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## Hydrogenation of Amorphous and Crystalline RE-Ni Alloys\*

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## Synopsis

Amorphous alloys with the combination of a rare earth metal (RE = Y, La, Ce, Pr and Sm) and nickel were prepared around the composition at an eutectic point by the melt-quenching technique. Amorphous Y-Ni and Sm-Ni alloys absorbed a large amount of hydrogen even in the amorphous state, while the other alloys in La-Ni, Ce-Ni and Pr-Ni systems were decomposed to a mixture of crystalline phase and hydride during hydrogenation at 323 K. An amorphous  $\text{SmNi}_2$  phase was also synthesized by reaction of hydrogen gas with the crystalline  $\text{SmNi}_2$  compound below about 500 K. The hydrogen absorption capacity of the melt-quenched amorphous Sm-Ni alloys was smaller than those of both the corresponding crystalline alloys and the amorphous  $\text{SmNi}_2$  alloy obtained by reaction of hydrogen.

## I. Introduction

Recently considerable attention has been attracted to hydrogen absorption properties of melt-quenched amorphous alloys and to the effect of hydrogen on the structural, electric and magnetic properties of amorphous alloys<sup>1)</sup>. However, many of investigations have been concerned with the alloys containing IVa group elements such as Ti, Zr and Hf<sup>2)-6)</sup> and little information is available on the hydrogen absorption properties of amorphous alloys consisting of rare earth and 3d transition metal. Such amorphous alloys may have several potential advantages over the crystalline counterparts. For instance, they may

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not disintegrate into powders during hydrogen absorption process. Further, they form a continuous series of alloy compositions which may prove advantageous for tailoring properties to specific applications.

In the present paper we report the results on the formation range and the crystallization temperature of the melt-quenched rare earth metal (RE = Y, La, Ce, Pr and Sm)-nickel amorphous alloys and on hydrogen absorption properties of these alloys. In addition, we report that the crystalline  $\text{SmNi}_2$  compound forms an amorphous phase by reaction of hydrogen.

## II. Experimental

RE-Ni mother alloys were prepared from pure metals [Y(99.6%), La(99.8%), Ce(99%), Pr(99.5%), Sm(99.8%) and Ni(99.9 %)] by arc melting under an argon atmosphere. Subsequently, these mother alloys were rapidly quenched using a single roller-type melt-quenching apparatus under an argon atmosphere. The quenched samples obtained were in the form of ribbon with 0.01-0.02 mm thickness and 1-2 mm width. Structure of the as-quenched samples was examined by an X-ray diffraction using  $\text{Cu-K}\alpha$  radiation in combination with an X-ray monochromator. The crystallization temperature,  $T_x$ , of the amorphous samples was measured in a purified argon atmosphere with a differential thermal analyzer (DTA) at a heating rate of  $1.67 \times 10^{-1}$  K/s. The hydrogenation treatment was conducted in a constant temperature reactor. Pulverized amorphous or crystalline samples were exposed to high pure hydrogen (7N) of 5 MPa in stainless steel reactor. The amount of hydrogen absorbed was determined from the pressure change in a known volume system. Structure of hydrogenated sample was identified with an X-ray diffractometer. The crystallization temperature and hydrogen desorption behavior of the amorphous Sm-Ni sample synthesized from the crystalline alloy were examined simultaneously by both DTA and TG (thermogravimetry) under an argon atmosphere at a heating rate of  $3.33 \times 10^{-1}$  K/s.

