Crystallization of Amorphous GdFe_2H_x Alloys Prepared by Hydrogen Absorption

Crystallization of Amorphous $GdFe_2H_x$ Alloys Prepared by Hydrogen Absorption *

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(Received October 22, 1988)

Synopsis

Amorphous a-$GdFe_2H_x$ alloys were prepared by two kinds of technique, i.e., the newly developed hydrogen-induced amorphization (HIA) of the Laves phase c-$GdFe_2$ and hyrogenation of the rapidly quenched amorphous a-$Gd_{33}Fe_{67}$ alloy. The formation of a-$GdFe_2H_x$ by hydrogen absorption was found to occur between 473 K and 573 K where the decomposition of c-$GdFe_2$ into the elemental hydride GdH_2 and α-Fe is suppressed. On the other hand, the rapidly quenched a-$Gd_{33}Fe_{66}$ alloy could absorb hydrogen in the amorphous state below 523 K. The crystallization behavior of the hydrogen-induced amorphous a-$GdFe_2H_{3.6}$ alloy was similar to that of the hydrogenated amorphous a-$Gd_{33}Fe_{67}H_{120}$ alloy. That is, the DSC curves of the a-$GdFe_2H_x$ alloys showed a broad endothermic peak resulting partial desorption of hydrogen together with two exothermic peaks. The first exothermic peak was associated with the crystallization of the amorphous phase into GdH_2 and α-Fe, and the second one was attributed to the growth of them. On the other hand, a-$Gd_{33}Fe_{67}$ crystallized polymorphously to the Laves phase c-$GdFe_2$ showing an exothermic peak.

I. Introduction

Within the past decade, hydrogen absorption characteristics of rapidly quenched amorphous alloys and characterizations of the hydrogenated amorphous alloys have received increased attention. Amorphous alloys offer specific advantages over crystalline alloys in regards to the hydrogen storage capacity, the resistance to the embrittlement, and the property modification through the substitutional alloying. Recently, it was demonstrated that a

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* The 1839th report of Institute for Materials Research
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hydrogen absorbed amorphous alloy can be synthesized by hydrogenation of Zr_3Rh having the $L1_2$ structure (1). Subsequently, it was found out that hydrogen-induced amorphization (HIA), i.e., the transformation from the crystalline to the amorphous state, occurs in many intermetallic compounds with the $L1_2$(2,3), C15(4-9), C23(10) and $D0_{19}$(11) structure, although its mechanism is still uncertain. Since amorphous alloys are thermally unstable, it is important to establish the thermal stability and the crystallization behavior of them. Although crystallization of rapidly quenched amorphous alloys have extensively been investigated so far, there has been little work on the hydrogen-induced amorphous alloy except for a-$SmNi_2H_x$(12). This paper describes a study of the formation of the a-$GdFe_2H_x$ alloys by hydrogen absorption and by hydrogenation of the rapidly quenched amorphous alloy, and of crystallization of the resultant amorphous alloys.

II. Experimental

The $GdFe_2$ compound was prepared by arc melting using high-purity metals [Fe(99.99%), Gd(99.9%)] in an argon atmosphere. The ingot was homogenized at 1073 K for 1 week in an evacuated quartz tube in order to obtain a single phase. Pulverized crystalline c-$GdFe_2$ samples (under 100 mesh) and amorphous a-$Gd_{33}Fe_{66}$ flakes prepared by rapid quenching of a melt in an argon atmosphere were reacted slowly with high purity hydrogen (7N) of 5 MPa at temperatures between 293 K and 673 K for 7.2 ks. Structures of the samples before and after hydrogenation were examined by powder x-ray diffraction (XRD) using a monochromated Cu K_α radiation. Some samples were further examined by transmission electron microscopy(TEM). The samples for TEM were prepared by crushing in ethanol. The amount of hydrogen absorbed or desorbed was determined by measuring the change of H_2 pressure in a constant volume reactor or analyzed the thermal conductivity of an argon-gas atmosphere in which the hydrogenated sample was remelted to desorb hydrogen. The crystallization behavior of the amorphous alloys prepared by two methods was investigated by differential scanning calorimetry (DSC) in a pure argon gas at a heating rate of 40 K/min. The nature of the observed heat effect was determined by heating the samples to distinct stages in the DSC run, followed by a rapid cooling to room temperature and subjecting them to TEM.

