

Microstructure of alloy $\text{MNi}_{3.75}\text{Co}_{0.75}\text{Mn}_{0.3}\text{Al}_{0.2}$ (M1—La rich mischmetal) during electrochemical hydriding-dehydriding process^①

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Abstract: Evolution of microstructures of alloy $\text{MNi}_{3.75}\text{Co}_{0.75}\text{Mn}_{0.3}\text{Al}_{0.2}$ (M1—La rich mischmetal) during the electrochemical hydriding-dehydriding process was studied by using in situ X-ray diffraction method. It is indicated that both the crystallite sizes of α phase (solid solution phase) and β phase (hydride phase) decrease with the hydrogen content increasing during this process. β phase is found to be composed of the plate-like and the needle-like crystallites, while the crystallite size of the former changes more rapidly than that of the latter during the hydriding-dehydriding process. It's also clearly found that strains along (110) plane and (001) plane of α phase and β phase are higher in the α - β region than those in the corresponding single phase region. Based on the microstructural studies, mechanism for the hydride growth has also been proposed.

Key words: in situ X-ray diffraction; crystallite size; hydrogen storage alloy; hydride

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1 INTRODUCTION

It's well known that the hydrogen absorption and desorption cycling in the LaNi₅-based AB₅-type alloys always induces high isotropic or anisotropic strains and therefore accelerates the rate of pulverization, which has been considered as the main reason for the degradation of hydrogen storage alloys in the electrochemical cycling^[1]. Therefore, it's necessary to study the properties of the hydrogen-cycling induced strains and other strain-related microstructures, such as the crystallite size, shape and defect that are generated during the hydrogen absorption and desorption cycling.

By using TEM technique, Kim et al^[2, 3] have revealed the dislocations generated during the hydrogen cycling for LaNi₅ system. Furthermore, the densities of dislocations were measured by using the conventional X-ray diffraction method to the activated alloy^[4-6]. However, one of the best ways to investigate the time-resolved structural or micro-structural changes of the alloy in the hydrogen cycling is in-situ X-ray diffraction method^[7-9]. In Ref. [10], we have indicated that the solid solution phase (α phase), the intermediate phase (γ phase) and the hydride phase (β phase) gradually appeared in the hydriding process of alloy $\text{MNi}_{3.75}\text{Co}_{0.75}\text{Mn}_{0.3}\text{Al}_{0.2}$. Transitions among them

can be presented as $\alpha \leftrightarrow \alpha + \gamma \leftrightarrow \beta \leftrightarrow \beta + \gamma \leftrightarrow \alpha$. Besides, a phase that remained in the whole cycling was observed. At the present work, the microstructures, including crystallite size and strain along different (*hkl*) planes are obtained by using in-situ X-ray diffraction method.

2 EXPERIMENTAL

2.1 Alloy preparation

An alloy ingot of $\text{MNi}_{3.75}\text{Co}_{0.75}\text{Mn}_{0.3}\text{Al}_{0.2}$ was prepared by frequency induction melting the La-rich mischmetal and high purity metals of Ni, Co, Mn, Al in an Ar atmosphere and annealing at 1473 K for 10 h. The ingot was further ground to the particle size of 30 μm for X-ray diffraction measurements.

2.2 Electrode preparation

450 mg of active material was combined homogeneously with 75 mg of carbon black and 30 mg of PTFE solution (30%). Then, this mixture was cold pressed onto a nickel foam. The product obtained had a diameter of 20 mm and thickness of 0.5 mm.

2.3 Electrochemical measurement

The electrodes were immersed in 6 mol/L

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KOH electrolyte. The potential was monitored against a Hg/HgO reference electrode. Before the in-situ XRD measurements, the electrode was activated by cycling for several times at C/10 for 12 h and D/10 with a cut-off voltage at 0.5 V (vs Hg/HgO). For in-situ X-ray diffraction measurements, the electrode was charged and discharged at 30, 45, and 60 mA/g, respectively. The cut-off voltage for discharging is 0.5 V (vs Hg/HgO).

2.4 In-situ X-ray diffraction measurement

In order to operate in-situ X-ray diffraction measurement, one special electrochemical cell was designed. It only caused a little loss of X-ray intensity and can be easily controlled as that in the conventional X-ray diffraction method. More details about this instrument can be found in Ref. [10].

2.5 Model for anisotropic line broadening caused by size and strain

It's well-known that most of the LaNi₅-based AB₅-type hydrogen storage alloys have characteristic of anisotropic diffraction-line broadening when subjected to hydrogen absorption and desorption cycling^[11-14]. In the Rietveld refinement method, one of the popular approaches to deal with this (*hkl*) dependent line broadening is using analytical expressions to model it directly. In this paper, the model proposed by Popa^[15] was used to study the crystallite size and strain that varied with the hydrogen absorption and desorption cycling. In this model, a 'composite crystallite' is supposed to give the same diffraction peaks as the crystallites related by the same symmetry operations of Laue group in polycrystals. Size of 'composite crystallite' can be derived by using the invariance condition where its surface is invariant to the operations of Laue group. This model can successfully reduce the number or refinable parameters and is correct for all of the Laue groups. More details for this approach can be found in Refs. [15] and [16].

