ErCo₂ C15 Laves 화합물의 수소유기 비정질화에 영향을 미치는 인자

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Factors Affecting Hydrogen Induced Amorphization of ErCo₂ C15 Laves Compound

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초록 : $ErCo_2$ 화합물에서 Co를 천이원소로 10% 만큼 치환한 $Er(Co_{0.9}M_{0.1})_2$ 화합물(M=Cr, Mn, Fe, Ni, Cu)의 비정질화 온도를 측정해서 수소유기 비정질화에 영향을 미치는 인자에 대해 살펴보았다. 비정질화 온도는 치환원소의 원자반경과 비례함을 알 수 있었다. 그러므로 $ErCo_2$ Laves 화합물에서 수소유기 비정질화에 영향을 미치는 인자는 확산과 밀접한 연관이 있는 원자의 크기임을 알 수 있다.

1. Introduction

As a new method for synthesizing amorphous phases by solid-state reaction, hydrogen-induced amorphization(HIA) was first developed by Yeh et al.[1] on the Zr₃Rh compound. Subsequently, many researchers[2-5] have also reported the phenomena of HIAs in RM₂ Laves phases(R=rare earths, M=transition metals). Especially Er-based C 15 Laves compounds are well known to be amorphized by hydrogen absorption[2, 4, 5]. There have been studies to investigate the factors affecting the HIA of ErCo₂ C15 Laves compound by substituting third elements for Co[4, 5]. However, due to the large amount of substituting element, the crystal structure or lattice parameter of the original compound is somewhat changed. So, they could not exclude the effect of the strain produced before hydrogenation on investigating the factors affecting the HIA.

In this study, the amount of the substituting transition elements was hold 10 atomic % in order to keep the original crystal structure and lattice parameter unchanged. By substituting transition

metals such as Cr, Mn, Fe, Ni and Cu for Co, it is possible to vary the properties such as the heat of formation, elastic modulus and atomic size of the transition elements of $ErCo_2$. Since the HIA in Er-based C15 Laves compounds is a thermally activated process[2], the amorphization temperature is closely related to the activation energy of transformation from a crystal to a amorphous phase. The amorphization temperature can be used as parameter to indicate the degree of difficulty of the HIA and it is measured to investigate the factors affecting the HIA in the $ErCo_2$ compound.

2. Experimental

The alloys were prepared from pure elements (99.9%) by arc melting in an argon atmosphere. The samples were checked by X-ray diffraction (XRD) using Cu-Kα radiation and were found to have single phases(cubic type-C15 Laves phase). All of the samples were then crushed into powder below 325 mesh before hydrogenation. Thereafter, hydrogen absorption treatment were carried out in a Sievert's type apparatus at a fixed hydrogen pressure of 50 atm H_2. The structural changes induced by hydrogen absorption were investigated by XRD. Some hydrogenated samples were observed by transmission electron microscopy(TEM) (200 kV Jeol 200CX microscope) to identify the amorphous phase and measure the amorphization temperature. The amorphization temperature is defined as the temperature at which the compound fully transforms to a amorphous phase at 50 atm H_2 in a charging time of 10 hours.

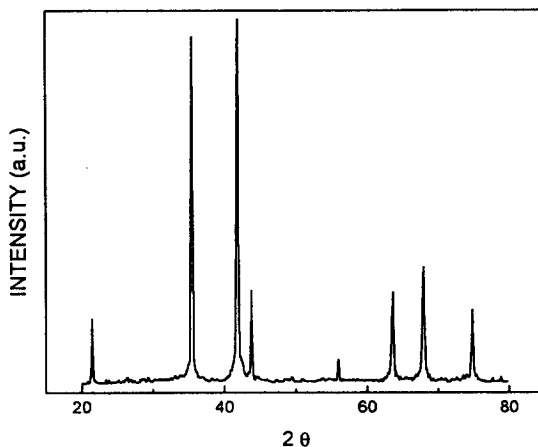## 3. Results and Discussion

Figure 1 shows a XRD pattern of the as cast

Fig. 1 XRD pattern of the as cast $ErCo_2$ compound.

