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Preparation of TiFe Hydrogen Storage Alloy Thin Films by Intense Pulsed Ion-Beam Evaporation

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Titanium iron (TiFe) is widely known as an intermetallic compound, which shows hydrogen storage characteristics. In the past, Ti-Fe thin films have been tried to prepare by sputtering methods, but crystallized thin films have not been prepared yet. In the present study, the preparation of crystallized TiFe thin films has been attempted by intense pulsed ion-beam evaporation. Using a Ti-50 at.%Fe target, thin films were deposited on soda lime glass substrates and was found to be of mixed phases of crystallized TiFe and $TiFe_2$. On the other hand, thin films deposited on Si(100) substrates consist of an amorphous phase. By using the Ti-40 at.%Fe target, a thin film of single phase TiFe has been successfully prepared on a soda lime glass substrate. Micro cracks were observed on the thin films prepared on a soda lime glass substrate. Even after hydrogenation treatments, the microstructures of the thin films were kept and micronization of the thin films were not observed.
Key words: TiFe, hydrogen storage alloy, thin film, crystallization, IBE

1. INTRODUCTION

Titanium iron (TiFe), widely known as an intermetallic compound, shows hydrogen storage characteristics. It reacts with hydrogen, producing metal hydride. In general, lattices of hydrogen storage alloys expand by absorbing hydrogen, and contract by desorbing hydrogen. However, there is a problem that the bulk hydrogen storage alloys would be micronized in repetitive contractions and expansions. Although, several phases such as TiFe, $TiFe_2$, and β-Ti alloy were known in Ti-Fe binary equilibrium system, TiFe is the only phase that shows hydrogen storage characteristics. In the past, Ti-Fe thin films have been tried to prepare by sputtering methods [1][2], but crystallized, single-phase TiFe thin films have never been prepared yet. Thus, new thin film preparation methods have to be developed to obtain single-phase crystallized TiFe thin films.

A new thin film preparation method of intense pulsed ion-beam evaporation (IBE) [3], has been developed. In this method, high-density ablation plasma is deposited on substrates that are placed near a target. Various kinds of crystallized thin films including intermetallic compounds such as TiAl [4] have been prepared by IBE. It is considered that the heat flux associated with the high temperature and high-density plasma tends to assist the crystallization without oxidation during the deposition on the substrates. In the present work, Ti-Fe thin films are prepared on Si and soda lime glass substrates at room temperature by IBE.

2. EXPERIMENTS

Figure 1 shows the schematic of the experimental arrangement for the preparation of thin films by IBE. The left-hand side represents the ion beam diode section to produce an intense pulsed light ion beam (LIB), while the right-hand side the preparation section of thin films. An intense pulsed-power generator "ETIGO-II" [5] was utilized in the experiment. Table I summarizes the experimental conditions. The preparation of the thin films was attempted using two kinds of targets with different compositions of Ti-50 at.%Fe and Ti-40 at.%Fe. Distance between anode and

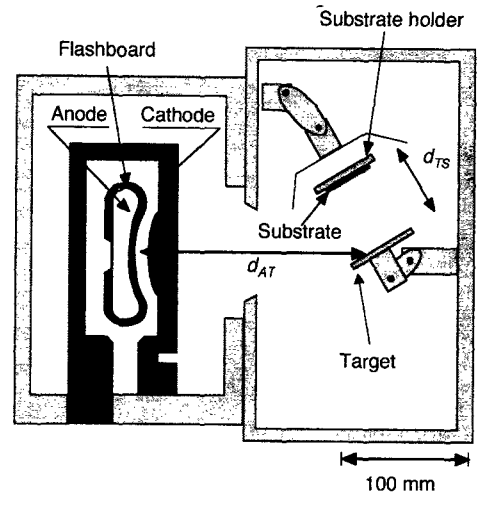

Fig.1 Outline of the experimental arrangement.

target (d_{AT}) and distance between target and substrate (d_{TS}) was changed. The chemical composition of the targets and the thin films were determined by X-ray fluorescence analysis (XRF) and energy-dispersive X-ray spectroscopy (EDX). The phases in the thin films were identified by X-ray diffraction (XRD) using CuKα radiation of 0.154 nm. In order to obtain the hydrogen storage characteristics, the thin films were kept in hydrogen gas at high temperature. The conditions of hydrogenation treatments were described in Table II.

Table I Experimental conditions.

