. Note sharp desorption features of H₂⁺ at 670 K and CO⁺ at 1070–1100 K, in distinction to other broader peaks. Ascription of the 1070–1100 K peak to CO⁺ rather than N₂⁺ (both having the same mass number 28) is based on the observation of minute quantities of C⁺ and O⁺ desorbed in the same temperature range.

The structure of the films was examined by X-ray diffraction using MAX80, a high-temperature, high-pressure X-ray diffraction apparatus installed at a synchrotron

Table 1 Bath composition and plating condition for the electrodeposition of Ni₆₄Fe₃₆ alloy films.

Bath composition	NiSO ₄ ·6H ₂ O	0.77 mol/l
	NiCl ₂ ·6H ₂ O	0.25 mol/l
	FeSO ₄ ·7H ₂ O	0.10 mol/l
	Carboxylate	20 g/l
	H ₃ BO ₃	45 g/l
	Saccharin group	3 ml/l
Plating conditions	pH	3.0
	Temperature	333 K
	Current density	5400 A/m ²
	Substrate	Steel (SCM)

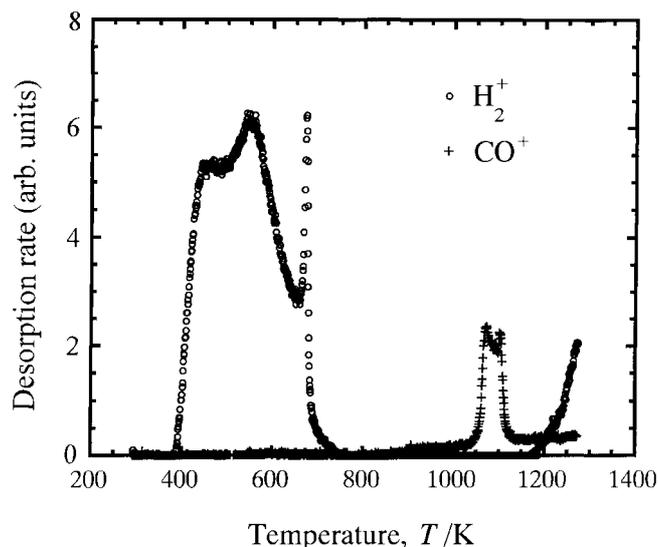


Fig. 1 Mass-spectrometry of thermally desorbed H₂⁺ and CO⁺ from an electroplated Ni₆₄Fe₃₆ alloy film. Measured 456 h after plating. Comparison of the relative magnitude of H₂⁺ and CO⁺ peaks is not meaningful.

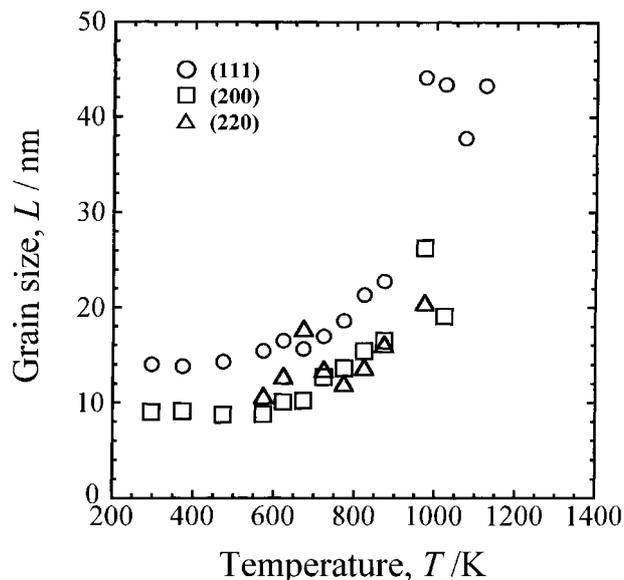


Fig. 2 Temperature dependence of the grain size of an electroplated Ni₆₄Fe₃₆ alloy film during heating under 5 GPa and 1053 K.

radiation facility of High Energy Accelerator Research Organization (KEK) in Tsukuba.²⁰⁾ The film was filed into a 400-mesh powder, and diluted 5 times in volume with a BN powder to reduce X-ray absorption, and subsequently formed into pellets of 1 mm in diameter.

First, the temperature-dependence of X-ray diffraction patterns was measured at a pressure of 5 GPa. The results showed that while the crystal structure was always face-centered cubic, the diffraction peaks were broad at room temperature, and became increasingly less broad as temperature was increased. Then, the temperature dependence of average grain size was extracted using Scherrer's formula, with results shown in Fig. 2. Initially, the film is composed of very fine grains of approximately 10 nm in diameter. A grain growth starts from 600 K, and proceeds rapidly at 700 K and above.

