ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 268–271

Journal of ALLOYS AND COMPOUNDS

Powder X-ray diffraction under a high-pressure hydrogen atmosphere for Zr–Cr based Laves phase alloys

S. Kuranaka*, T. Gamo, Y. Morita

Human Environment Research Laboratory, Corporate Research Division, Matsushita Electric Industrial Co., 3-1-1, Yagumo-Nakamachi, Moriguchi, Osaka 570, Japan

Abstract

Zr–Cr based Laves phase alloys were investigated by powder X-ray diffraction under a high-pressure hydrogen atmosphere and/or high temperature in order to compare two crystal structures of the same composition. These alloys were synthesized in either the C14 or the C15 type and absorb hydrogen at room temperature. We observed the X-ray diffraction peaks of the C14 type in as-cast ingots and the C15 type in annealed ingots. Line broadening of the X-ray diffraction profile upon hydriding was not observed in either the C14 or C15 phase. The C14 H-free alloys had an axial ratio c/a slightly smaller than $\sqrt{(8/3)}$, and the C14 hydrides had an axial ratio c/a slightly larger than $\sqrt{(8/3)}$. Under a high-pressure hydrogen atmosphere, the cell volume of both the C14 and C15 hydrides decreases with an increase in temperature. These phenomena are explained by the change in hydrogen concentration. At constant hydrogen concentration, the cell volume expansion of the C15 phase upon hydrogenation was larger than that of the C14 phase.

Keywords: Zr–Cr based Laves phase; Powder X-ray diffraction; Cell volume expansion; C15 phase; C14 phase

1. Introduction

Ti–Mn based Laves phase alloys have high hydrogen capacities and good lifecycle properties [1,2]. Zr–Cr based Laves phase alloys also have good hydrogen storage properties. The stoichiometric compound $ZrCr_2$ can be synthesized in either the C14 or the C15 type and absorb 3.4 H (formula unit)$^{-1}$ at room temperature for the C14 type [3], and 4 H (formula unit)$^{-1}$ for the C15 type [4]. The C14 type and the C15 type structures of the alloys and hydrides were determined by X-ray and neutron diffraction [5,6]. The non-stoichiometric C14 type Laves phase compound in the Zr–Cr system can absorb hydrogen, to a concentration of $H/M=0.9–1.0$ at 423 K for the C14 type [7]. At equilibrium there are three Laves phases in the Zr–Cr system, γ $ZrCr_2$, β $ZrCr_2$ and α $ZrCr_2$, with C14 (hexagonal), C36 (hexagonal) and C15 (cubic) structures, respectively. At room temperature, the C15 phase is the stable one [8]. These structures differ in the stacking of the hexagonal layers [9–11]. When the C14 phase has the axial ratio $c/a=\sqrt{(8/3)}$ and the lattice constant $a=2/\sqrt{3}\ a'$, (where a' is the lattice constant of the C15 phase), the dimension of the stacking layer unit of the C14 phase is the same as that of the C15 phase. Consequently, in powder X-ray diffraction patterns, all the C15 characteristic peak positions overlap with some of the C14 peak positions. In this work, we synthesized alloys with the C14 and C15 type structure having identical compositions. They were investigated by powder X-ray diffraction under a high-pressure hydrogen atmosphere and/or high temperature. The pressure-composition isotherms were measured to investigate the static hydrogenation properties. The C14 and C15 type crystal structures of the same composition have been compared in view of the relationships between the lattice parameters and the static hydrogenation properties.

2. Experimental details

The alloys were prepared by arc-melting the raw metals. The starting elements were Zr sponges (99.5% purity) and Cr plates (99% purity) and their nominal composition for $ZrCr_2$ and $ZrCr_{2.15}$. Then they were arc-melted on a water-cooled copper crucible under an argon atmosphere. We remelted the initially melted button-type sample five or six times, turning it over between each melt. In order to obtain the C15 phase, we annealed the ingots at 1373 K for 20 h in vacuum.

Both as-cast and annealed samples were analyzed by

---

*Corresponding author.

PII S0925-8388(96)03030-7

powder X-ray diffraction and by measuring pressure-composition isotherms. The powder X-ray diffraction patterns under high-pressure hydrogen atmosphere and/or high temperature were obtained by a Rigaku diffractometer equipped with a high-pressure chamber and a sample heater. The pressure-composition isotherms were measured four times after hydrogen absorption and desorption. The pressure-composition isotherms were measured based on vacuum conditions (at 423 K for 1 h) as described in the Japanese Industrial standard JIS H 7201.