III. Results and discussion

(1) Formation of an amorphous phase by hydrogen absorption

Figure 1 shows powder x-ray diffraction (XRD) patterns of the $GdFe_2H_x$ samples hydrogenated at various temperatures. The XRD pattern of the homogenized sample indicates that this consists of a single phase having the $MgCu_2$ type Laves structure. $GdFe_2$ absorbs hydrogen in the crystalline state at 293 K, although the position of the Bragg peaks shifts to the lower angle side, indicating the volume expansion of the lattice. On hydrogenation at 373 K, a broad maximum appears overlapped with the Bragg peaks. In the XRD pattern of the sample hydrogenated between 473 K and 573 K, Bragg peaks disappear and are replaced by the broad maximum. At higher hydrogenation temperature of 623 K, two types of Bragg peaks corresponding to GdH_2 and α-Fe are observed.

Figure 2 shows a bright-field image (a) and the corresponding diffraction pattern (b) of the $GdFe_2H_x$ sample showing a broad maximum (hydrogenated at 473 K). The microstructure is featureless and the diffraction pattern shows a diffuse halo. These indicate that the alloy has become amorphous by hydrogen absorption. The amount of hydrogen absorbed is 1.2(H/M) (expressed as the hydrogen to metal atom

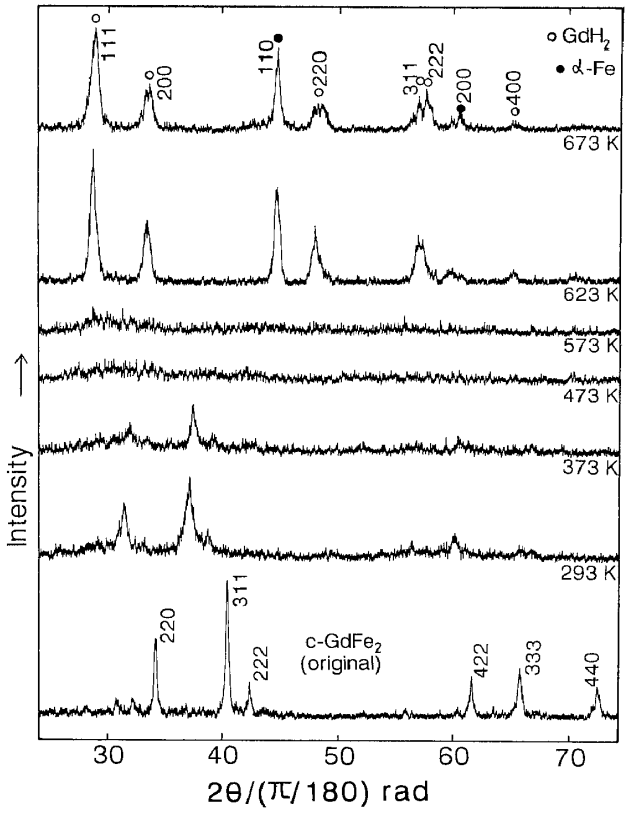

Figure 1
X-ray diffraction patterns of the $GdFe_2$ compounds hydrogenated at various temperatures.

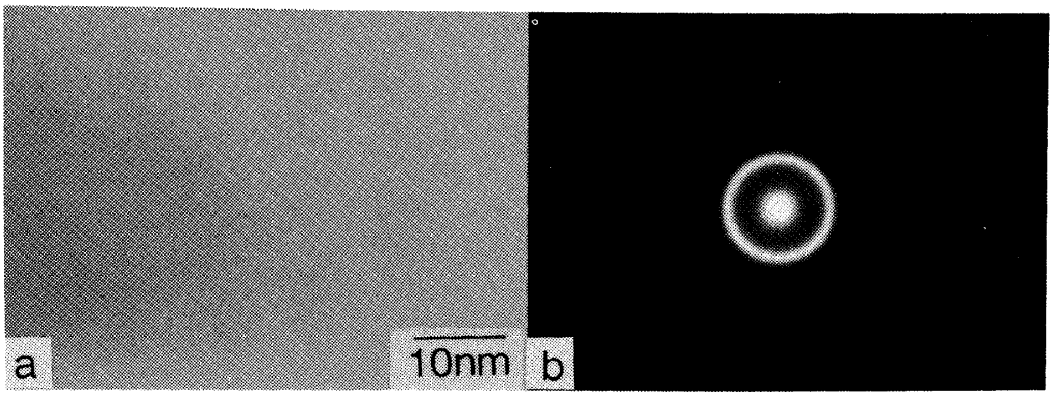

Figure 2 A transmission electronmicrograph (a) and the diffraction pattern (b) of the $GdFe_2H_{3.6}$ alloy hydrogenated at 473 K.