## III. Results and Discussion

### 1. Formation range of amorphous phase and crystallization temperature

Prior to hydrogen absorption experiments, the alloy compositions producing an amorphous phase were investigated. As an example, the structures of as-quenched La-Ni alloys are displayed on the equilib-

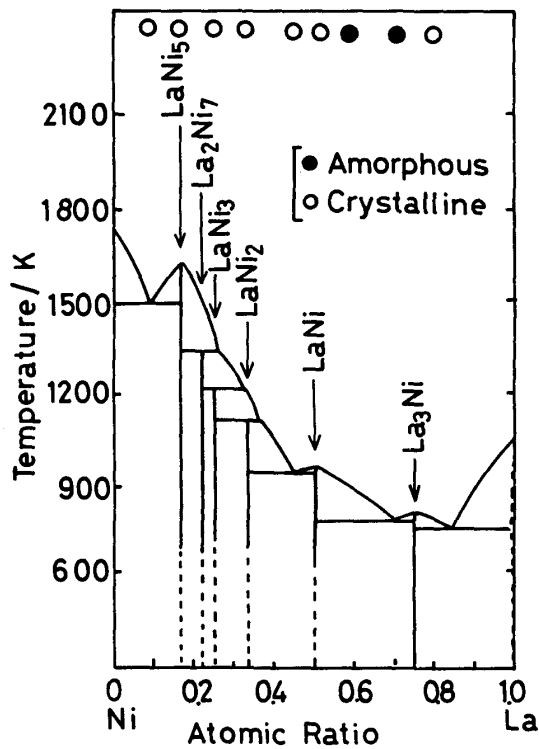


Fig. 1 Structure of La-Ni alloy samples obtained by the melt-quenching. Close circles show the amorphous phase and open circle the crystalline phase.

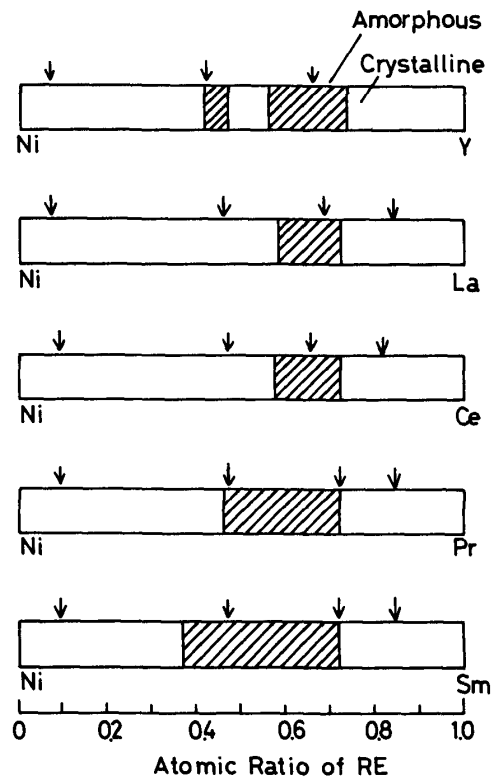


Fig. 2 Formation ranges of amorphous RE-Ni alloys obtained by melt-quenching.

rium phase diagram<sup>7)</sup> shown in Fig. 1. It can be seen in this figure that amorphous phase is obtained in a narrow composition range of 0.6-0.7 atomic ratio of La, at the present quenching condition. However, no amorphous phase is obtained at the composition of the well-known hydrogen absorbing alloys,  $\text{LaNi}_5$ .

The formation ranges of amorphous RE-Ni alloys are collectively shown in Fig. 2. In this figure, arrow marks show the composition of the eutectic points. The amorphous RE-Ni phases are produced around the composition close to the eutectic points in the same manner as usual melt-quenched amorphous alloys. Among these alloy systems, the amorphous Sm-Ni phase is obtained in the widest composition range, 0.4-0.7.

Fig. 3 shows DTA curves of the as-prepared amorphous Sm-Ni alloys. As seen in the figure, the amorphous Sm-Ni alloys exhibit two exothermic peaks at about 450-520 K. From these DTA curves, the crystallization temperature  $T_x$ , was determined as the temperature corresponding to the intersection of the extrapolated base line and the steepest tangent of the first exothermic peak.  $T_x$ 's of the melt