3. Results and discussion

The alloys $ZrCr_2$ and $ZrCr_{2.15}$ show X-ray diffraction patterns of the C14 type in as-cast ingots and of the C15 type in annealed ingots. Their hydrides have the same type of structure as the alloys. In the case of AB_5 compounds, anisotropic line broadening is observed in the activated sample [12]. However, in this case, line broadening by hydriding is not observed in either the C14 or C15 phase.

Figs. 1 and 2 show the changes in the lattice constants for the C14 and type C15 structure under vacuum and a high-pressure hydrogen atmosphere (3 MPa) respectively. All vacuum samples were hydrogen-free alloys, and all 3 MPa samples were hydrides. Under vacuum the lattice constants of both the C14 and C15 alloys slightly increase with an increase in temperature due to thermal expansion. On the other hand, the lattice constants of both the C14 and C15 hydrides decrease with an increase in temperature. These phenomena can be explained by the change in the hydrogen concentration of the hydride.

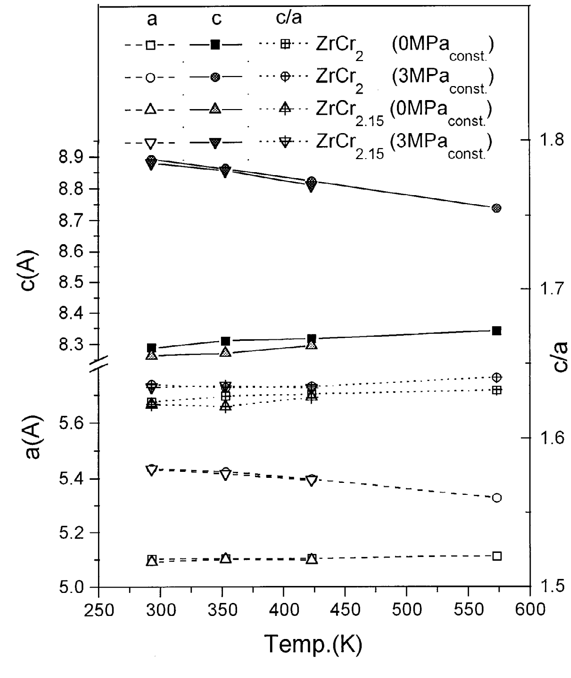

Fig. 1. Lattice constants—isobaric lines for the C14 type.

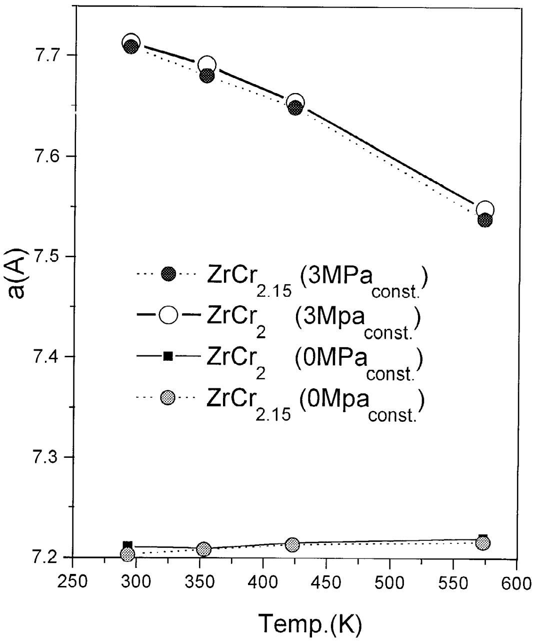

Fig. 2. Lattice constants—isobaric lines for the C15 type.

As shown in Fig. 1, the axial ratio c/a of both the C14 hydrogen-free alloys and the hydrides deviate from their ideal value $\sqrt{(8/3)} \fallingdotseq 1.63$ as a function of pressure and temperature. In order to compare these results with those published [5,6], the lattice constants of the C14 type compound $ZrCr_2$ and its hydride are tabulated in Table 1. The axial ratio c/a of the former is slightly smaller than 1.63 and that of the latter is slightly larger than 1.63.

Under all conditions, the lattice constants for $ZrCr_{2.15}$ were slightly smaller than those for $ZrCr_2$ but the differences are small. Therefore, we shall discuss mainly $ZrCr_2$ below.

Figs. 3 and 4 show the changes of the lattice constants for the C14 and C15 type compounds, respectively, at constant temperature. In the same manner as in Fig. 1, the C14 type $ZrCr_2$ hydride has an axial ratio c/a slightly larger than that of the C14 type ZrC_2 alloy. The lattice constants of both the C14 and C15 type compounds increase with pressure. These phenomena can also be explained by a change in hydrogen concentration.

