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Lattice defects introduced during hydrogen absorption–desorption cycles and their effects on *P–C* characteristics in some intermetallic compounds

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Abstract

The generation of lattice defects and their effects on hydrogen sorption properties described in terms of pressure–composition (*P–C*) isotherms have been investigated as a function of the number of hydrogen sorption cycles for $LaNi_5$ and FeTi. For $LaNi_5$, while the desorption pressure does not significantly depend on the number of cycles, the absorption pressure drastically decreases between the first and second cycles. Numerous dislocations of edge character with Burgers vectors of the $1/3\langle 1\bar{2}10\rangle$-type as well as numerous cracks are introduced during the first absorption cycle. The introduction of numerous lattice defects such as *a*-type edge dislocations and the formation of severe cracks seems to be completed during the first cycle, resulting in the reproducible *P–C* characteristics for the subsequent cycles. In contrast, FeTi exhibits ever-changing *P–C* characteristics with cycle number. The introduction of dislocations and cracks occurs during each of the absorption cycles. However, the extent to which this occurs is considerably smaller in each absorption cycle of FeTi than in the first absorption cycle of $LaNi_5$. The difference in material response to hydrogenation seems to be closely related to the difference in ductility of these two intermetallics.

Keywords: $LaNi_5$; FeTi; Hydrogen-storage alloy; Dislocation; Crack

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1. Introduction

There is considerable interest in the research and development of hydrogen-storage materials because of the growing demands for environmental safety. Hydrogen atoms should readily be absorbed and desorbed in these hydrogen storage materials at ambient temperatures and pressures in a reproducible manner. Many intermetallic compounds, such as $LaNi_5$ with a hexagonal $CaCu_5$ structure, $TiMn_2$ with a hexagonal C14 structure and FeTi with a cubic B2 structure, are known to be typically classified into this class of material [1]. However, why and how hydrogen atoms are readily absorbed and desorbed in some particular materials as listed above has remained largely unknown. Of these intermetallics, $LaNi_5$ and FeTi are known to behave differently when their hydrogen properties are described in terms of *P* (pressure)–*C* (composition) isotherms. $LaNi_5$ has been recognized to be rather easily activated; the activation only needs a few to several cycles of hydrogen sorption, after which reproducible absorption–desorption characteristics are obtained. The only hydride of concern for the $LaNi_5$–H system is $LaNi_5H_6$, which involves lattice expansion of more than 20% upon hydride formation [2–4]. On the other hand, the activation of FeTi has been recognized to be difficult. In addition to the FeTi–H solid-solution (designated to be α), two different hydrides, FeTiH (β) and $FeTiH_2$ (γ), are known to appear during measurements of *P–C* isotherms at ambient temperatures. As a result, the *P–C* isotherms usually exhibit two plateaus corresponding to $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations [5–8]. Unlike in $LaNi_5$, *P–C* characteristics of FeTi continuously change as the cycle number increases without showing any reproducible characteristics [5,8]. However, almost nothing is known about why these two typical hydrogen-storage intermetallics, $LaNi_5$ and FeTi, behave so differently in response to hydrogenation. We believe that some physically important changes occur in the bulk of these intermetallics during hydrogen absorption–desorption cycles causing their *P–C* characteristics to change accordingly.

In the present study, we thus investigate microstructure evolution in $LaNi_5$ and FeTi as a function of the number of hydrogen sorption cycles in order to establish the relation-

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ship between microstructure and hydrogen absorption–desorption properties described in terms of *P–C* isotherms.

2. Experimental procedures

Ingots of $LaNi_5$ and FeTi were prepared by Ar-arc melting of high purity elements (either 99.9 or 99.99%) followed by annealing in vacuum at 1000°C for 48 h. These ingots were crushed mechanically and sieved. *P–C* isotherms were measured by the Sieverts method at 30°C.

Cracking and pulverization behaviors were monitored as a function of the number of hydrogen sorption cycles by scanning electron microscopy (SEM). Microstructure evolution in the bulk of powder specimens was examined by transmission electron microscopy (TEM). Thin foils for TEM observations were prepared by ion-milling $LaNi_5$ and FeTi particles embedded in a Ni plate formed by electroless plating [9].

3. Results

3.1. Microstructure evolution and P–C isotherms in $LaNi_5$

P–C isotherms of $LaNi_5$ with an initial particle size of 150–300 μm are shown in Fig. 1 for the first five cycles of hydrogen absorption–desorption. While the desorption pressure does not significantly depend on the number of cycles (0.2 MPa), the absorption pressure drastically decreases from 0.9 MPa for the first cycle to 0.3 MPa for the second cycle. For further cycles, the absorption pressure stays almost constant at 0.3 MPa.