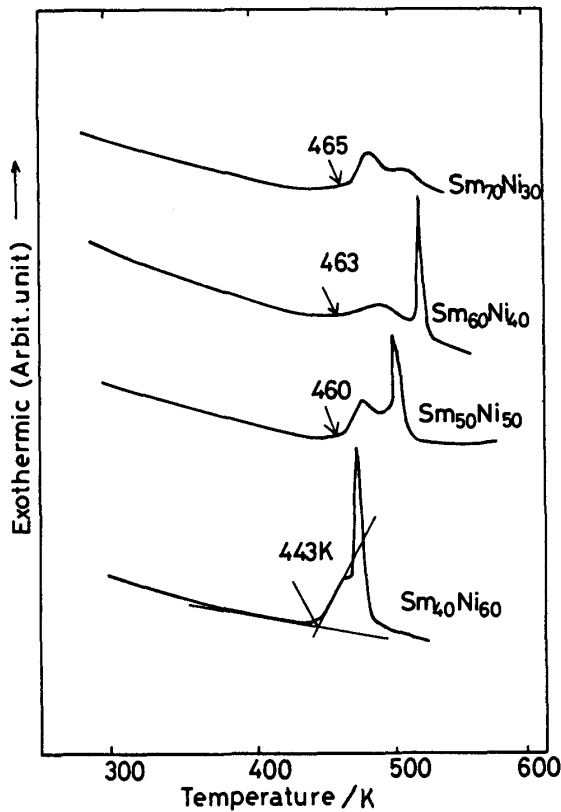


Fig. 3 DTA curves of the melt-quenched Sm-Ni amorphous alloys.

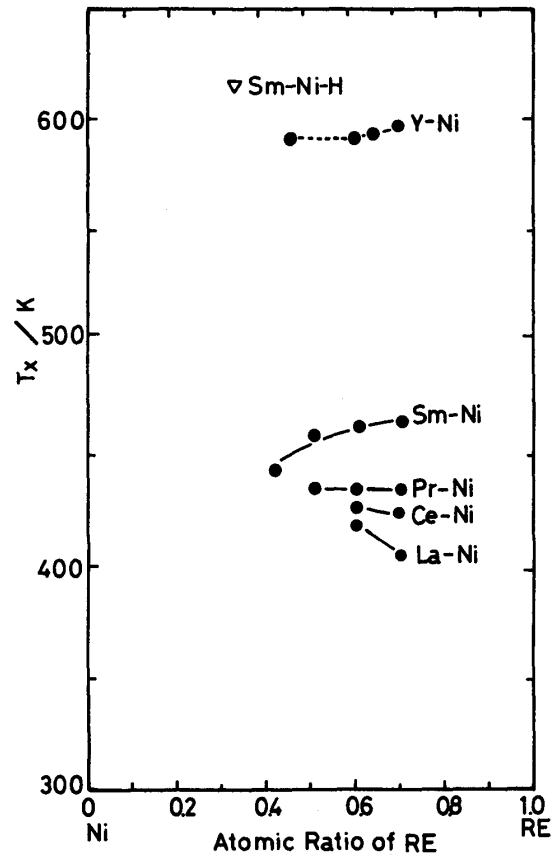


Fig. 4 Crystallization temperatures of amorphous RE-Ni alloys.

quenched amorphous RE-Ni alloys are shown as a function of alloy composition in Fig. 4.  $T_x$ 's of the amorphous RE-Ni alloys containing La, Ce, Pr and Sm are between 400-470 K, being considerably lower compared with those of usual metal-metal type amorphous alloys. On the other hand,  $T_x$ 's of the amorphous Y-Ni alloys are higher than those of the other amorphous RE-Ni alloys by about 100-200 K, probably due to their high melting points.

## 2. Structure change of amorphous $RE_{60}Ni_{40}$ alloys by hydrogenation

In order to make clear whether the RE-Ni alloys absorb a large amount of hydrogen in the amorphous state, the amorphous  $RE_{60}Ni_{40}$  alloys produced by rapid quenching were heat treated at 323 K for 86.4 ks under a pressure of 5 MPa hydrogen gas. Fig. 5 shows X-ray diffraction (XRD) patterns of the as-quenched and hydrogenated amorphous  $Sm_{60}Ni_{40}$  alloys. The profile of the XRD pattern of the sample hydrogenated at 323 K is similar to that of the as-quenched