Targets	Sintered Compact (Ti-50 at.%Fe, Ti-40 at.%Fe)
Substrate	Si(100), Soda Lime Glass
d_{AT}	170-180 mm
d_{TS}	90 mm
Number of Shots	3
Substrate Temperature	Room Temperature
Ambient Pressure	10^{-2} Pa

Table II Conditions of hydrogenation treatments.

Step	Holding Time (h)	Holding Pressure (MPa)	Holding Temperature (°C)	Evacuation Time (h)
1st	8	3.4	350	2
2nd	6	3.4	350	2
3rd	8	3.4	350	2
4th	6	3.4	350	2
5th	13	3.4	350	2
6th	6	3.4	350	2

3. RESULTS AND DISCUTTIONS

Ti-Fe thin films were deposited on Si(100) wafer and soda lime glass substrates. The thickness of all thin films was about 500-600 nm. Figure 2 shows the XRD patterns of the thin films deposited by using the Ti-50 at.%Fe target on (a)

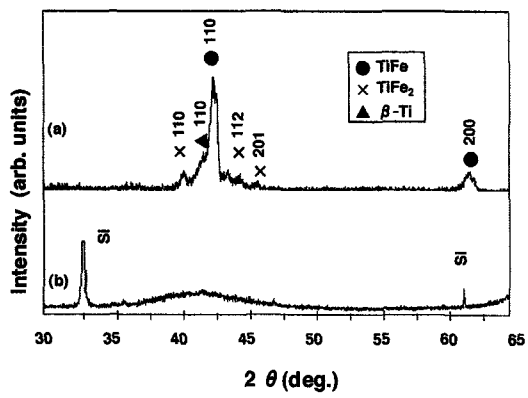

Fig. 2 XRD patterns of the thin films deposited by Ti-50 at.%Fe target at d_{AT} = 170 mm and d_{TS} = 90 mm on (a) glass substrate, (b) Si(100) substrate.

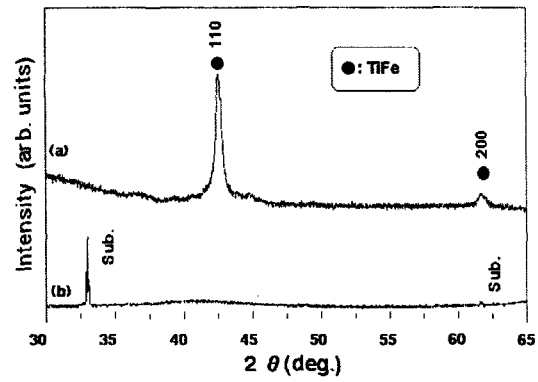

Fig. 3 XRD patterns of the thin films deposited by using Ti-40 at.%Fe target at d_{AT} = 180 mm and d_{TS} = 90 mm on (a) glass substrate, (b) Si(100) substrate.

the soda lime glass substrate and (b) the Si(100) substrate. From the result of EDX analysis for the Ti-Fe thin film prepared on the Si(100) substrate, the chemical composition of the thin films was Ti-49 at.%Fe, which was almost the same as that of the target. The thin film deposited on the glass substrate has been well crystallized (Fig. 2(a)). The strongest peak at 43° corresponds to the 110 reflection of TiFe phase. This result indicates that TiFe phase was successfully crystallized in the thin film prepared by IBE. Since small peaks for $TiFe_2$ phase also exist in Fig. 2(a), small amount of $TiFe_2$ grains co-exists in the thin film. In the meantime, since the XRD pattern in Fig. 2(b) shows a harrow peak of amorphous, the thin film deposited on the Si(100) substrate has not been crystallized. This difference in crystallinity between the thin films may come from the difference in thermal conductivity of substrates [6].

Figure 3 shows the XRD patterns of the thin films deposited by using the Ti-40 at.% Fe target on (a) the soda lime glass substrate and (b) the Si(100) substrate. From the result of EDX analysis, the actual thin film composition was observed to be Ti-37 at.%Fe. The thin film deposited on the Si(100) substrate (Fig. 3(b)) has not been crystallized. This is similar to the thin films prepared using the Ti-50 at.% Fe target (Fig. 2(b)). From Fig. 3(a), the XRD pattern for the thin film deposited on the glass substrate has two peaks. Both peaks correspond to reflections from TiFe phase. This result indicates that the thin film of almost single phase TiFe has been successfully prepared by IBE.