Creation of fresh and clean surfaces that are free from adsorbed gas molecules as a result of cracking and pulverization has been believed to be very important in the activation of $LaNi_5$ [1]. However, this may not be the case, since the increase in absorption pressure of the sample subjected to three cycles followed by exposure in air for 48 h is very small; the absorption pressure is 0.3 MPa before air-exposure and 0.35 MPa after air-exposure. This indicates that the change in surface properties does not play a decisive role in significantly decreasing the absorption pressure between the first and second cycles, and suggests that some physically important changes should occur in the bulk of $LaNi_5$ particles during the fist absorption cycle.

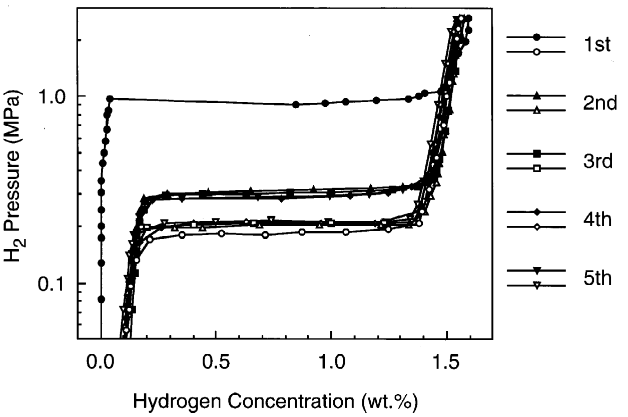

Fig. 1. *P–C* isotherms of $LaNi_5$ with an initial particle size of 150–300 μm for the first five cycles of hydrogen absorption–desorption. Data points plotted with closed and open symbols indicate those corresponding to the absorption and desorption cycles, respectively.

SEM images of powder samples with an initial particle size of 150–300 μm subjected to one and five cycles are shown in Fig. 2(a),(b) and (c),(d), respectively. The particle size decreases quickly as the cycle number increases, so that the majority of particles exhibit a particle size of 10–20 μm after five cycles. Uchida et al. [10] reported that after ~30 cycles, the average particle size saturates to a certain value around 15 μm, which is comparable to the particle size presently observed after five cycles. Although many particles remain large (greater than 100 μm) after one cycle, close examination at a higher magnification (Fig. 2(b)) reveals that most of large particles observed after one cycle are severely cracked and that the size of sub-particles delineated by cracks is comparable to that of particles observed after five cycles. This indicates that the first cycle plays a decisive role in pulverization of powder samples.

A typical example of TEM images of samples subjected to one cycle of hydrogen absorption–desorption is shown in Fig. 3. A tremendously high density of dislocations with Burgers vectors parallel to the *a*-axis is seen to align parallel to the *c*-axis without showing any tendency for tangling. The density of these *a*-type edge dislocations (with Burgers vectors of the $1/3\langle 1\bar{2}10\rangle$-type) is considerably high and is estimated to be of the order of 10^{12}–10^{13} cm^{-2}, which is comparable to the upper limit of dislocation density in most crystalline solids. Because of the high density of dislocations introduced in the first absorption cycle, all features of lattice defects introduced in the second and further cycles cannot be resolved by TEM. The occurrence of these numerous *a*-type dislocations is consistent with anisotropic line broadening observed for $\{hk0\}$-type reflections in X-ray and neutron diffraction studies [4,11–13]. Of importance to note here is that when referring to the results of our plastic deformation experiments on single crystals [14], $LaNi_5$ is very brittle, exhibiting the onset temperature for plastic flow as high as 700°C when slip on $\{1\bar{1}00\}$ [1] is operative and *a*-type dislocations can not move so easily in response to uniaxial stresses. We thus believe that these *a*-type dislocations are introduced in response to hydrogenation as misfit dislocations formed at interfaces between the $LaNi_5$ matrix and hydride. Recently, the introduction of numerous vacancies was also reported to occur in $LaNi_5$ during the first absorption cycle through positron lifetime spectroscopy by Shirai and co-workers [15].