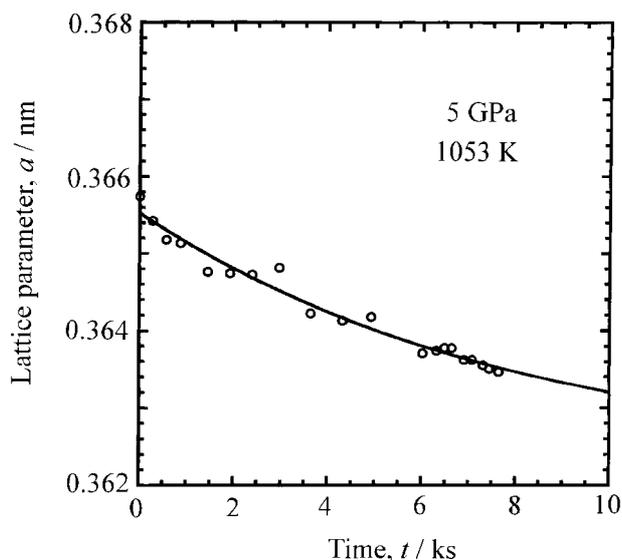


Fig. 3 Temporal variation of the lattice parameter of electroplated $\text{Ni}_{64}\text{Fe}_{36}$ alloy films under a hydrogen pressure of 5 GPa and 1053 K.

Next, in order to examine possible vacancy formation, X-ray diffraction was observed under a hydrogen pressure of 5 GPa at an elevated temperature of 1053 K. Details of high hydrogen-pressure experiments are described elsewhere.²⁾ Figure 3 shows the variation of the lattice parameter over long holding times. The lattice contraction, occurring over several ksecs, is a clear indication of the introduction of a large number of vacancies.¹⁻³⁾

2.2 TDS measurements

In thermal desorption measurements, a specimen (~ 10 mg) was placed in a vacuum chamber, sealed after evacuation to 10^{-4} Pa, and subsequent pressure increase was measured by a Pirani gauge during heating of the specimen at a fixed rate (5 K/min). The system was calibrated by Ta-H alloys of known composition, and the maximum sensitivity attained was 10^{-8} mol H_2 . Thermal desorption spectra were obtained by numerical differentiation. Generally, the desorption temperature is shifted upwards with increasing heating rates, due to finite diffusion time across the specimen, but this effect is small enough at the present heating rate for the film specimens of 40 μm thick.

Figure 4 shows the thermal desorption spectra measured at different times, between 8 and 2887 h, after electrodeposition. Hydrogen was desorbed in several stages, and the height of the desorption peaks at lower temperatures decreased as time elapsed, indicating that the amount of hydrogen retained decreased in time. The desorption peaks are designated as P_0 - P_5 from low temperatures upwards, and the temperatures of these peaks are summarized in Table 2. (The sharp peak at 1100 K is due to CO^+ desorption, and is therefore excluded from the table.) There is an indication that another desorption peak (P_6) exists at still higher temperatures (> 1270 K).

To help identifying the origin of these desorption peaks, TDS measurements were also made on specimens prepared under high temperature and high hydrogen pressure. Figure 5 shows a thermal desorption spectrum of an electrodeposited film heat-treated at 1165 K for 10 h at a hydrogen pressure of

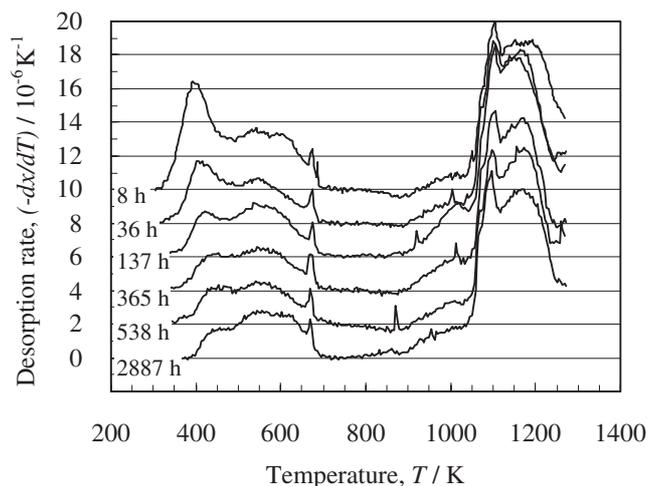


Fig. 4 Temporal variation of the thermal desorption spectra of hydrogen after electrodeposition of $\text{Ni}_{64}\text{Fe}_{36}$ alloy films. Each curve is shifted by one digit for the sake of clarity.

Table 2 Desorption peak temperatures observed in electroplated $\text{Ni}_{64}\text{Fe}_{36}$ alloy films.

Peak	Peak temperature (K)		
	As-plated*	As-plated**	Heat-treated***
P_0	395	—	385
P_1	—	440	—
P_2	~ 560	560	590
P_3	670	670	—
P_4	~ 980	~ 960	—
P_5	1170	1170	1210
P_6	> 1270	> 1270	> 1270

*Measured 8 h after plating.