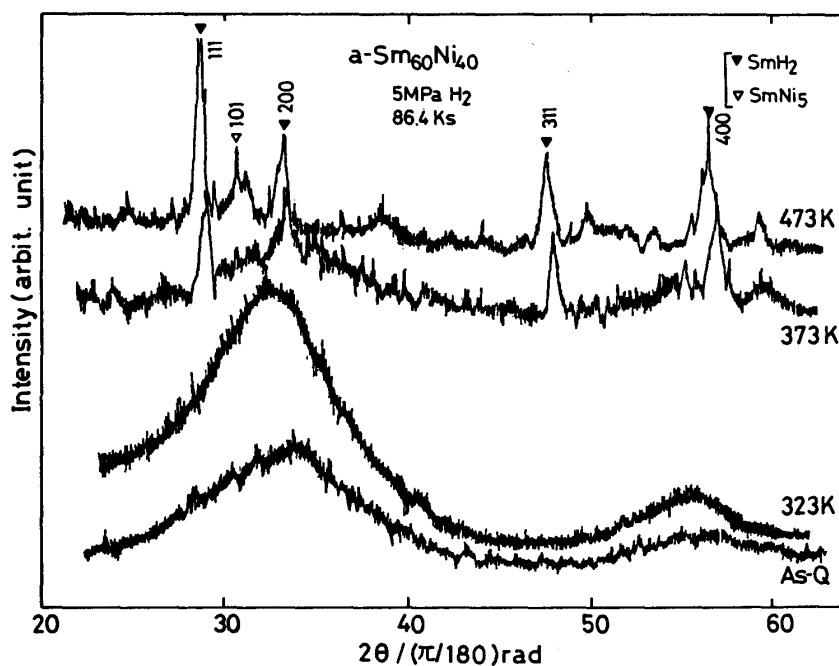


Fig. 5 X-ray diffraction patterns of the amorphous  $\text{Sm}_{60}\text{Ni}_{40}$  alloys hydrogenated at various temperatures for 86.4 ks under hydrogen pressure of 5 MPa.

sample, which is characterized by broad peaks typically observed in many other amorphous alloys. However, the peak position for the hydrogenated sample is seen to shift slightly towards lower angle side, indicating that the absorption of hydrogen results in a volume expansion of the sample. For the sample hydrogenated at 373 K, on the other hand, several diffraction peaks of the samarium hydride  $\text{SmH}_2$  appear overlapping with the amorphous peaks, and they become stronger with increasing temperature. At 473 K, the amorphous peaks completely disappear and the diffraction peaks of  $\text{SmNi}_5$  compound appear in addition to the peaks of  $\text{SmH}_2$ .

Table 1 shows the structures of various  $\text{RE}_{60}\text{Ni}_{40}$  alloy samples hydrogenated at 323 K for 86.4 ks. Amorphous  $\text{Y}_{60}\text{Ni}_{40}$  and  $\text{Sm}_{60}\text{Ni}_{40}$  alloys absorb a large amount of hydrogen as remaining the amorphous state, while the other alloys containing La, Ce and Pr with lower crystallization temperatures are crystallized by an exothermic reaction of hydrogen absorption. From these results, further investigation was focused to the Sm-Ni system, in which the amorphous phase is formed in wider composition range and absorbs a large amount of hydrogen in the amorphous state.

Table 1 Structures of amorphous  $RE_{60}Ni_{40}$  alloys after hydrogenation at 323 K for 86.4 ks under 5 MPa hydrogen.

Alloys	Structure		Crystallization temperature
	As-quenched	Hydrogenated	
$Y_{60}Ni_{40}$	Am	Am[1.8 (H/M)]	585 K
$La_{60}Ni_{40}$	Am	Crystalline	414 K
$Ce_{60}Ni_{40}$	Am	Crystalline	427 K
$Pr_{60}Ni_{40}$	Am	Crystalline	435 K
$Sm_{60}Ni_{40}$	Am	Am[1.25 (H/M)]	456 K

### 3. Hydrogen absorption capacity

In Fig. 6, hydrogen absorption capacity, (H/M), defined as the number of hydrogen atom per metal atom at the maximum hydrogen content, is plotted against the concentration of Sm for the amorphous and crystalline alloys of Sm-Ni series. As seen in the figure, the Sm-Ni alloys have a large absorption capacity even at 283 K in both the amorphous and crystalline states and the values in the amorphous state are always lower than those in the crystalline state.