$ErCo_2$ compound. From indexing, the sample has an $MgCu_2$ type C15 Laves phase $ErCo_2$, which is found to be in single phase with lattice parameter of 7.154Å. All the substituted $Er(Co_{0.9}Cr_{0.1})_2$ compounds(M = Cr, Mn, Fe, Ni, Cu) are observed to have also C15 Laves phases with cubic structures from XRD patterns. The XRD patterns of the $Er(Co_{0.9}Cr_{0.1})_2$ compound hydrogenated at 50 atm H_2 and in a charging time of 10 hours with various hydrogenation temperatures are shown in Figure 2. At 290℃, it is observed that crystalline hydride with extended lattice parameter is formed, but the original cubic structure is still retained. As the hydrogenation temperature increases, the crystalline peak gradually decreases and only a broad maxima pattern remians as shown in Figure 2. To confirm whether the broad pattern in Figure 2(c) is due to the formation of the amorphous phase, it has been examined by TEM. Figure 3 shows the TEM image and corresponding diffraction pattern. The bright field image shows a mottled structure and the electron diffraction pattern exhibits diffuse halo rings, which are indicative of an amorphous
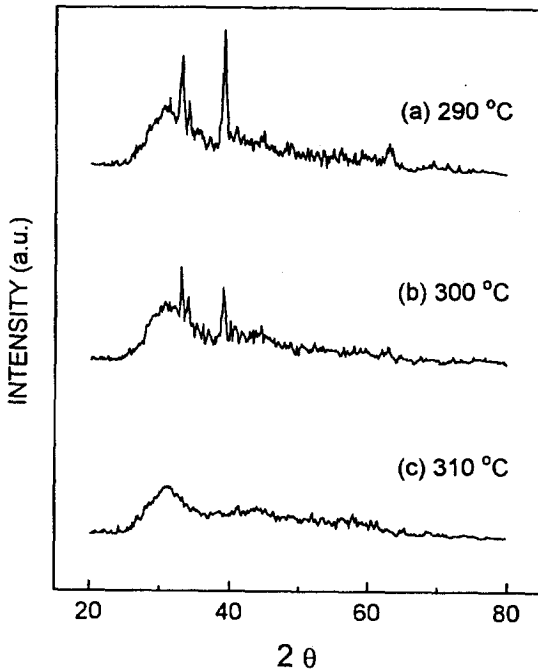
Fig. 2 XRD patterns of the $Er(Co_{0.9}Cr_{0.1})_2$ compound hydrogenated at 50 atm H_2 and for 10 hours with various hydrogenation temperature.
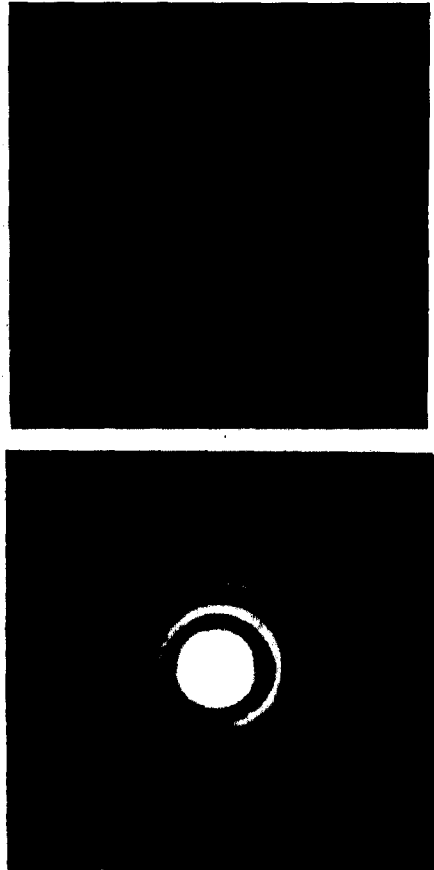

Fig. 3 Bright-field transmission electron micrograph and the corresponding electron diffraction pattern for $Er(Co_{0.9}Cr_{0.1})_2$ hydrogenated at 310°C for 10 hours.

state.