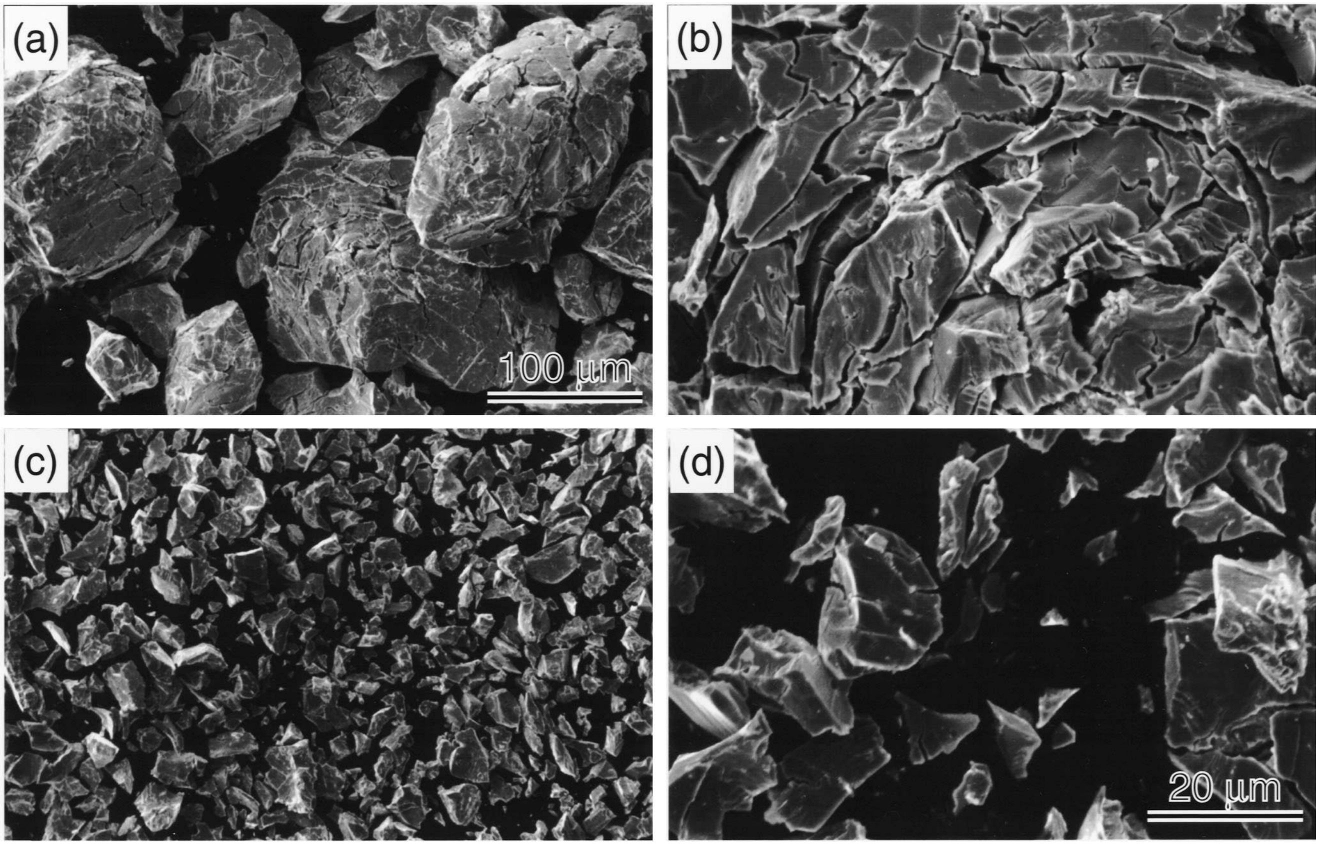

Fig. 2. SEM images of $LaNi_5$ samples after (a), (b) one cycle, and (c), (d) five cycles.

The absorption pressure for the first cycle depends on the initial particle size of powder samples, as tabulated in Table 1. It decreases from 0.9 MPa for particles of 150–300 μm to 0.68 MPa for particles of 20–40 μm. It should be noted is that the absorption pressure for samples subjected to three cycles followed by annealing at 800°C to eliminate the introduced lattice defects is 0.65 MPa, which is comparable to the absorption pressure for the first cycle of samples with the initial particle size of 20–40 μm. This indicates that the absorption pressure for the first cycle has nothing to do with the chemistry of the sample if the particle size is large and that the absorption pressure for the first cycle is determined by over-pressure required to produce many cracks as a result of lattice expansion upon hydride formation.