In order to obtain the hydrogen storage characteristics of the thin films, the hydrogenation treatments were carried out. The thin films deposited by using the Ti-40 at.%Fe target at d_{AT} = 180 mm and d_{TS} = 90 mm on soda lime glass substrate were kept in hydrogen atmosphere at 350 °C. The details of hydrogenation conditions were described in Table II. The thin films could be considered to

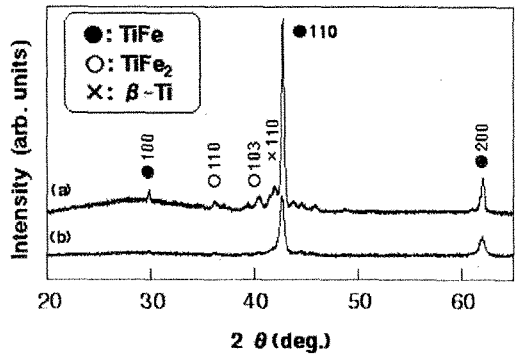

Fig. 4 XRD patterns of the thin films (a) before and (b) after hydrogenation treatments.

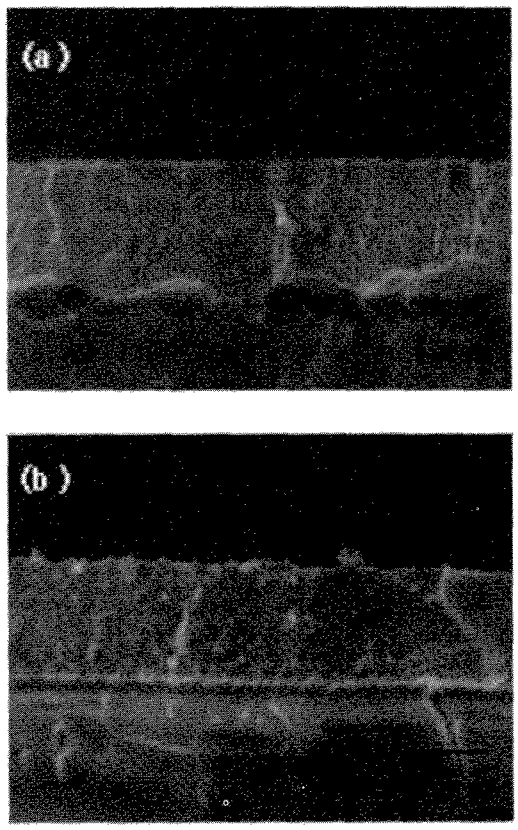

Fig.5 SEM images of the thin films deposited by using Ti-40 at.%Fe target (a) before hydrogenation (b) after hydrogen desorbing.

undergo hydrogen absorbing and desorbing by this hydrogenation conditions. The XRD patterns of thin films before and after the hydrogenation treatments were shown in Fig. 4(a) and (b), respectively. The thin films kept TiFe structure as a main phase even after the hydrogenation treatments, and the structural change of TiFe phase could not been observed after the hydrogenation. The second phases ($TiFe_2$ and β-Ti) which were observed in Fig. 4(a) were disappeared in Fig. 4(b). These second phases seem to be transformed to TiFe phase due to annealing effect during the hydrogenation treatments.

Figure 5 shows the cross sectional SEM images of the thin films (a) before and (b) after the hydrogenation treatments respectively. In Fig.5 (a), it was found that the thin film consisted of small grains, and layer boundaries could not be observed. The grain size of the thin film after hydrogenation, as showing in Fig. 5(b), seems to be larger than that of the thin films before hydrogenation as shown in Fig. 5(a). It is considered that this grain growth was occurred by annealing effect keeping at 350 °C during hydrogenation treatment. However, no cracks or micronization of the thin films could not been observed after hydrogenation.

4. CONCLUSIONS

We have attempted to prepare thin films of Ti-Fe intermetallic compounds by IBE. Chemical composition and phases in the thin films were investigated, and the following conclusions were drawn.

(1) Thin films of Ti-Fe intermetallic compounds could be prepared by IBE.
(2) Using a Ti-50 at.%Fe target, the thin film has been found to be the mixed phases of TiFe and $TiFe_2$.
(3) Using a Ti-40 at.%Fe target, the thin film of single phase TiFe was successfully prepared on a soda lime glass substrate.
(4) The thin films deposited on a Si(100) substrate consisted of amorphous phases.
(5) TiFe phase was remained in the thin films after the hydrogenation treatments.

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