From the followed hydrogenation treatment for the rest of the $Er(Co_{0.9}Cr_{0.1})_2$ compounds, it was found out that these substituted compounds show the similar hydrogenation reactions and amorphization behaviors for the $Er(Co_{0.9}Cr_{0.1})_2$ compound. However, the amorphization temperatures are measured to be different each other as shown in Figure 4.

In table 1, lattice parameters, heats of formation, Young's moduli, atomic radii of the substituting transition metals and amorphization temperatures in the $Er(Co_{0.9}Cr_{0.1})_2$ compounds are summarized.

The lattice parameters of the $Er(Co_{0.9}Cr_{0.1})_2$ com-

pounds differ from that of $ErCo_2$[6] only 0.42%. So, it is believed that the original crystal structure and the lattice parameter are nearly unchanged. The heats of formation are calculated using the Miedema's model [7] and the Young's moduli of compounds by rule of mixture of the constituents. It is reported that the elastic modulus of the Laves
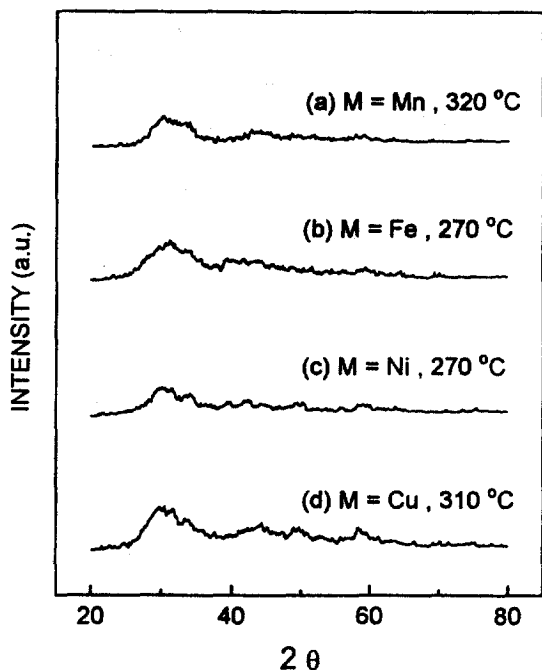
Fig. 4 XRD patterns of the Er(Co$_{0.9}$M$_{0.1}$)$_2$ compound at 50 atm H$_2$ and for 10 hours with (a) M=Mn, T=320℃ (b) M=Fe, T=270℃ (c) M=Ni, T=270℃ and (d) M=Cu, T= 310℃.

Table 1. Lattice parameters, heats of formation, Young's moduli and atomic radii of the substituting transition elements and the amorphization temperatures of the Er(Co$_{0.9}$Cr$_{0.1}$)$_2$ compounds.

M	Cr	Mn	Fe	Ni	Cu
Lattice parameter of Er(Co$_{0.9}$M$_{0.1}$)$_2$ (A)	7.174	7.157	7.164	7.147	7.157
Heat of formation (kJ/mole)	-31.71	-33.66	-31.97	-35.97	-31.78
Young's modulus (GPa)	168.6	162.7	164.1	163.3	158.7
Atomic radius (A)	1.28	1.37	1.26	1.25	1.28
Amorphization temperature (°C)	310	320	270	270	310