3.2. Microstructure evolution and P–C isotherms in FeTi

P–C isotherms of FeTi with initial particle size of 150–300 μm are shown in Fig. 4 for the first, second, 10th and 50th cycles of hydrogen absorption–desorption. Two plateaus corresponding to $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations are clearly observed for both absorption and desorption isotherms of the first cycle. The second plateau corresponding to the $\beta \rightarrow \gamma$ transformation could not be completed in the first four cycles because of the pressure limitation (9.0 MPa) of our apparatus. For the first plateau corresponding to the $\alpha \rightarrow \beta$ transformation, while the desorption pressure does not significantly depend on the number of cycles, the absorption pressure progressively decreases as the cycle number increases with the most significant decrease occurring between the first and second cycles. The decrease in absorption pressure of the first plateau persistently occurs even when the cycle number is increased to 50, in contrast to the case of $LaNi_5$. The significant decrease in absorption pressure of the first plateau between the first and second cycles is similarly observed in $LaNi_5$ (Fig. 1). However, the origins seem to be somewhat different from each other, since our preliminary results indicate that the absorption pressure of the first cycle in FeTi is sensitive to both the surface conditions and particle size. The second plateau corresponding to the $\beta - \gamma$ transformation is inclined more steeply than the first plateau for both absorption and desorption cycles. The inclination of the second plateau becomes more marked for both absorption and desorption cycles as the cycle number increases, resulting in the distortion of the second plateau in the direction of higher pressure. As a result, the hydrogen capacity tends to decrease with the increase in cycle number. This is consistent with previous reports [5,6].

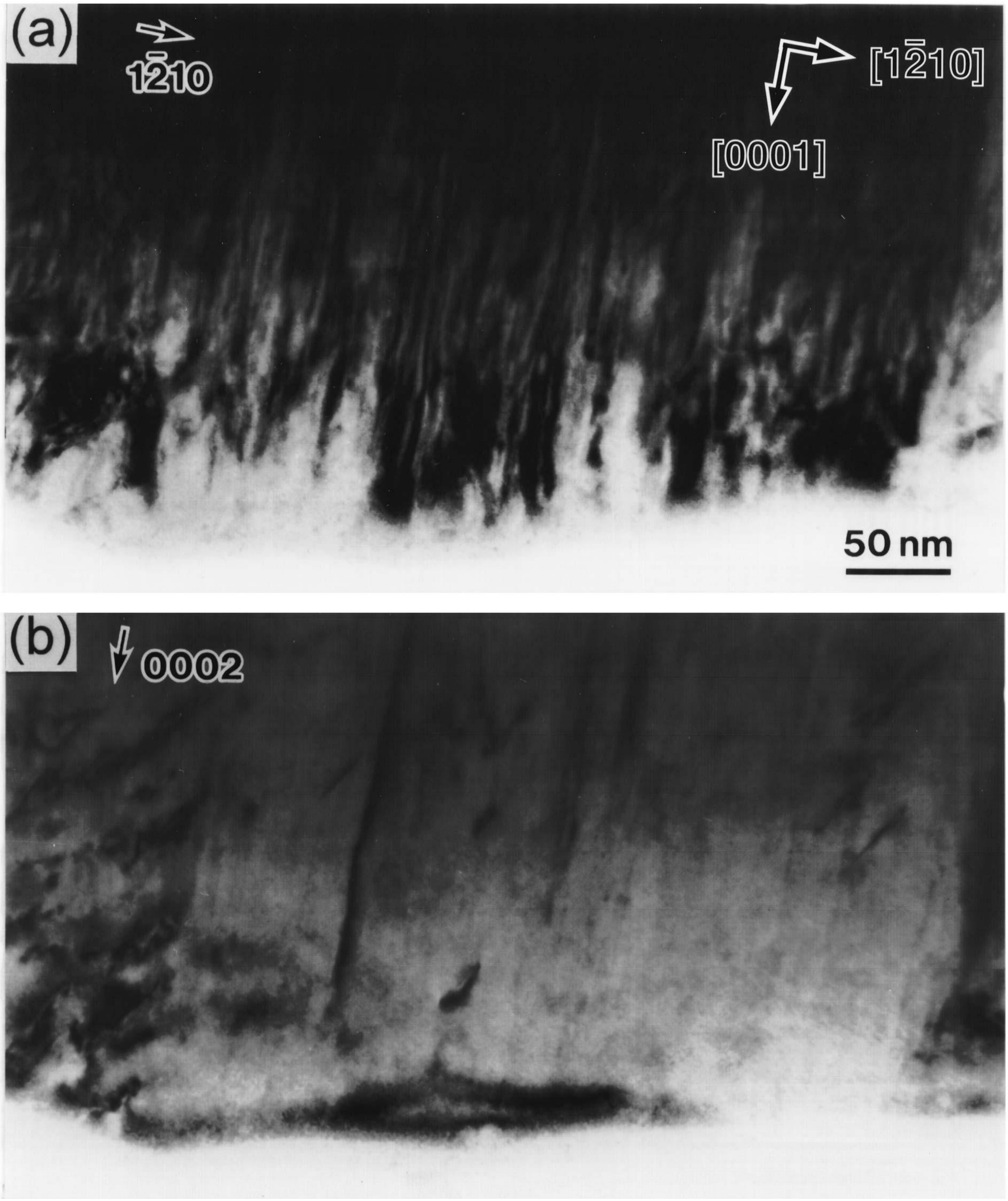

Fig. 3. TEM microstructures of a LaNi$_5$ sample subjected to one cycle of hydrogen absorption–desorption. The images were taken with (a) **g** (reflection vector)=$1\bar{2}10$ and (b) **g**=0002, respectively. The crystallographic directions are indicated in (a).