**Measured 365 h after plating.

***Hydrogen pressure 3 GPa, 1165 K for 10 h.

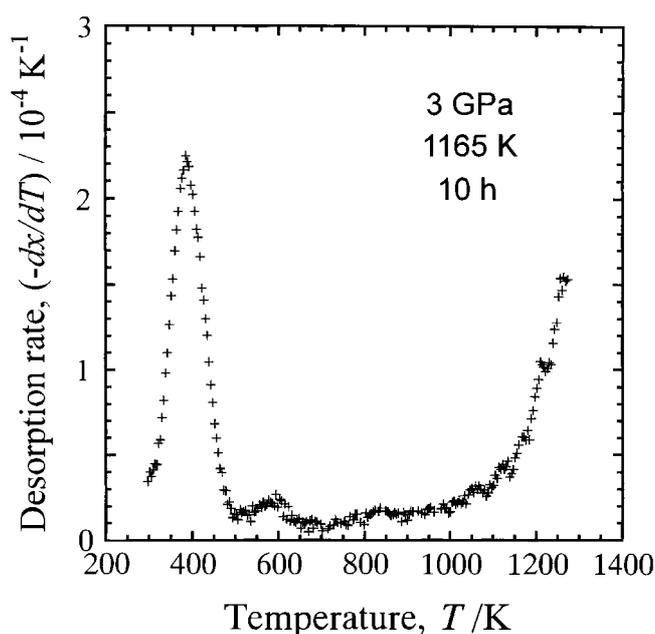


Fig. 5 Thermal desorption spectrum of an electroplated $\text{Ni}_{64}\text{Fe}_{36}$ alloy film, heat-treated at 1165 K for 10 h under a hydrogen pressure of 3 GPa. Measured 30 min after recovery.

3 GPa, and quenched to ambient conditions. Approximately 30 min elapsed before the TDS measurement was started. Note the different scale from Fig. 4; the amount of hydrogen desorbed from the heat-treated specimen is two orders of magnitude larger than from electrodeposited ones. An additional measurement on a specimen heat-treated for a short time (10 min) revealed only the lowest-temperature peak. The observed peak temperatures are included in Table 2.

2.3 Discussion regarding the state of hydrogen and its temporal variation

Comparison of the TDS spectra of electrodeposited specimens with those of heat-treated ones shows that desorption peaks P_0 , P_2 and P_5 (P_6) occur at nearly the same temperatures. Among these peaks, an unambiguous assignment can be made for P_0 ; the fact that only P_0 is produced by heating for a short period indicates that this is due to desorption of hydrogen dissolved on regular interstitial sites. By analogy with other fcc metals, Ni and Cu, P_1 and P_2 may be assigned to detrapping from single vacancies, and $P_4 \sim P_6$ from divacancies and larger vacancy complexes (voids).^{1,3,16)}

Because the effect of variable diffusion times before degassing is negligibly small in the present experiments, the width of desorption peaks should be due to the distribution of binding energies of the traps. The observation that, in the lower-temperature range, desorption peak P_0 became smaller in size and shifted to higher temperatures with time indicates that desorption starts with shallowly trapped hydrogens, progressing to more deeply trapped hydrogens. Two sharp peaks at 670 and 1100 K, which disappeared upon heat treatment, were ascribed to the products (H_2^+ and CO^+) of decomposition of small amounts of C-H complexes.¹⁸⁾ These peaks, largely irrelevant to the present purpose, will not be considered further.

Based on these observations, the following inference can be made on the change of state of hydrogen and vacancy-hydrogen clusters.

In the P_1 - P_2 temperature range, the hydrogen atoms that have been trapped by single vacancies are released, and immediately desorbed from the surface. The single vacancies left behind are not as mobile as hydrogen atoms, but, given the Stage-III temperature of pure Ni being 340 K (at which single vacancies start migration),²¹⁾ the single vacancies in the present alloy specimens are believed to move a short distance in this temperature range. Increasingly larger number of vacancies should become mobile as they release trapped hydrogen atoms, and their movement should occur on a large scale towards the end of $P_1 \sim P_2$ temperature range. Thus, single vacancy-hydrogen clusters, originally dispersed in the film, should be transformed into larger clusters in the process of heating of TDS measurements. Hydrogen atoms are more strongly trapped by these larger clusters, to be released at higher temperatures.