Fig. 7 illustrates the number of hydrogen atom absorbed per one Sm atom, H/Sm, replotted as a function of alloy composition. The values of H/Sm for the crystalline alloys are scattering within the range from 3 to 4 probably depending on their crystal structure, while those for the amorphous ones are approximately at the level of 2. Such a large difference in the H/Sm value between amorphous and crystalline phases may be explained by the type and size of vacant sites contained in both the structures. Unfortunately, however, we have a little information about the sites of hydrogen atoms in amorphous and crystalline Sm-Ni alloy system at the present time.

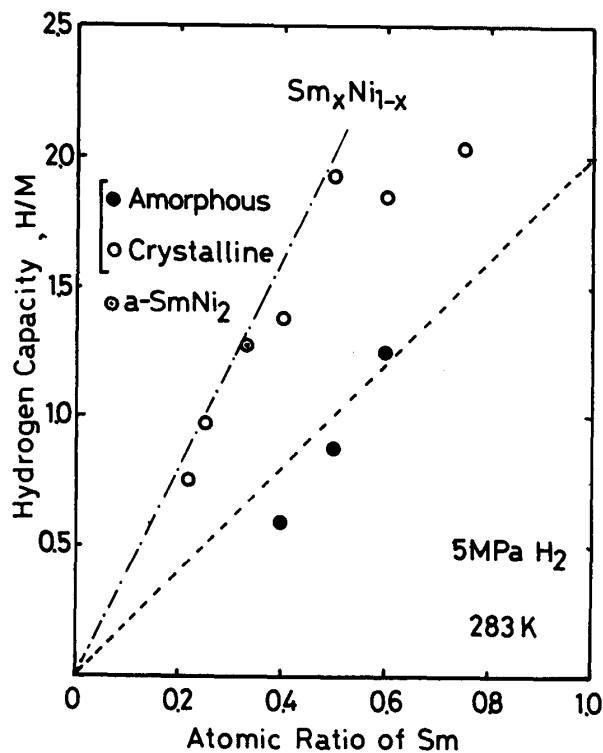


Fig. 6 Compositional dependence of the hydrogen absorption capacity, H/M, for the amorphous and crystalline Sm-Ni alloys.

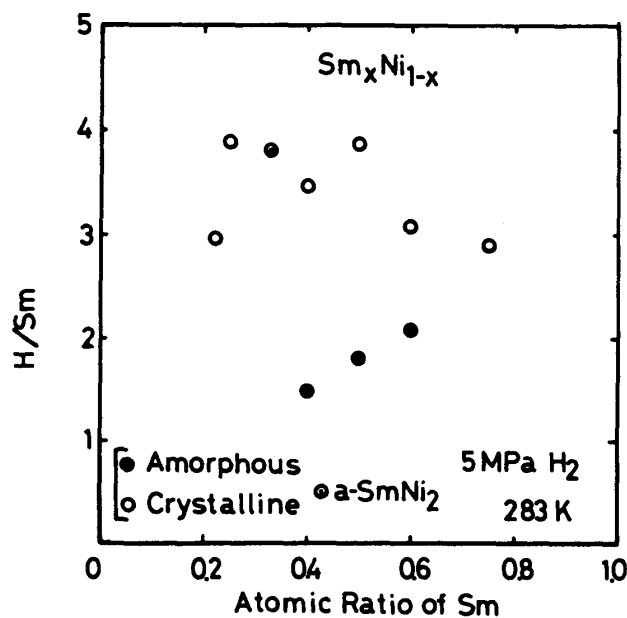


Fig. 7 Compositional dependence of the number of hydrogen atoms absorbed per one Sm atom for the amorphous and crystalline Sm-Ni alloys.