SEM images of powder samples after one and 50 cycles are shown in Fig. 5(a),(b) and (c),(d), respectively. As the number of cycles increases, the particle size gradually decreases. The rate of the decrease in particle size with cycle number is considerably smaller in FeTi than in LaNi$_5$. Even after 50 cycles, the particle sizes of many powders remain greater than 100 μm, although many smaller particles are also observed. Close examination at a higher magnification (Fig. 5(b),(d)) reveals that many cracks are also observed for particles subjected to one and 50 cycles. This indicates that cracking and pulverization in FeTi occur progressively and very slowly in each of the

Table 1
The initial particle size dependence of the absorption pressure for the first cycle of $LaNi_5$

Particle size range (μm)	Absorption pressure (MPa)
150–300	0.91
150–180	0.80
90–106	0.78
20–45	0.68

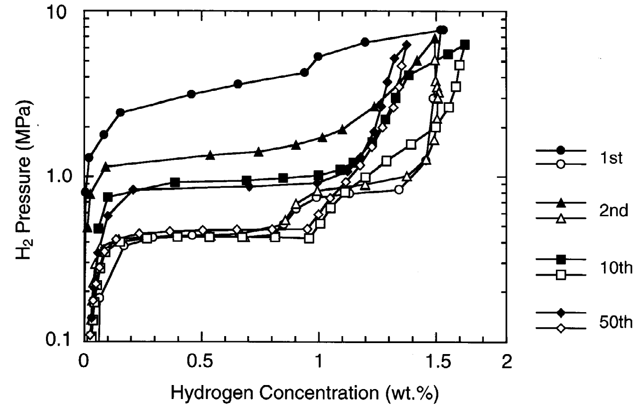

Fig. 4. *P–C* isotherms of FeTi with initial particle size of 150–300 μm for the first, second, 10th and 50th cycles of hydrogen absorption–desorption. Data points plotted with closed and open symbols indicate those corresponding to the absorption and desorption cycles, respectively.

absorption cycles, in contrast to the case of $LaNi_5$ in which the first cycle plays a decisive role in pulverization of powder samples.

Typical TEM images of samples subjected to one and three cycles of hydrogen absorption–desorption are shown in Fig. 6(a) and (b), respectively. In contrast to the observation by Schober [16], a high density of dislocations is observed heterogeneously in the form of tangles for both samples subjected to one and three cycles. Although no quantitative estimation is made, the dislocation density seems to increase with the increase in cycle number. This is further confirmed by our preliminary investigation with the X-ray line broadening technique. Burgers vectors of most dislocations are determined to be of the ⟨100⟩-type through conventional contrast analysis. Takasugi et al. [17] reported that plastic deformation of FeTi polycrystals occurs above 400°C by slip on {110}⟨100⟩. Our preliminary results on plastic deformation of single crystals of FeTi indicates that plastic deformation can occur at temperatures as low as room temperature [18]. Both dislocation tangling and Burgers vectors of the ⟨100⟩-type, which is consistent with those observed after plastic deformation, indicate that dislocations observed after hydrogen sorption cycles (Fig. 3) are lattice dislocations set in motion in order to relieve elastic strains generated during $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ trans-