3. Stabilizing Heat Treatments of Electrodeposited Films

3.1 Application of the electrodeposited film as magnetostrictive torque sensor

A Ni-Fe alloy film was electrodeposited on the surface

of a carburized chrome-molybdenum steel shaft to form a magnetostrictive torque sensor. This sensor detected torque as changes in the impedance of a solenoid coil wound around the deposited film. In order to enable the sensor to detect the torque direction, magnetic anisotropy was attached to the film by applying a proper sequence of twisting and high-frequency pulse heating. More details of sensor fabrication technique will be described elsewhere. Suffice it to say in the present context that a condition of the high-frequency pulse heating is so chosen as to remove the strain in the film, without affecting its structure or the rigidity of the shaft. As the grain growth of the film proceeds rapidly above ~ 700 K, the temperature of pulse heating was limited to 668 K in less than 1 s.

Additional heat treatments aimed at eliminating long-term drifts of the magnetostriction are described in the next section.

3.2 Effects of heat treatments on the state of hydrogen

In order to test the effectiveness of the heat treatment for stabilizing the magnetostrictive properties of the film, TDS measurements were performed after each heat treatment, with and without applying additional aging treatment at 383 K for 400 h. This aging treatment simulates, approximately, the condition required for actual automobile application. The stabilizing treatment may be judged sufficient if no further change of state is induced by the aging.

Table 3 summarizes the conditions of heat treatments adopted in the present experiment.

Figure 6 compares the total amount of hydrogen desorbed (a) and the desorption rate (b) of the films, 8 h and 2887 h (approximately 4 months) after electrodeposition, and the one pulse-heated to 668 K. The results show that the high-frequency pulse heating reduces the desorption on the low-temperature side (≤ 440 K), eliminating P_0 and a lower-temperature side of P_1 .

Figure 7 shows the effect of aging, following the high-frequency pulse heating. The total amount of hydrogen desorbed is reduced, and the peak is shifted to high temperatures, indicating that hydrogen atoms have moved from shallow traps to deeper traps during aging. Thus, the high-frequency pulse heating is very effective, but not sufficient for stabilizing the state of hydrogen in the film.

Figure 8 shows the effect of additional stabilizing heat treatment at 453 K for 1 h and 2.5 h. The total amount of hydrogen is reduced further, and desorption is shifted to still higher temperatures.

Table 3 Heat treatments of electrodeposited $Ni_{64}Fe_{36}$ alloy film specimens.

Specimens	Heat treatments		
	Pulse heating	Annealing	Aging
Pulse heating	668 K	none	none
Aging added	668 K	none	383 K \times 400 h
Stabilization heat treatment	668 K	453 K	none
Aging added	668 K	453 K	383 K \times 400 h
Stabilization heat treatment + electrolytic charging	668 K	453 K	none
Aging added	668 K	453 K	383 K \times 400 h

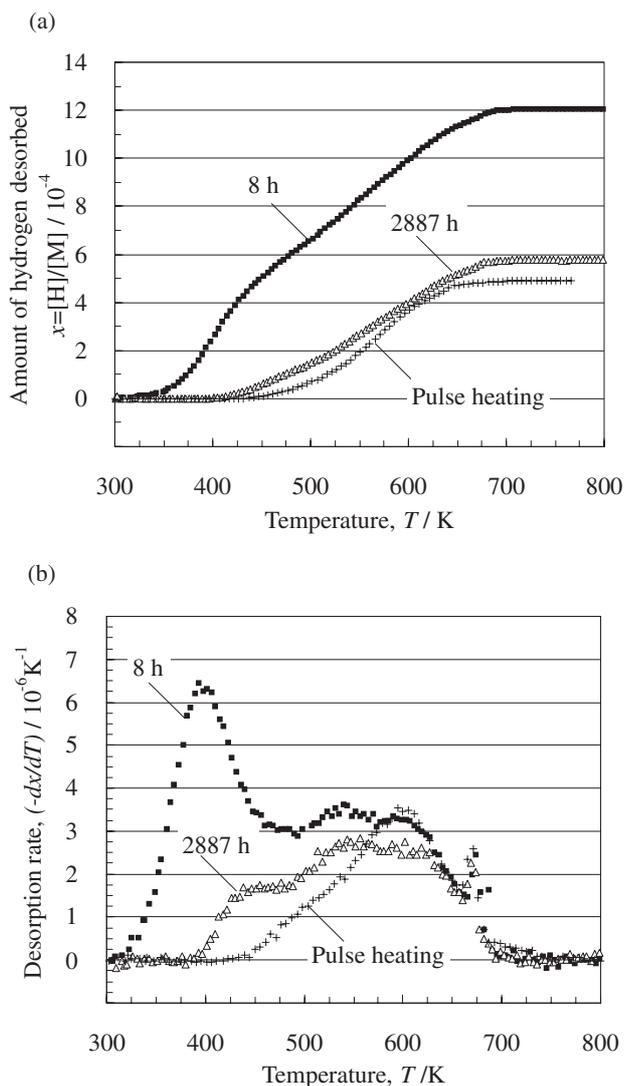


Fig. 6 Comparison of thermal desorption behaviors of $Ni_{64}Fe_{36}$ alloy films, 8 h and 2887 h after electrodeposition, and the one pulse heated to 668 K. The pulse heating is very effective in removing hydrogen to be desorbed at lower temperatures (≤ 440 K). Total amount desorbed (a), and desorption rate (b).