ratio), so that the amorphous alloy is written as a-$GdFe_2H_{3.6}$. The single phase a-$GdFe_2H_{3.6}$ is formed between 473 K and 573 K where the decomposition of the compound into GdH_2 and α-Fe is suppressed. On the other hand, the rapidly quenched a-$Gd_{33}Fe_{67}$ alloy can absorb 1.2 (H/M) hydrogen below 523 K, so that the alloy is written as a-$Gd_{33}Fe_{67}H_{120}$. However, it decomposes into GdH_2 and α-Fe above 550 K. A same amount of hydrogen dissolves in two amorphous alloys prepared by the different methods. This suggests that the structure of both amorphous alloys is nearly same.

Figure 3 shows a scanning electron micrograph (SEM) of the a-$GdFe_2H_{3.6}$ samples prepared by hydrogenation at 473 K. Unexpectedly, the samples retain their original shape and size, i.e., no spontaneous disintegration occurs. The hydrogen absorbed samples are so brittle that they pulverize easily into fine powders by the grinding or the crushing. Therefore, we propose that HIA is a promising method

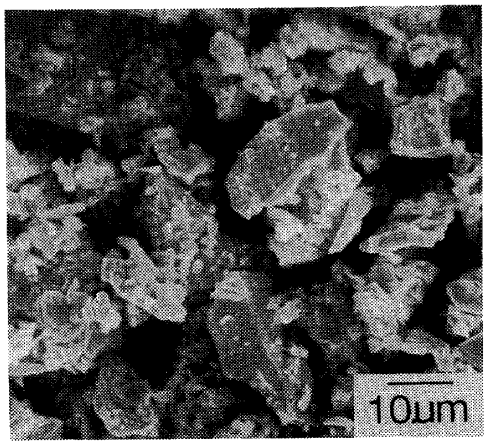

Figure 3
A scanning electron micrograph (SEM) of the amorphous a-$GdFe_2H_{3.6}$ alloy prepared by hydrogenation at 473 K.

for the preparation of amorphous fine powders. The disappearance of Bragg peaks in the XRD pattern of hydrogenated intermetallic compounds has sometimes been reported (13-14). However, it was uncertain until recently whether the alloys showing no Bragg peak are amorphous or not, because compounds disintegrate into fine powders by hydrogenation and the Bragg peak width is inversely proportional to the particle size, leading to the disappearance of sharp Bragg peaks. Therefore, the simple observation of the XRD pattern is insufficient to distinguish amorphization from the disintegration into fine powders. The present authors have recently, confirmed the amorphous nature of the hydrogenated $CeFe_2H_x$ by XRD, TEM, DSC and magnetic property measurements(15). The present TEM and SEM results support the amorphous nature of the hydrogen-induced amorphous $GdFe_2H_x$.

(2) Crystallization behavior

The DSC curves of three amorphous alloys,i.e., a-$GdFe_2H_{3.6}$, a-$Gd_{33}Fe_{67}H_{120}$ and a-$Gd_{33}Fe_{67}$ are shown in Figure 4. The curves of the hydrogen absorbed alloys exhibit a broad endothermic peak and two exothermic peaks, while the curve of the as-quenched alloy only an exothermic peak. A hydrogen content of both the amorphous alloys fall to 0.67 (H/M) after heating to 873 K. That is, about half of the hydrogen [0.53 (H/M)] is released. Thus a same amount of hydrogen [1.2(H/M)] is absorbed and desorbed [0.53(H/M)] in the a-$GdFe_2H_x$ alloys prepared by two different methods. This suggests the similarity