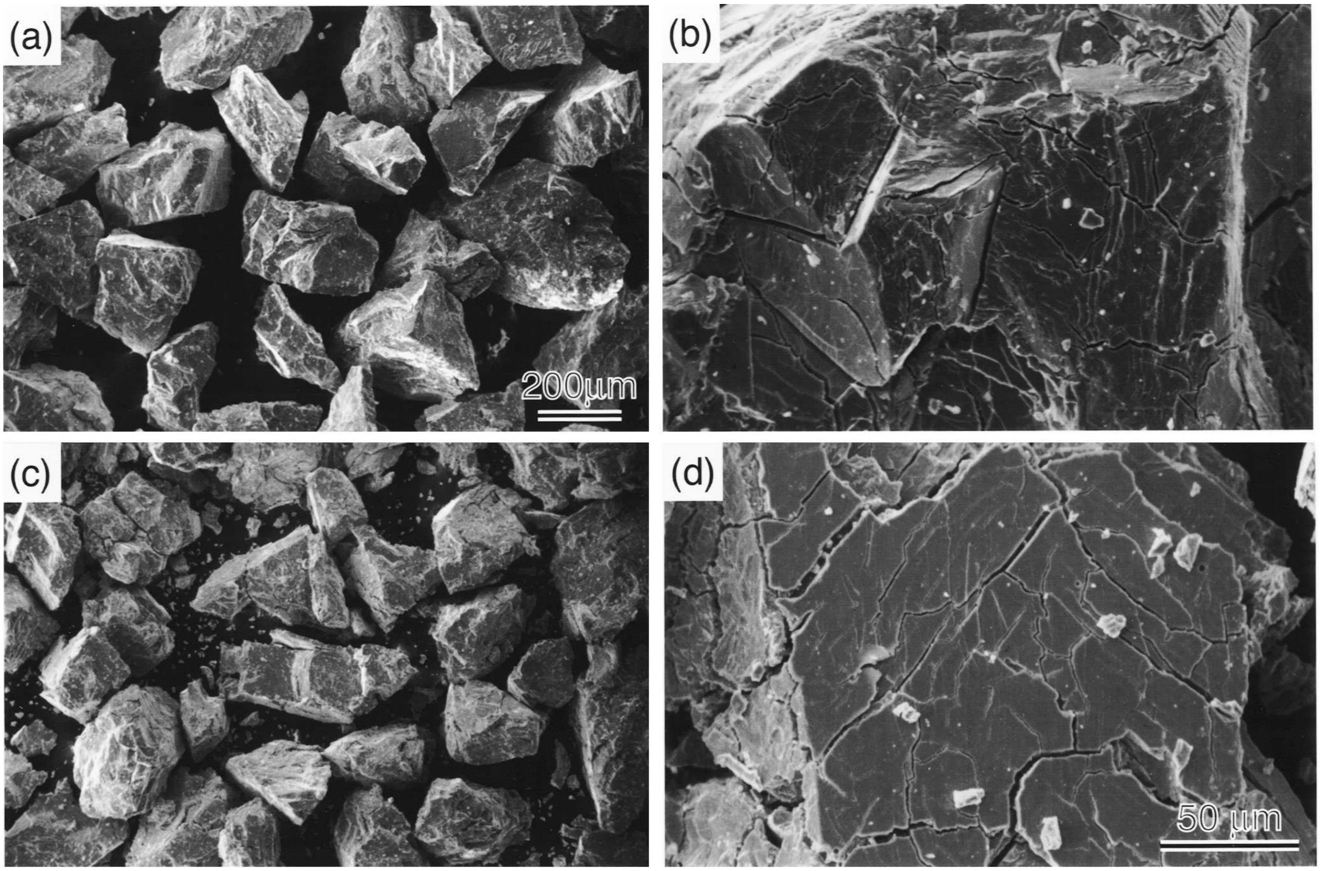

Fig. 5. SEM images of FeTi samples after (a), (b) one cycle, and (c), (d) 50 cycles.