The effect of aging on the films after the stabilizing heat treatment for 1 h and 2.5 h is shown in Figs. 9 and 10, respectively. A small aging effect is still observable for the 1 h annealing, but eliminated completely for the 2.5 h annealing.

Finally, in order to verify the stability of the film as a torque sensor, temporal variation in the sensor performance following application of the stabilizing heat treatment was studied. After the stabilizing treatment for 1 h or 2.5 h, no impedance changes were observed after aging, and the sensor output characteristics were therefore judged to be sufficiently stable.

3.3 Effects of heat treatment on the state of vacancies

Although a close correlation between the changes of TDS spectra of hydrogen and magnetostriction as described above helped in establishing the condition of stabilizing heat treatments, it is still desirable to know exactly what has happened for vacancies during or after the heat treatments.

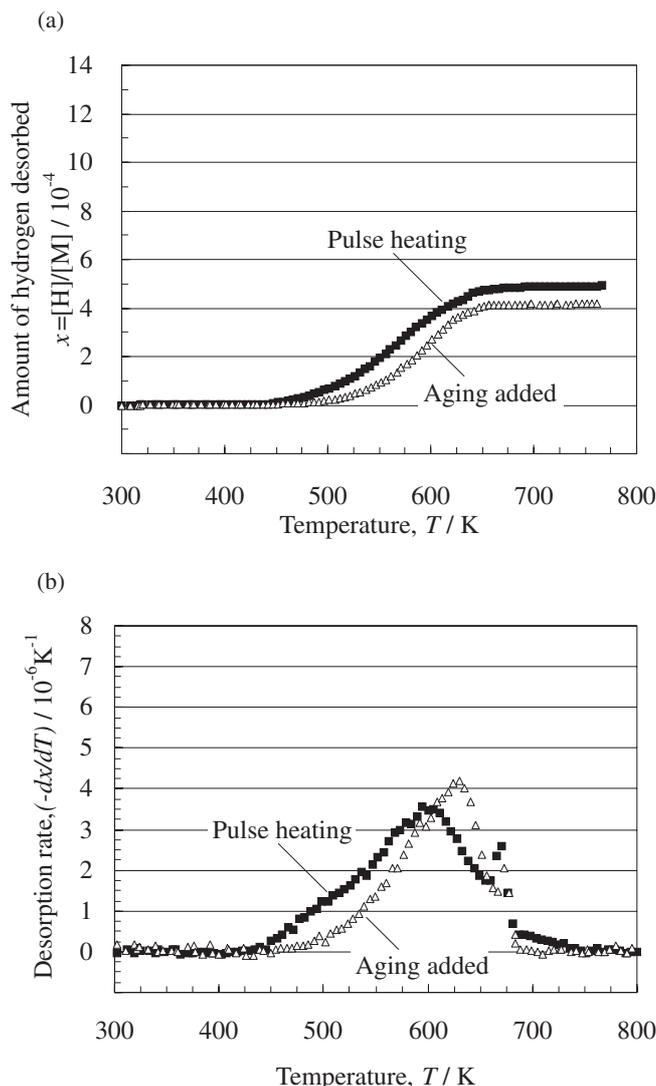


Fig. 7 Effects of aging $383 K \times 400 h$, after a pulse heating to 668 K. Total amount desorbed (a), and desorption rate (b).

For the desorption of hydrogen from single vacancy-hydrogen clusters (in P_1 and P_2), the following two processes can be conceived of: Either that vacancy-hydrogen clusters as a whole disappear after migration to the surface, or that hydrogen atoms released from vacancies are desorbed, leaving single vacancies behind.

In order to distinguish between these two possibilities, hydrogen was charged electrolytically after the stabilizing heat treatment (pulse-heating + $453 K \times 1 h$), and thermal desorption was measured again. (The electrolytic charging was performed in 0.05 mol/l sulfuric acid with a current density of $2000 A/m^2$ for 1 h.)

Figure 11 shows a comparison of TDS spectra for three specimens, (1) pulse-heated, (2) pulse-heated and annealed $453 K \times 1 h$, (3) pulse-heated, annealed $453 K \times 1 h$ and electrolytically charged. The desorption caused by the annealing is completely recovered by the subsequent electrolytic charging. This indicates that the annealing only released trapped hydrogen atoms, and single vacancies left behind were replenished with hydrogen by the subsequent electrolytic charging.