In order to estimate the hydrogen concentration (H/M) of the $ZrCr_2$ hydride in Figs. 1–4, measurements of

Table 1
The lattice constants for the C14 $ZrCr_2$

Sample	Alloys			Hydrides		
	a	*c*	*c*/*a*	*a*	*c*	*c*/*a*
[5]	5.102	8.294	1.626	5.385	8.830	1.640
[6]	5.106	8.292	1.624	5.385	8.832	1.640
293 K	5.102(2)	8.288(9)	1.624	5.434(2)	8.891(8)	1.636
353 K	5.104(2)	8.310(6)	1.628	5.423(1)	8.861(4)	1.634
423 K	5.103(2)	8.316(7)	1.630	5.396(2)	8.822(7)	1.635
573 K	5.111(1)	8.341(3)	1.632	5.325(2)	8.736(7)	1.641

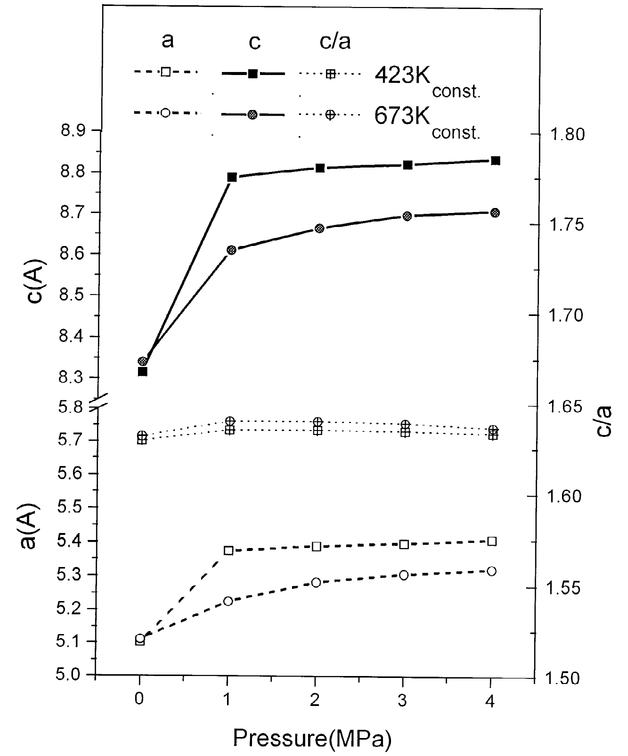

Fig. 3. Lattice constants—isotherms for the C14 $ZrCr_2$.

pressure-composition isotherms for the C14 and the C15 $ZrCr_2$ hydrides were performed at 293 K, 353 K and 423 K. There was no obvious plateau region for the pressure-composition isotherms and little difference in hydriding properties between the C14 and the C15 $ZrCr_2$ hydrides.

Fig. 5 shows the cell volume expansion for the $ZrCr_2$ hydride. The points of C14 isobaric, C15 isobaric, C14 isotherm and C15 isotherm were taken respectively from Figs. 1–4. Their cell volume expansion increased with an increase in hydrogen concentration (H/M) of the $ZrCr_2$ hydride. The slope of the lines of C14 and C15 agreed with those of the C14 and isobaric C15 isotherms, respectively. The experimental results showed that the effect of temperature was not very large. When the hydrogen concentration of the hydride was the same, the cell volume expansion of the C15 type phase per hydrogen atom was larger than that of the C14 phase. This phenomena can be explained by the change of the axial ratio *c/a* of the C14 phase because the C14 type structure is more flexible with respect to a cell volume expansion compared to the C15 type structure where expansion is constrained by the cubic symmetry.

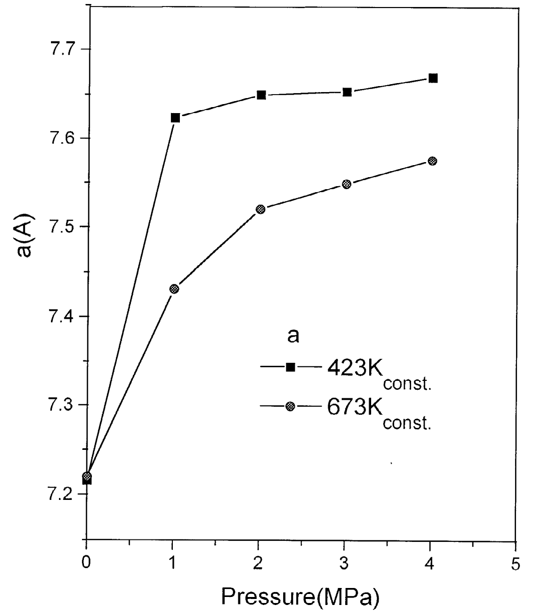

Fig. 4. Lattice constants—isotherms for the C15 $ZrCr_2$.