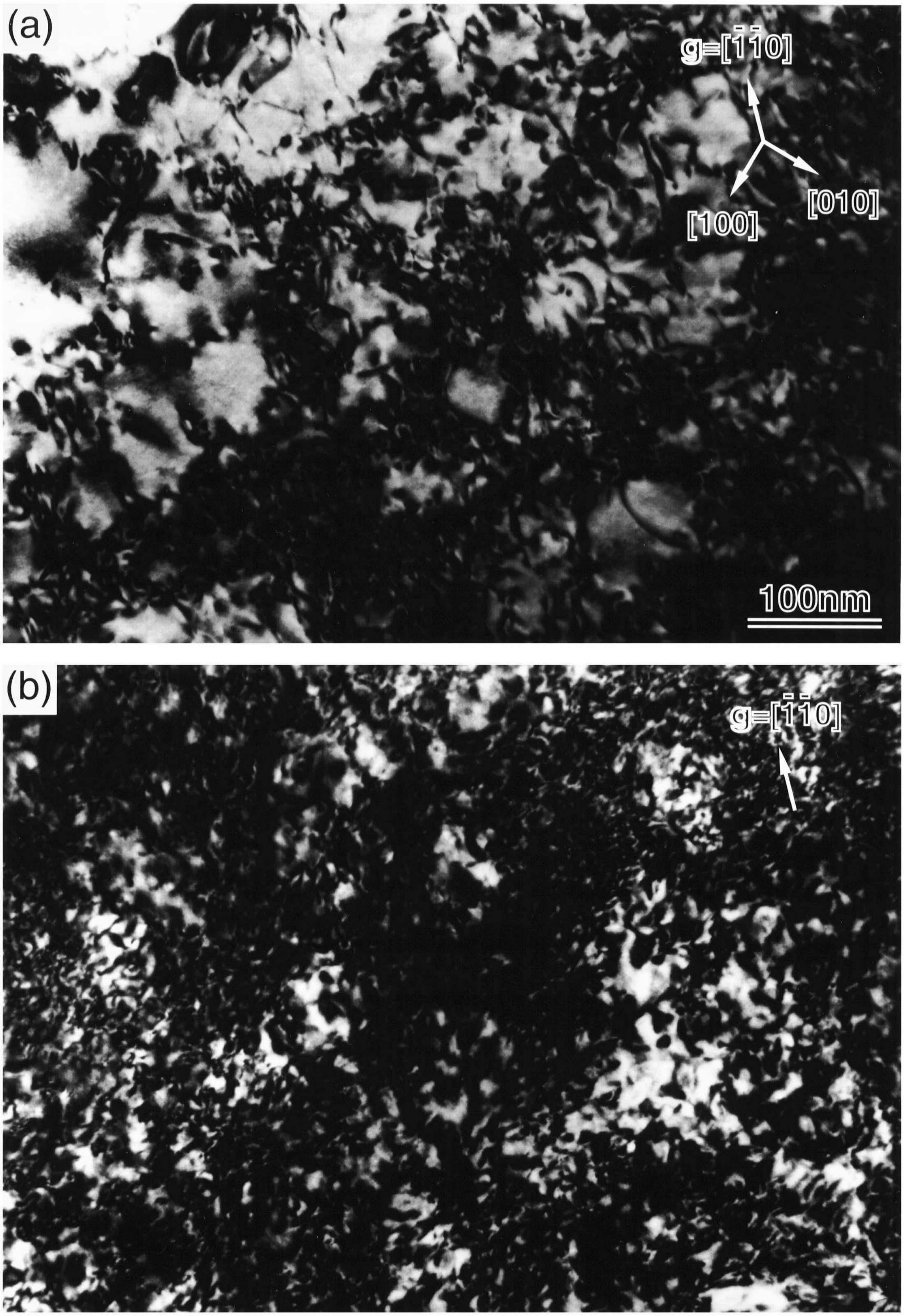

Fig. 6. TEM microstructures of FeTi samples subjected to (a) one cycle and (b) three cycles of hydrogen absorption–desorption. The image was taken with **g**=110. The crystallographic directions are indicated in (a).

formations. In contrast to $LaNi_5$, FeTi seems to be quite ductile, since some deformability is noted also during mechanical crushing in sample preparation. Many dislocations are indeed observed similarly in the form of tangles in as-crushed samples, although the density is considerably smaller in as-crushed samples compared to samples subjected to hydrogen cycles.

These facts indicate that the introduction of lattice defects and cracks which occurs persistently in each of the cycles is responsible for the ever-decreasing absorption pressure for the first plateau corresponding to the $\alpha \rightarrow \beta$ transformation and that the accumulation of dislocations causes the distortion of the second plateau corresponding to the $\beta \rightarrow \gamma$ transformation in the direction of higher pressure for both absorption and desorption cycles. We believe that high ductility is the origin of the persistent introduction of lattice defects and cracks in FeTi.

4. Discussion

While the desorption pressure of $LaNi_5$ does not depend much on the number of cycles, the absorption pressure for the first cycle is very high when compared to that for the subsequent cycles. The significant decrease in absorption pressure between the first and second cycles observed for $LaNi_5$ is due to the formation of severe cracks, which corresponds to pulverization, and the introduction of lattice defects such as *a*-type dislocations, both of which processes are almost complete within the first absorption cycle. This indicates that the reproducible *P–C* characteristics of $LaNi_5$ can be achieved only when such numerous lattice defects are introduced in the bulk of $LaNi_5$. Indeed, the absorption pressure increases upon annealing at high temperatures because of the loss of lattice defects. The extent of the decrease in absorption pressure between the first and second cycles due to the introduction of lattice defects such as dislocations does not depend on the initial particle size. On the other hand, the extent of the decrease due to the formation of cracks depends on the initial particle size, since over-pressures required to form cracks as a result of the formation of hydride depend on the initial particle size. Judging from Table 1, the initial particle size around 20 μm corresponds to the critical value below which over-pressures are not needed to form cracks. This value may correspond to the mean free path for cracks that are spontaneously formed upon hydride formation. This has yet to be clarified. The absorption pressure for the first cycle has nothing to do with the chemistry of the sample if the particle size is large and the absorption pressure is determined by over-pressure required to produce many cracks and lattice defects such as dislocations during the first absorption cycle, as schematically illustrated in Fig. 7. Since both the formation of cracks and the introduction of lattice defects are almost complete within the first absorption cycle, *P–C* isotherms are reproducible and do not depend much on the number of cycles for the second and further cycles.