#### 4. Formation of amorphous phase by hydrogenation of crystalline $\text{SmNi}_2$ compound

It has been known so far that the La-Ni compounds such as  $\text{La}_7\text{Ni}_3$ ,  $\text{LaNi}_2$ ,  $\text{LaNi}_3$  and  $\text{La}_2\text{Ni}_7$  change to the amorphous phase by hydrogenation at room temperature<sup>8)</sup>. Therefore, we have tried the same treatment against the Sm-Ni series alloys. As a result, only  $\text{SmNi}_2$  compound among six intermetallic compounds in Sm-Ni system was found to become an amorphous phase at room temperature by hydrogenation treatment.

Fig. 8 shows the change of XRD pattern after hydrogenation at each temperature for 86.4 ks for the as-quenched crystalline  $\text{SmNi}_2$  samples. The diffraction pattern of the as-quenched sample indicates that this sample consists mainly of  $\text{SmNi}_2$  compound with  $\text{MgCu}_2$  crystal structure. However, in the diffraction pattern of samples hydrogenated at 283 and 373 K, these sharp peaks completely disappear and only a broad peak is observed. This fact means that the amorphous phase has been formed from the crystalline  $\text{SmNi}_2$  phase by hydrogenation. At the higher hydrogenation temperature of 773 K, two types of diffraction peaks corresponding to  $\text{SmH}_2$  and  $\text{SmNi}_5$  are observed.

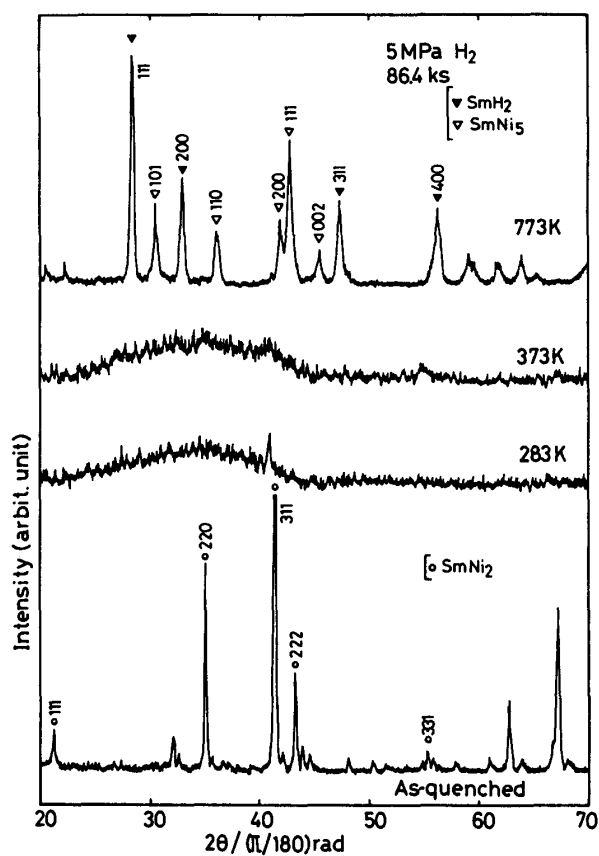


Fig. 8 X-ray diffraction patterns of the as-quenched  $\text{SmNi}_2$  alloys hydrogenated at various temperatures for 86.4 ks under hydrogen pressure of 5 MPa.

Fig. 9 shows DTA and TG curves of an amorphous sample obtained by hydrogenation of the as-quenched  $\text{SmNi}_2$  crystalline phase. This amorphous sample exhibits a single exothermic peak at about 630 K. The crystallization temperature,  $T_x$ , indicating by arrow mark in the figure is also plotted in Fig. 4. It is seen that the  $T_x$  value of amorphous  $\text{SmNi}_2$  phase synthesized from the crystalline compound is considerably higher compared with those of the as-quenched amorphous Sm-Ni phases. From the data of DTA and TG, it seems that desorption of hydrogen stored in sample takes place accompanying a slight weight loss during heating above about 300 K and almost a half part of hydrogen is desorbed below  $T_x$ . This fact seems to show that the presence of hydrogen in SmNi phase holds an amorphous structure in more stable state. However, the mechanism of transformation from crystalline state to amorphous one by hydrogenation is still unclear.