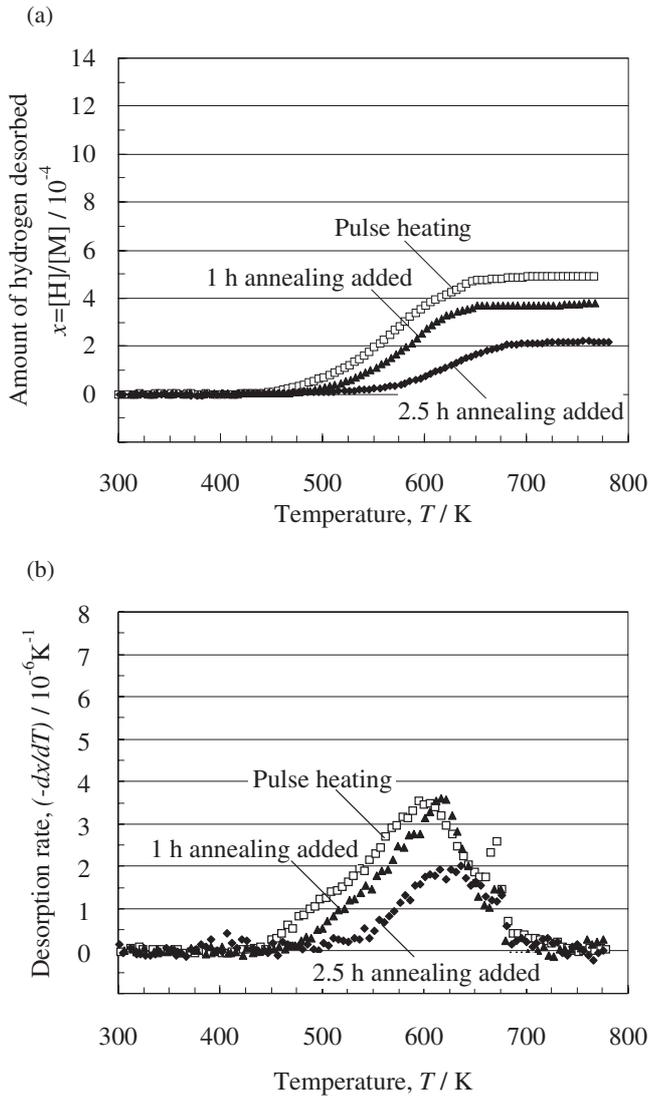


Fig. 8 Comparison of thermal desorption behaviors of electrodeposited $Ni_{64}Fe_{36}$ alloy films, with and without annealing $453 K \times 1 \sim 2.5 h$ after pulse heating to 668 K. The annealing reduces the lower-temperature side of the desorption peak. Total amount desorbed (a), and desorption rate (b).

It may be expected, then, that single vacancies free of trapped hydrogen atoms will become over-saturated and tend to disappear at the surface or forming internal voids. To determine the temperatures at which the free vacancies start migrating, TDS measurements were made on specimens, annealed for 5 min at different temperatures to liberate trapped hydrogen and subsequently charged electrolytically.

Figure 12 shows the total amount of hydrogen desorbed during heating to 773 K as a function of temperature of annealing for 5 min. The total amount of hydrogen desorbed (*i.e.*, the amount of hydrogen retained in the film) starts decreasing from the annealing temperature of around 500 K, and becomes nearly zero at 673 K. Thus, single vacancies that trap hydrogen largely disappear by annealing at 673 K, and replaced by multiple vacancies and voids that release hydrogen at higher temperatures.

These results lead to the following picture for hydrogen and vacancies in the electrodeposited films. At room temperature, hydrogen atoms dissolved interstitially in the lattice during electrodeposition is gradually desorbed, leaving only