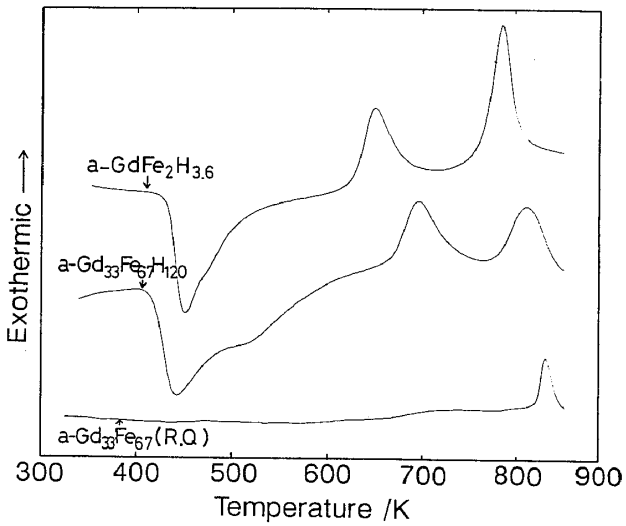

Figure 4 The DSC curves of a-$GdFe_2H_{3.6}$, a-$Gd_{33}Fe_{67}H_{120}$ and a-$Gd_{33}Fe_{67}$ alloys heated in an argon gas.

of the structure of both amorphous alloys.

The crystallization temperature T_x and the enthalpy change ΔH_c of crystallization are listed in Table 1. In the present work, T_x was defined as the temperature corresponding to the intersection of the extrapolated base line and the steepest tangent to the first exothermic peak, and the ΔH_c was determined from the area of the exothermic peak. T_x's of the hydrogen absorbed amorphous alloys are lower than that of the hydrogen free amorphous alloy by about 200 K. On the contrary, the enthalpy change of the hydrogen absorbed amorphous alloys is far larger than that of the hydrogen free alloy. To clarify the differences in the crystallization behavior, structures of the samples heated to several temperatures were examined. The arrows in the figure show the temperatures where DSC runs were terminated to obtain samples for TEM. The electron diffraction pattern of a-$GdFe_2H_{3.6}$ heated to 543 K shows only a halo and the hydrogen content decreases to 0.4 (H/M), so that it is concluded that the endothermic peak is attributed to partial desorption of hydrogen. From the DSC curve, it is seen that hydrogen desorption starts about 430 K.

Figure 5 shows a bright field image (a) of a-$GdFe_2H_{3.6}$ heated above the first exothermic peak (to 673 K) and the corresponding diffraction pattern (b). The bright field image shows homogeneous precipitates and the diffraction pattern shows Debye-Scherrer rings. The diffraction pattern can be satisfactorily indexed on the basis of a phase mixture consisting of GdH_2 having the C1 structure with a lattice parameter of 0.534 nm and α-Fe with the lattice parameter of 0.284 nm. Therefore, it is concluded that the first exothermic peak is attributed to crystallization of the amorphous alloy.

Table 1 The crystallization temperature T_x, the enthalpy change ΔH_c of crystallization, and the hydrogen content of the $GdFe_2H_x$ alloys before and after heating to 873 K in DSC.

Alloys	Absorbed H_2 (H/M)	T_x (K)	ΔH_c (kJ/mol)	Desorbed H_2 (H/M)
a-$GdFe_2H_{3.6}$(573 K,H_2)	1.2	633	-4.7 -6.7	0.53
a-$Gd_{33}Fe_{67}$ (RQ)		681	-4.6 -3.7	
a-$Gd_{33}Fe_{67}H_{120}$(473 K,H_2)	1.2	841	-1.3	0.53

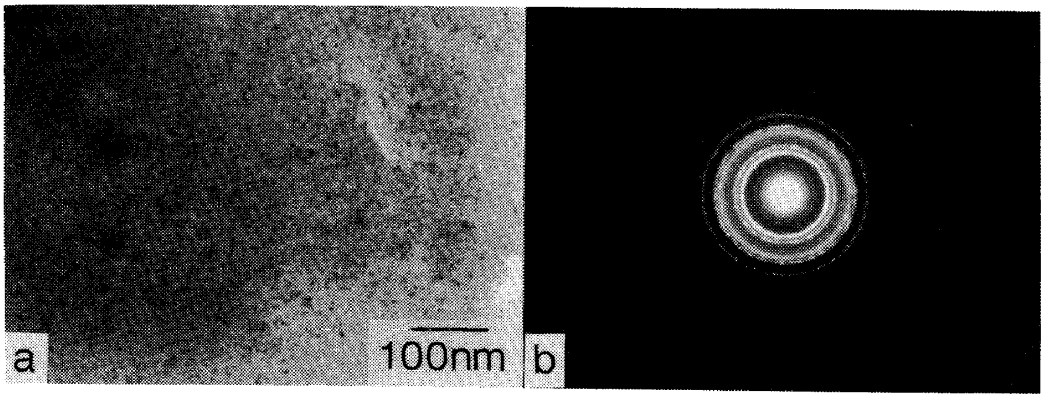

Figure 5 A bright field image (a) of a-$GdFe_2H_{3.6}$ heated above the first exothermic peak (to 673 K) and the corresponding diffraction pattern (b).