In Figs. 6 and 7, the hydrogen absorption capacity and the number of H/Sm of amorphous  $\text{SmNi}_2$  phase are plotted together with those of amorphous Sm-Ni series alloys. The hydrogen absorption capacity is much higher than other amorphous alloys and is comparable to those of Sm-Ni crystalline alloys. Also the number of hydrogen atom absorbed per one Sm atom is about 4 corresponding to the case of Sm-Ni crystalline alloys. This fact implies that the structure of amorphous  $\text{SmNi}_2$  phase prepared from the crystalline state may be different with that of hydrogenated amorphous alloys.

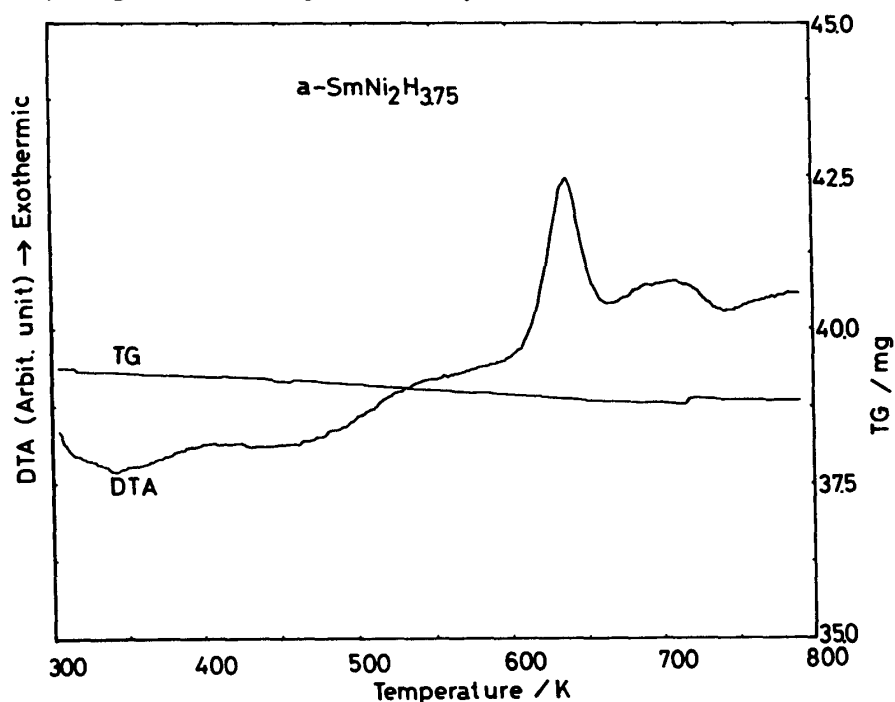


Fig. 9 DTA and TG curves of the amorphous  $\text{SmNi}_2$  sample obtained by hydrogenation at 323 K.

## IV. Conclusions

Rare earth metal (RE = Y, La, Ce, Pr and Sm)-nickel binary amorphous alloys were prepared in the form of ribbon by the melt-quenching technique. The formation ranges of these amorphous alloys were located mainly in the vicinity of the eutectic points. The amorphous Y-Ni and Sm-Ni alloys absorbed a large amount of hydrogen in the amorphous state, while the amorphous La-Ni, Ce-Ni and Pr-Ni alloys were decomposed to crystalline phase due to exothermic reaction by hydrogen absorption during hydrogenation treatment. On the other hand, it was found that amorphous  $\text{SmNi}_2$  phase is formed by hydrogenation of crystalline  $\text{SmNi}_2$  compound at lower temperatures below 500 K. The hydrogen absorption capacity of the melt-quenched amorphous Sm-Ni alloys was smaller than those of both the corresponding crystalline alloys and the amorphous  $\text{SmNi}_2$  alloy obtained by hydrogenation.

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