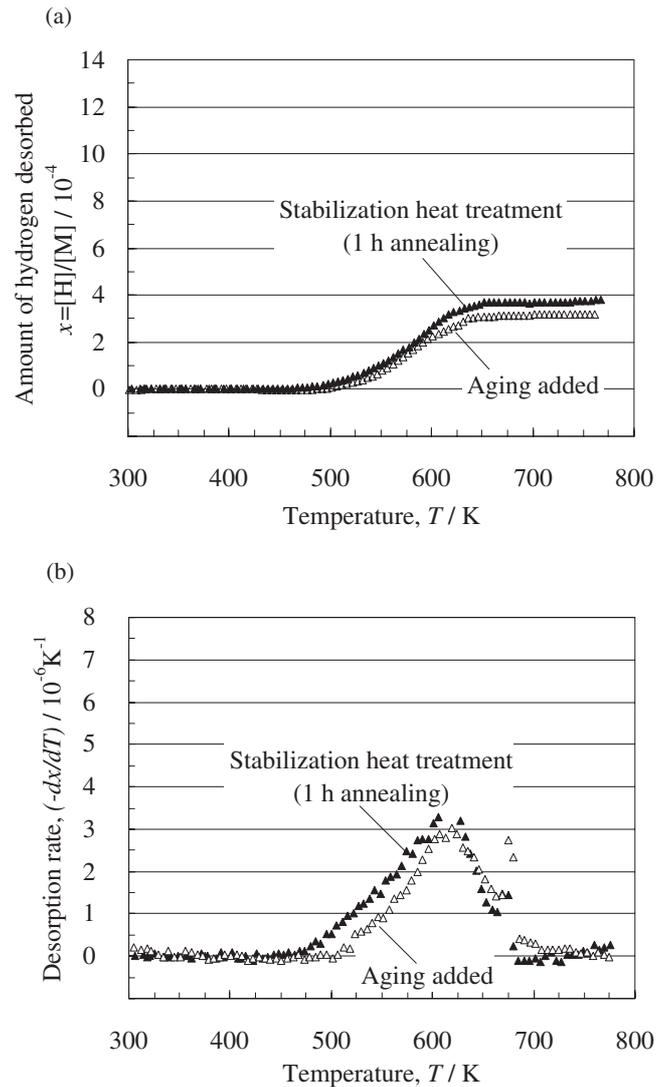


Fig. 9 Effects of aging $383 K \times 400 h$, after stabilization heat treatment (a pulse heating to 668 K and a subsequent annealing $453 K \times 1 h$). Total amount desorbed (a), and desorption rate (b).

those trapped by vacancies after 365 h. Upon heating, hydrogen atoms trapped by single vacancies are released and desorbed between 420–670 K. The number of single vacancies becomes almost zero at 673 K, where the hydrogen has been completely released from the single vacancies. This indicates that immediately following the release of the trapped hydrogen, the single vacancies become mobile and form multiple vacancy-hydrogen clusters or voids. The migration of metal atoms, occurring on a large scale during the grain growth above $\sim 600 K$, is believed to be promoted by these multiple vacancy-hydrogen clusters.

4. Summary and Conclusion

The film of $Ni_{64}Fe_{36}$ alloy, produced by rapid electrodeposition, consists of nano-crystals of approximately 10 nm in size, and undergoes grain growth when heated to above 600 K. Hydrogen and vacancy-hydrogen clusters are introduced during electrodeposition. The hydrogen is gradually desorbed at room temperature, whereas single vacancies move at $\geq 500 K$, and disappear above 673 K. The temporal

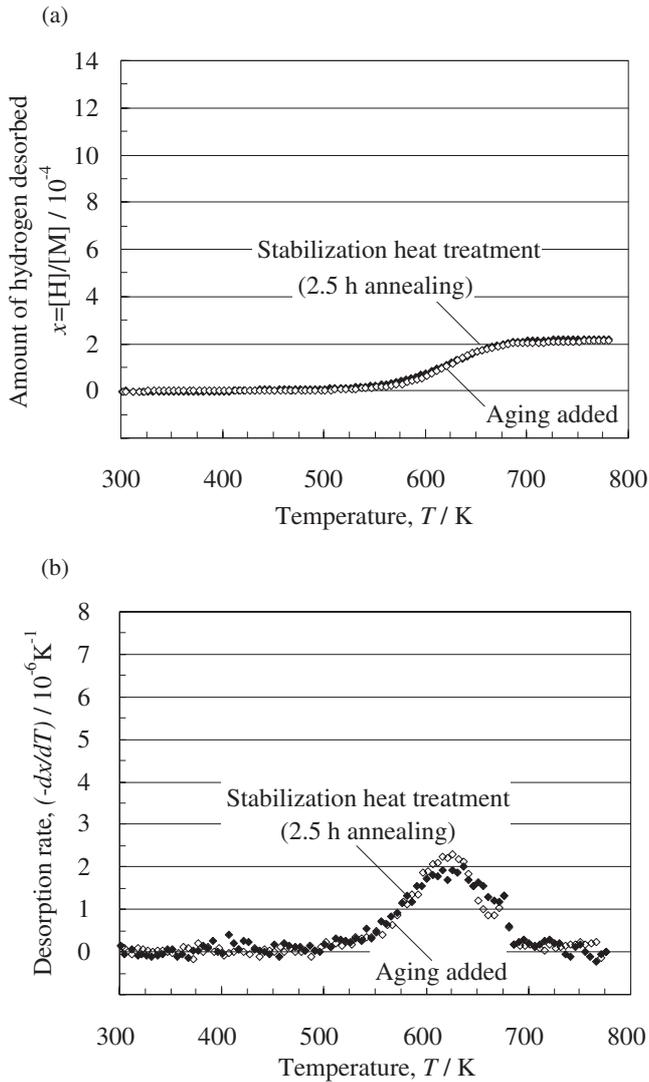


Fig. 10 Effects of aging 383 K \times 400 h, after stabilization heat treatment (a pulse heating to 668 K and a subsequent annealing 453 K \times 2.5 h). Total amount desorbed (a), and desorption rate (b).