Figure 6 shows a bright field image (a) of a-$GdFe_2H_{3.6}$ heated above the second exothermic (to 873 K) and the corresponding diffraction pattern (b). The diffraction pattern can also be indexed on the basis of a phase mixture of GdH_2 and α-Fe. The differences in the bright field image and the diffraction pattern in Fig. 5 and Fig. 6 are only the size and the shape of the GdH_2 and α-Fe. Therefore, it is concluded that the second exothermic peak is attributed to the growth of the GdH_2 and α-Fe phases. As seen from Fig. 1 and Fig. 6, the crystallization products of a-$GdFe_2H_{3.6}$ heated in an argon atmosphere are same as those formed during the hydrogen absorption process at elevated temperatures. This implies that hydrogen in a-

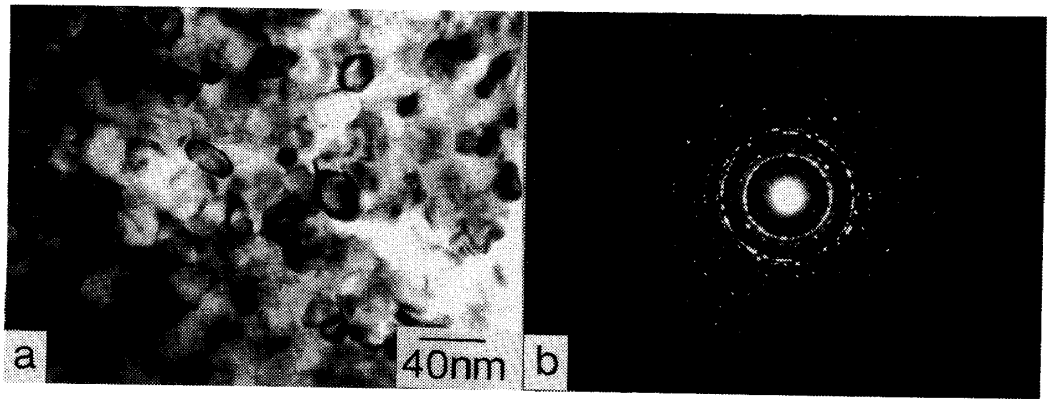

Figure 6 A bright field image (a) and the corresponding diffraction pattern (b) of a-$GdFe_2H_{3.6}$ heated above the second exothermic peak (to 873 K).

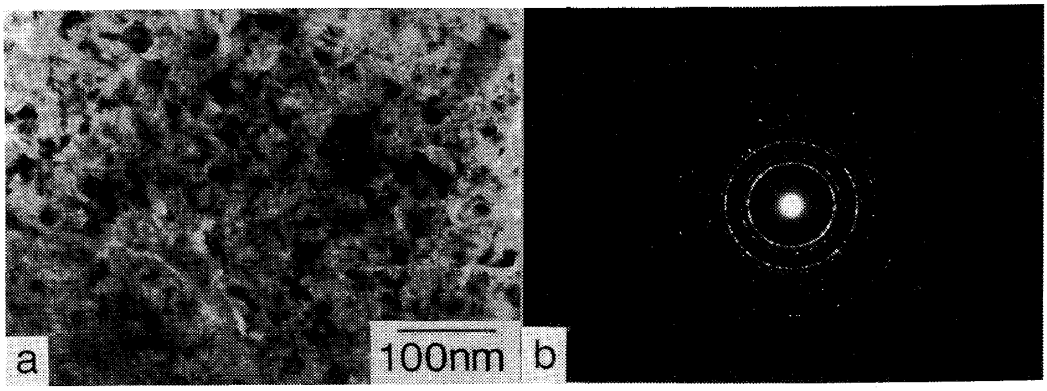

Figure 7 A bright field image (a) and the corresponding diffraction pattern (b) of a-$Gd_{33}Fe_{67}H_{120}$ heated above the second exothermic peak(to 873 K).

