Journal of Alloys and Compounds 253–254 (1997) 29–33

Effects of nonmetal addition on hydriding properties for Ti–Mn Laves phase alloys

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

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

Abstract

The effects of nonmetal addition such as B, C, O, S and Se, on hydriding properties were investigated for $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ Laves phase alloys. It was found that for both as-cast and annealed samples, the addition of nonmetal elements such as S, Se and C greatly increases the plateau pressure, improves the plateau slope factor, and expands the hysteresis. The effect of increasing the plateau pressure was strongest for the S addition. These phenomena are possibly related to the appearance of manganese-rich minute particles as observed by scanning electron microscopy. The above effects pave the way for increasing the hydrogen storage capacity of the Ti–Mn Laves phase alloys.

Keywords: Hydrogen storage alloy; Laves phase; Ti–Mn alloy; Nonmetal addition; PCT diagram

1. Introduction

AB_2-type Laves phase alloys are regarded as a possible choice for hydrogen storage materials used for hydrogen suppliers, heat pumps and nickel–metal hydride batteries in the future [1–7]. Ti–Mn AB_2-type Laves phase alloys consisting of multi-components have attracted considerable interest because of their superior hydriding properties. We have investigated the effects of nonmetal addition such as B, C, O, S and Se on hydriding properties for the Ti–Mn alloys. As a result, it was found that these nonmetal additions affect considerably the hydriding properties of the alloys. In this report, the improved pressure–composition temperature (PCT) characteristics will be discussed, and it will be shown that these additions lead to an increase of the hydrogen storage capacity and a simplification of the alloy-manufacturing process.

2. Experimental details

A $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.3}V_{0.2}$ alloy was chosen as a typical Ti–Mn Laves phase alloy which has superior hydrogen absorbing properties [1]. Each $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ alloy containing a nonmetal element such as B, C, O, S and Se of about 1 at% quantity was arc-melted in an argon atmosphere. The starting materials were elemental Ti, Zr, Mn, Cr and V metals with a 2N purity, and Ti based compounds for the nonmetal additions. The ingots had a weight of about 30 g. The alloys obtained were homogenized for 24 h at 1100°C. These samples were characterized by chemical analysis, optical micrograph, scanning electron microscopy (SEM), X-ray diffraction and PCT measurements. For the latter, the samples were sealed in a stainless steel holder subsequent to being crushed into a powder which was introduced into an automated PCT apparatus.

3. Results and discussion

The compositions of the arc-melted ingots were analyzed by a chemical method. It was ascertained that each nonmetal element was completely dissolved in the Ti–Mn alloy i.e., the composition of B, C, O, S and Se were 1.0, 0.5, 1.5, 0.8 and 1.0 at%, respectively. The only notable losses were flux during the fusion process of manganese, but they remained small.

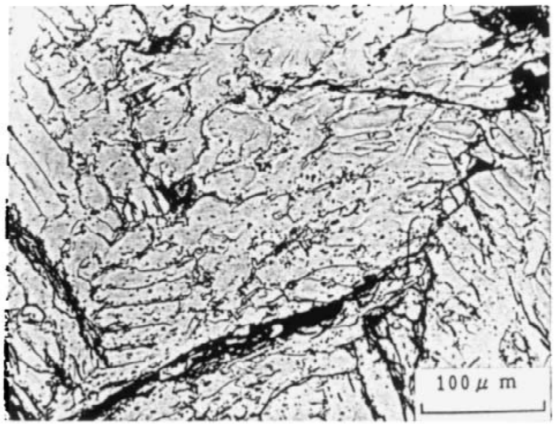
Fig. 1 shows an optical micrograph for the as-cast alloy without nonmetal addition and one for the S-containing alloy. Both contain two regions, of which the major part is considered to be the Laves phase and the minor part the finally solidified phase. No significant difference can be seen between these two microstructures. Similar features were observed for alloys containing other nonmetal ele-

---

*Corresponding author.