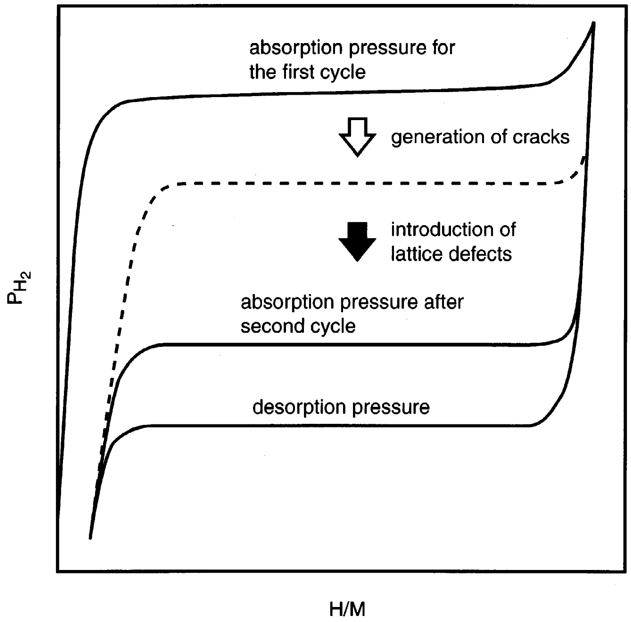

Fig. 7. Schematic illustration of *P–C* isotherms of $LaNi_5$ showing the contribution of over-pressures require to form lattice defects and cracks.

On the other hand, while the desorption pressure for the first plateau of FeTi does not significantly depend on cycle number, the absorption pressure progressively and persistently decreases as the cycle number increases. We believe that the introduction of lattice defects and cracks occurring persistently in each of the cycles is responsible for the ever-decreasing absorption pressure for the first plateau. This occurs because FeTi is ductile enough to set lattice dislocations with Burgers vector of the ⟨100⟩-type in motion in order to relieve elastic strains generated during the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations. Thus, the extent of cracking for each of the absorption cycles in FeTi is greatly reduced when compared to that for the first absorption cycle in $LaNi_5$. Because of this, the rate of the decrease in particle size is considerably smaller in FeTi than in $LaNi_5$. We suspect that the decrease in absorption pressure for the first plateau of FeTi will be minimized when the initial particle size is as small as that attained, for example, after thousands of cycles. In this case, the absorption pressure for the first plateau is expected to be low from the first cycle and the pressure hysteresis with respect to cycle number is also expected to be quite low. The inclination of the second plateau of FeTi becomes more marked for both absorption and desorption cycles as the cycle number increases, resulting in the distortion of the second plateau in the direction of higher pressure. We believe that this is due to the accumulation of dislocations in the bulk of FeTi. The distortion of the second plateau is indeed reported to recover upon annealing [8]. However, the reason why the accumulated dislocations cause the distortion of the second plateau has yet to be clarified. The fact that the desorption pressure of the first plateau does not depend on cycle number even in the presence of the accumulated dislocations may provide a key to the clarification.

5. Conclusions

(1) Numerous dislocations are introduced and significantly severe cracking occurs during the first cycle of hydrogen absorption–desorption in $LaNi_5$. The majority of dislocations introduced are *a*-type edge dislocations, which account for anisotropic line broadening observed for {*hk0*}-type reflections by neutron and X-ray diffraction studies. Reproducible (reversible and stable) $P–C$ characteristics of $LaNi_5$ can be achieved only when such numerous dislocations and cracks are formed in the bulk of $LaNi_5$.

(2) Since both the formation of cracks and the introduction of lattice defects are almost complete within the first absorption cycle, $P–C$ isotherms are reproducible and do not depend much on the number of cycles for the second and further cycles.

(3) The introduction of dislocations (lattice defects) and cracks occurs persistently in each of the cycles in FeTi because FeTi is ductile enough to set lattice dislocations with Burgers vectors of the $\langle 100 \rangle$-type in motion in order to relieve elastic strains generated during the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations. Thus, $P–C$ characteristics of FeTi continuously change with cycle number without showing any reproducibility.

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