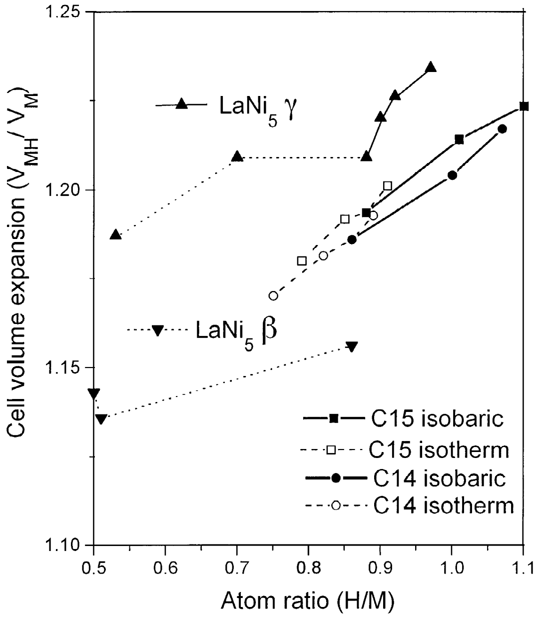

Fig. 5. Cell volume expansion for $ZrCr_2$ hydrides.

The points of $LaNi_5$ β and $LaNi_5$ γ shown in Fig. 5 were taken from [12,13]. The dotted line for γ $LaNi_5$ indicates the coexistence with β $LaNi_5$. Therefore, the hydrogen contents of the hydride in this region are not well determined. The cell volume expansion of the $ZrCr_2$ hydride is smaller than that of γ $LaNi_5$.

4. Conclusions

We have compared the C14 and C15 type crystal structures of Zr–Cr based Laves phase alloys by powder X-ray diffraction under a high-pressure hydrogen atmosphere and/or high temperature. The lattice parameters of both phases increased with hydrogen content. At similar hydrogen contents the cell volume expansion of the C15 type phase upon hydrogenation was larger than that of the

C14 phase. Also, the cell volume expansion of the $ZrCr_2$ type hydride was smaller than that of the $LaNi_5$ hydride.

Acknowledgments

This study was conducted as a part of the Eco-Energy City Project by Matsushita Electric Industrial Co. under consignment from NEDO (New Energy and Industrial Technology Development Organization) and ECC (Energy Conservation Center).

References

[1] T. Yamashita, T. Gamo, Y. Moriwaki and M. Fukuda, *Nippon Kinzoku Gakkaishi*, *41* (1977) 148.
[2] T. Gamo, Y. Moriwaki, N. Yanagihara and T. Iwaki, *J. Less-Common Met*, *89* (1983) 495.
[3] A. Pebler and E.A. Gulbransen, *Electrochem. Technol.*, *4(5–6)* (1966) 211.
[4] D. Shaltiel, I. Jacob and D. Davidov, *J. Less-Common Met*, *53* (1977) 117.
[5] J.L. Soubeyroux, M. Bouovdina, D. Fruchart and L. Pontonnier, *J. Alloys Comp.*, *219* (1995) 48.
[6] J.L. Soubeyroux, M. Bouovdina, D. Fruchart and P. de Rango, *J. Alloys Comp.*, *231* (1995) 760.
[7] M. Uchida and S. Suda, *The Research Report of Kougakuin University*, *71* (1991) 41.
[8] T.B. Massalski, *Binary Alloy Phase Diagrams*, 2nd ed., ASM International, 1990.
[9] Y. Komura, *Acta Cryst.*, *15* (1962) 770.
[10] K. Kanematsu, *J. Phys. Soc. Japan*, *27* (1969) 849.
[11] J. Huot, E. Akiba and Y. Ishido, *J. Alloys Comp.*, *231* (1995) 85.
[12] S. Ono, K. Nomura, E. Akiba and H. Uruno, *J. Less-Common Met.*, *113* (1985) 113.
[13] E. Akiba, K. Nomura and S. Ono, *J. Less-Common Met.*, *129* (1987) 159.