$GdFe_2H_x$ is tightly trapped, because if hydrogen is desorbed easily, GdH_2 is not formed during crystallization. The crystallization behavior of a-$Gd_{33}Fe_{67}H_{120}$ is nearly same as that of a-$GdFe_2H_{3.6}$, that is, the first exothermic peak is attributed to crystallization to GdH_2 and α-Fe phases and the second peak is the growth of them. As an example, a bright field image of a-$Gd_{33}Fe_{67}H_{120}$ heated to 873 K in an argon atmosphere (a) and the corresponding diffraction pattern (b) are shown in Figure 7. On the other hand, the exothermic peak for a-$Gd_{33}Fe_{67}$ is due to the polymorphous cystallization to the Laves phase c-$GdFe_2$.

IV. Summary and conclusions

Amorphous a-$GdFe_2H_x$ alloys were prepared by two kinds of technique, i.e., the newly developed hydrogen-induced amorphization (HIA) of the Laves phase c-$GdFe_2$ and hydrogenation of the rapidly quenched amorphous a-$Gd_{33}Fe_{67}$ alloy. The present investigation has demonstrated that it is possible to produce an amorphous phase by hydrogen absorption of the Laves phase $GdFe_2$ between 473 K and 573 K where the decomposition of $GdFe_2$ into GdH_2 and α-Fe is suppressed. On the other hand, the rapidly quenched a-$Gd_{33}Fe_{66}$ alloy could absorb hydrogen in the amorphous state below 523 K. The crystallization behavior of the hydrogen-induced amorphous a-$GdFe_2H_{3.6}$ alloy, which was investigated by differential scanning calorimetry (DSC) in combination with transmission electron microscopy (TEM), was similar to that of the hydrogenated amorphous a-$Gd_{33}Fe_{67}H_{120}$ alloy. That is,

the DSC curves of the a-$GdFe_2$ H_x alloys showed a broad endothermic peak together with two exothermic peaks. The endothermic peak was attributed to the partial desorption of hydrogen. The first exothermic peak was associated with the crystallization of the amorphous phase into GdH_2 and α-Fe, and the second one was attributed to the growth of them. A same amount of hydrogen [1.2(H/M)] is absorbed and desorbed [0.53(H/M)] in the a-$GdFe_2H_x$ alloys prepared by two different methods.On the other hand, a-$Gd_{33}Fe_{67}$ crystallized polymorphously to the Laves phase c-$GdFe_2$ showing an exothermic peak.

Acknowledgment

The present work was supported in part by a Grant-In-Aid for the Science Research on Priority Areas, New Functionality Materials-Design, Preparation and Control, The Ministry of Education, Science and Culture (63604506).

References

(1) X.L.Yeh, K.Samwer and W.L.Johnson, Apply. Phys. Letters, 42(1983)242.

(2) M. Komatsu, H.Fujita and Y.Ishii, Collected Abstract Annual Spring Meeting Japan Inst. Metals (1984)209.

(3) K.Aoki, X-G Li, K.Chattopadhyay and T.Masumoto, Scripta Metall.,22(1988)991.

(4) K.Aoki, K.Shirakawa and T.Masumoto, Sci.Rep. RITU,A-32,(1985)239.

(5) K.Aoki,T.Yamamoto, K.Fukamichi and T. Masumoto, Sci. Rep. RITU,A-33,(1986)163.

(6) K.Aoki, T.Yamamoto and T. Masumoto, Scripta Metall.,21 (1978)27.

(7) K.Aoki,A.Yanagitani,X-G.Li and T.Masumoto, Mater.Sci. and Eng.,97(1988)35.

(8) K.Aoki,X-G.Li,A.Yanagitani and T.Masumoto, Supplement to Trans.Jpn.Inst.Metals,29(1988)101.

(9) V.P.Boncour,A.P.Guegan,M.Diaf and J.C.Achad,J.Less-Common Met.,131(1987)201.

(10) K.Aoki,X-G.Li and T.Masumoto,Proc.of MRS Int.Meeting on Advanced Materials, Sunshine City,Tokyo, May 30-June 3,1988.

(11) X-G.Li, K.Aoki and T.Masumoto, Supplement to Trans. Jpn.Inst. Metals,29(1988)105.

(12) K. Chattopadhyay, K.Aoki and T. Masumoto, Scripta Metall., 21(1987)365.
(13) H.Oesterreicher, J.Clinton and H.Bittner, Mater. Res. Bull., 11(1977)117.
(14) K.H.J.Buschow, Solid State Comm., 22(1976)421.
(15) K.Aoki,T.Yamamoto,Y.Satoh,K.Fukamichi and T.Masumoto, Acta Metall.,35(1987)2465.