variation of magnetism at room temperature can therefore be ascribed to the change of state of hydrogen in the film. A high-frequency pulse heating to 668 K removed hydrogen dissolved interstitially in the lattice, and additional annealing 453 K \times 1~2.5 h removed shallowly trapped hydrogen atoms. Aging tests (383 K \times 400 h) performed after stabilizing heat treatments (pulse heating + annealing 453 K \times 1~2.5 h) showed that the change of state of hydrogen after aging was substantially reduced. The TDS measurements described here have helped in achieving detailed understanding of the change of state of hydrogen and vacancy-hydrogen clusters in electrodeposited Ni-Fe alloy films, and the stabilizing heat treatment devised on this basis proved to be effective in eliminating the temporal variation of the output characteristics of the film employed as a torque sensor. The authors wish to thank Wataru Senju of the Shibaura Institute of Technology for his help in the TDS measurements. X-ray diffraction experiments were performed at a synchrotron radiation facility of the High Energy Accelerator Research Organization (KEK) under approval 02G08.

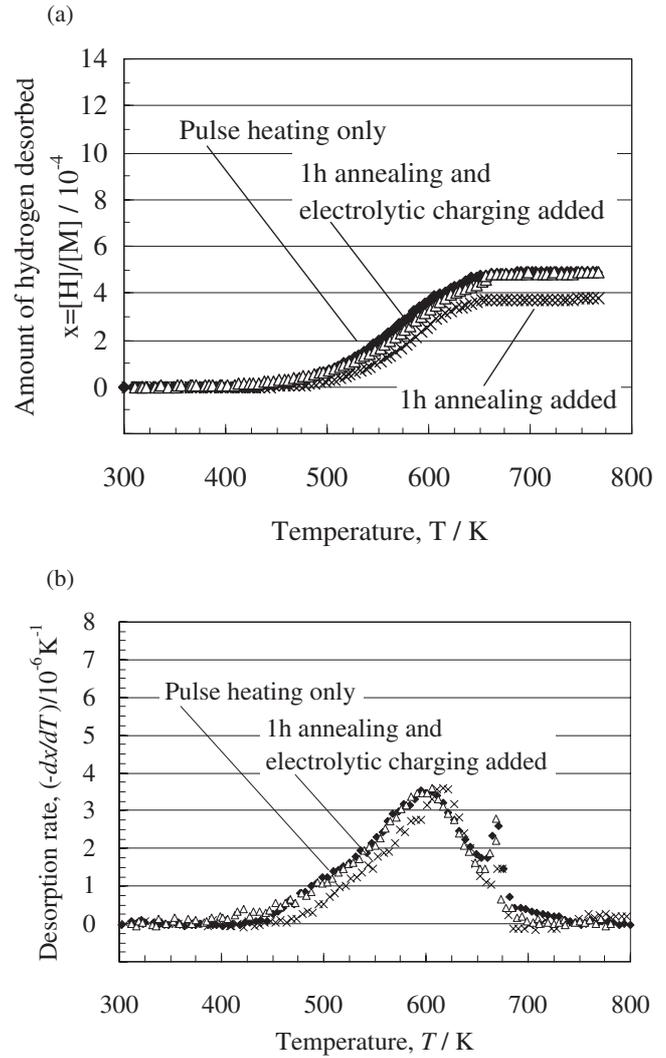


Fig. 11 Comparison of thermal desorption behaviors of electrodeposited $Ni_{64}Fe_{36}$ alloy films, pulse-heated to 668 K, with and without 453 K \times 1 h annealing, with and without electrolytic charging. The desorption caused by the annealing is completely recovered by the electrolytic charging. Total amount desorbed (a), and desorption rate (b).

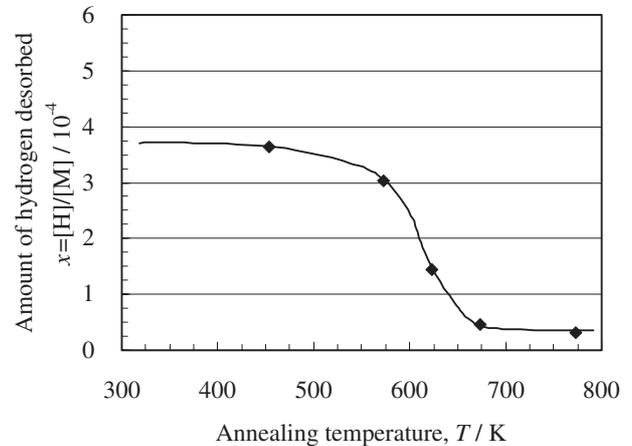


Fig. 12 Total amount of hydrogen retained after heat treatments at different temperatures (for ≤ 5 min) and subsequent electrolytic charging. The data provide a measure of the amount of single vacancy-hydrogen clusters retained after the heat treatments.

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