This size-strain model has been imposed in the Rietveld refinement program MAUD^[17] and the crystallite shape can be drawn out according to the crystallite size along the different (*hkl*) planes.

3 RESULTS AND DISCUSSION

In Ref. [10], it has been indicated that besides α phase and β phase there are also remaining phase and intermediate γ phase in the hydriding-dehydriding cycling. However, because of their small content, results of their micro-structural analysis are therefore excluded in this paper.

3.1 Crystallite size and strain of solid solution phase

Fig. 1 presents the variations of the crystallite size and shape of the solid solution phase (α phase) and the hydride phase (β phase) during the hydrogen absorption and desorption cycling. It indicates that during the cycling, the crystallite shape of the solid solution phase keeps the form of columnar, which is the same as that of the fresh alloy. However, it can also be found in Fig. 1 that in the $\alpha + \beta$ region of the hydriding process, the crystallite size of α phase has a dramatic decrease when the β phase is clearly found. It reveals that the hydride

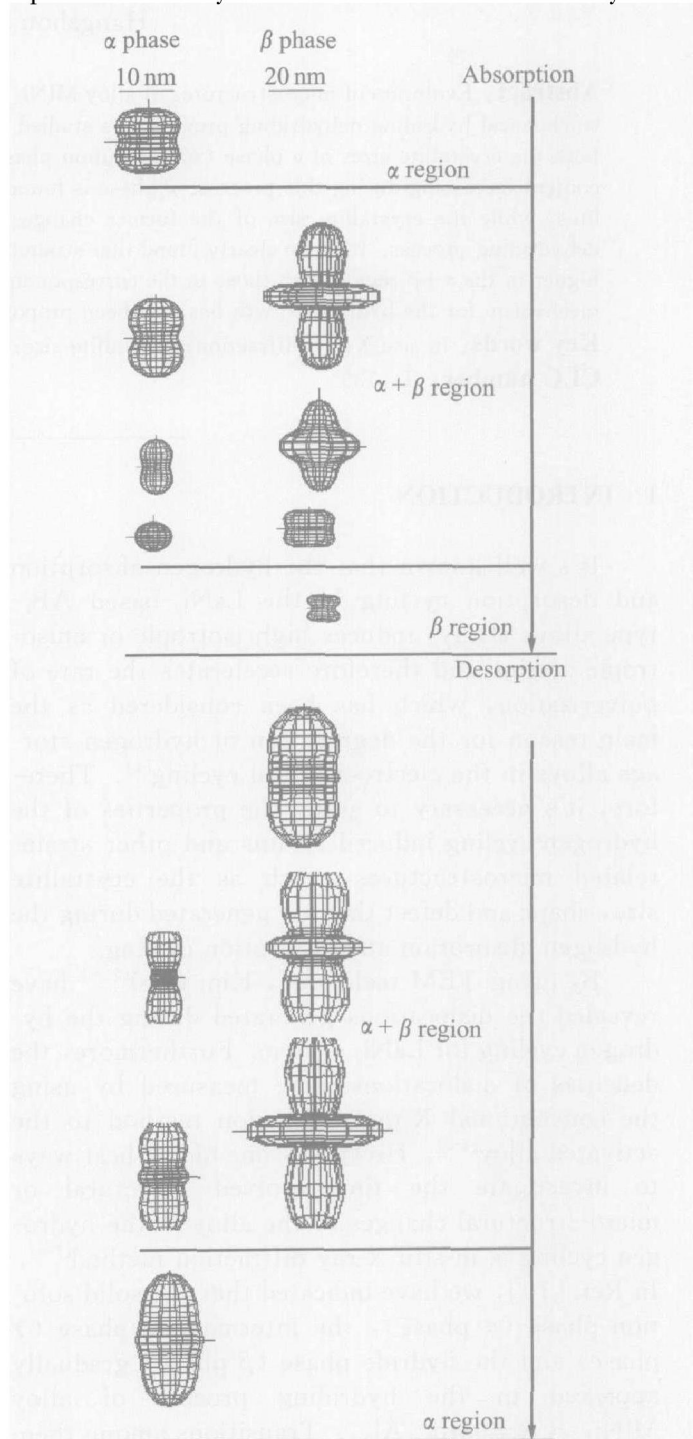


Fig. 1 Evolution of composite crystallite size and shape of matrix (α phase) and hydride precipitates (β phase) during hydrogen absorption-desorption cycling

(β) phase precipitates in the same domains with α phase. This can be confirmed by the facts that strain of α phase and β phase is much higher in the $\alpha + \beta$ region than that in the single phase region, as shown in Figs. 2 (a) and (b). It's commonly believed that the strain, especially along (110) plane, is induced by the discrete lattice expansions between α phase and β phase^[8].