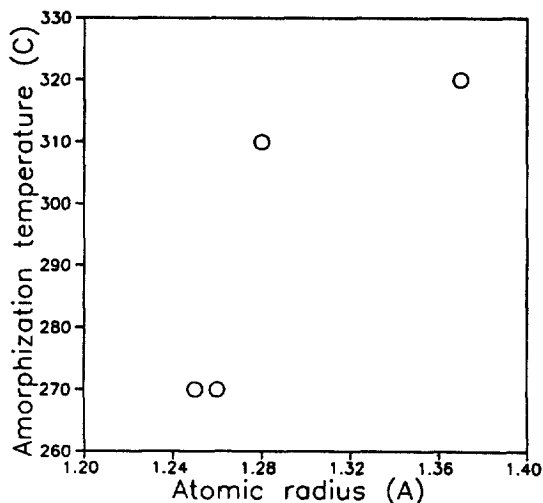

Fig. 5 Plot of amorphization temperatures vs. atomic radii of the substituting elements in the Er(Co$_{0.9}$M$_{0.1}$)$_2$ compounds.

compounds calculated from the elastic modulus of each constituent element by means of the rule of mixture agrees well with the experimental results [8]. The atomic size is the Goldschmidt radius. From the result of Table 1, there is no correlation of the amorphization temperature with the heat of formation and Young's modulus. But the amorphization temperature appears to be only proportional to the atomic size of the substituting element. Figure 5 shows plot of the amorphization temperatures with the atomic radii of the substituting elements of the Er(Co$_{0.9}$Cr$_{0.1}$)$_2$ compounds.

Generally, the activation energy for interstitial diffusion of transition metals in rare earth metals is lower when the ratio of the atomic sizes of transi-
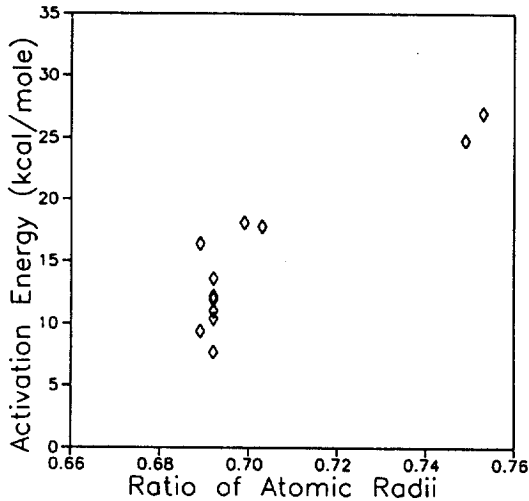
Fig. 6 Variation of the activation energy for interstitial diffusion of transition metals in rare earth metals with the ratio of the atomic sizes of transition metals to those of rare earth metals. The data are collected from Ref.[9] and the atomic sizes are Goldschmidt radii.

tion metals to those of rare earth metals is smaller, as shown in Figure 6. It is said that the diffusion of transition metal is easier as the atomic size is smaller. From the relation of the amorphization temperature to the atomic size of the substituting element, the HIA in the $ErCo_2$ compound is mostly affected by the atomic radius and this fact is a evidence that the amorphization of the $ErCo_2$ compound is due to the diffusion of transition element.

Recently, Kim and Lee [5] have reported that the elastic modulus of the compound plays a critical role in the HIA of the $Er(Co_{1-x}Fe_x)_2$ ($x=0 \sim 1$) Laves phases. In that case, large elastic strain is initially produced before hydrogenation because of large amount of the substituting element, up to 100 % of Fe and accordingly the change of lattice parameter reaches about 1.76%. The strain effect could not be excluded. But in this study, content of the substituting element is low so that the crystal structure of the original compound is kept nearly unchanged and elastic strain is scarcely produced. Consequently, the atomic size of transition metal is an intrinsic factor affecting the HIA in the $ErCo_2$ compound.

4. Conclusions

The amorphization temperatures of the $Er(Co_{0.9}Cr_{0.1})_2$ compounds are found to be proportional to the atomic size of the substituting transition metal. This indicates that the atomic size of the transition element is a factor affecting the HIA in the $ErCo_2$ Laves compound and the amorphization is related with the diffusion of transition element.

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