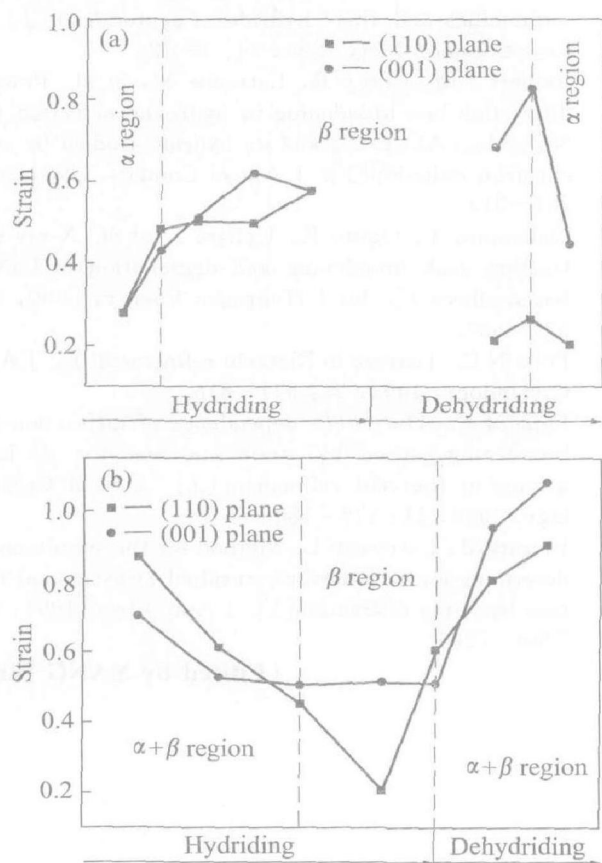


Fig. 2 Lattice strain of α phase(a) and β phase(b) along (001) plane and (110) plane

The above in-the-same-domains mechanism for hydride growth is different from that proposed by Nakamura et al^[9]. Based on the crystallite size of β phase, the hydride phase grows domain by domain. However, as those will be discussed as follows, the crystallite size of β phase is affected by many factors and can't be used as the evidence.

3.2 Crystallite size and strain of hydride phase

Different from the columnar crystallites of the matrix (α phase), crystallites of hydride precipitates (β phase) are composed of the needle-like and the plate-like phases, as shown in Fig. 1. It seems that the size of the plate-like crystallites changes more rapidly than that of the needle-like ones in the hydriding-dehydriding process.

In general, there are two factors that can influence the crystallite size of hydrides. One is the lattice expansion induced by hydrogen absorption. The volume of the crystallites can be increased up

to 25% if they are fully hydrogenated. However, during the hydriding process, lots of dislocations will be formed by lattice strain. As it can be seen in Fig. 2, at the beginning of $\alpha + \beta$ region, strain along (110) plane is much higher than that along (001) plane. The former results in the dislocation at the basal plane. This is in good agreement with those reported by Lim et al^[2, 3] and Wu et al^[4] that the dislocation system $E1 (1/3 \langle \bar{2}110 \rangle (0001))$ with Burgers vector a gliding in the basal planes is dominant at the beginning of the $\alpha + \beta$ region. It has been shown by the fracture studies that this type of dislocation will split the hydrides precipitates along the a -axis in the basal planes into the smaller plate-like precipitates^[6]. However, with the increasing of hydrogen content in the alloy, strains along (110) plane and (001) plane decrease rapidly because the content of α phase that coexists with β phase in the same domains is continuously decreased. However, strain along (110) plane decreases more rapidly than that along (001) plane. Therefore, at this stage, dislocations are mainly induced at the prismatic planes by the lattice strain along (001) plane. As indicated by Lim et al^[2, 3] and Wu et al^[4], the dominant dislocation comes to be $E2 (1/3 \langle \bar{2}110 \rangle (0110))$ which has the Burgers vector a but gliding in the prismatic planes and therefore can change the plate-like precipitates into the needle-like ones^[6].

During the hydrogen desorption process, the lattice strains of hydride along (110) plane and (001) plane increase because the discrete lattice contraction of α phase and β phase and therefore crystallite size and shape change in a way that reverses to that in the hydrogen absorption process, as shown in Fig. 1.

4 CONCLUSIONS

Crystallite size and shape of hydrides of $\text{Mn}_{13.75}\text{Co}_{0.75}\text{Mn}_{0.3}\text{Al}_{0.2}$ vary with the hydrogen content during the electrochemical hydriding-dehydriding process. This variation can be ascribed to the effects of dislocations induced by strains along (001) plane and (110) plane, respectively. Also, a conclusion has been made at the present work that hydrides grow in the same domains as α phase, which have been proved by the changes of strain and evolution of crystallite size of α phase during the hydrogen-induced cycling.

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