0925-8388/97/$17.00
PII S0925-8388(96)03056-3

$Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ (as-cast)



$Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}S_{0.03}$ (as-cast)

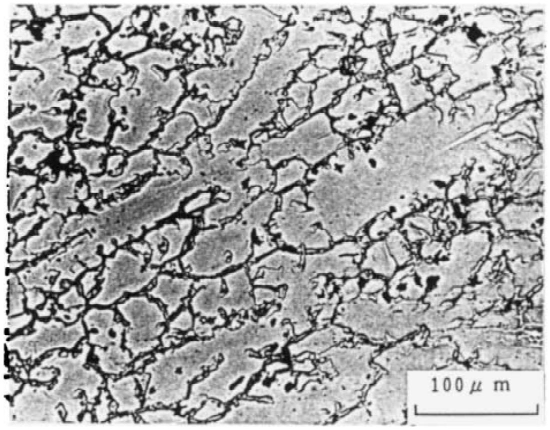


Fig. 1. Optical micrographs for as-cast $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ and $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}S_{0.03}$ alloys.

ments. From these results, one can conclude that the nonmetal addition at the 1 at% level barely influences the microstructure.

X-ray diffraction patters confirm the hexagonal C14-type structure for both the as-cast and the annealed alloys as shown in Fig. 2 for $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}S_{0.03}$. The diffraction peaks for both alloys could all be fitted to the reflections of the $MgZn_2$ type structure. There were no reflections corresponding to the cubic C15-type structure. The lattice constants a and c for the C14-type structure as calculated from these patterns are shown in Fig. 3. For the as-cast samples, they are generally smaller for alloys containing nonmetal additions than for alloys which do not contain nonmetal additions. Moreover, the lattice constants decrease in the order of B, C, O, S and Se, as expected from the atomic size of the added elements. On the other hand, there is a difference in lattice constants between as-cast and annealed samples. In the case of the S-containing sample element, the diffraction peaks of the annealed alloy are shifted toward lower diffraction angle, (see Fig. 2), which means that the lattice constants of the annealed sample are bigger than those of the as-cast sample. Similarly, the alloys C, O and Se containing alloys show increased lattice constants, after annealing, whereas the B containing alloys show decreased lattice constants. Consequently, all lattice constants of the annealed samples all have nearly the same value. As to the reason for this behaviour, we suppose, as a hypothesis, that the vacancy concentration in as-cast alloy increases as nonmetal elements having a larger atomic size are introduced into the C14-type structure, thus reducing the lattice constants. The heat-treatment tends to release the vacancy containing state, thus leading to almost the same lattice constants in annealed samples.

Fig. 4 shows the PCT diagrams for the as-cast alloys with and without S additions as measured at 5°C. The addition of S causes a remarkable increase in the plateau pressure, flattens the plateau slope and expands the hysteresis in comparison with the S-free alloy. The pressure difference is about 0.9 MPa during absorption and 0.3 Mpa during desorption at the hydrogen/metal ratio $H/M=0.5$. The PCT diagrams measured at 7°C and 27°C for the annealed alloys with and without C addition are exhibited in Fig. 5. The C addition also raises the plateau pressure, flattens the plateau slope, and expands the hysteresis. In this case, the pressure difference measured at 27°C is about 1.0 Mpa during absorption and 0.4 Mpa during desorption at $H/M=0.5$. In both Figs. 4 and 5, the maximum hydrogen storage capacity barely differs between the addition free and the nonmetal added alloys. So far, we have found that the addition of nonmetal elements such as S, Se and C greatly increase the plateau pressure, decreases the plateau slope, and expands the hysteresis as shown in Table 1. The plateau slope factor Sf was evaluated as ln $(P_{0.75}/P_{0.25})$ where $P_{0.75}$ and $P_{0.25}$ are the pressures at 0.75 and 0.25 maximum hydrogen storage capacity, respectively. The hysteresis factor Hf was evaluated as $\ln(P_a/P_d)$ where P_a and P_d are the absorption and desorption pressures at 0.5 of maximum hydrogen storage capacity, respectively [5]. The effect of increasing the plateau pressure was strongest for the S addition in case of both as-cast and annealed samples. The Zr additions in Ti(Zr)–Mn based Laves phase alloys have a similar effect on decreasing the plateau pressure and increasing the absorbing capacity [5,8,9]. Thus S-containing Ti–Mn alloys can contain larger quantities of Zr than S-free alloys, which indicates that the hydrogen storage capacity of the S-containing alloys increases. On the other hand, the improvement of the plateau slope factor suggests for as-cast alloys that nonmetal addition such as S and C will simplify the alloy-manufacturing process, because the plateau slope factor is generally improved by heat treatment.

It is well known from experience that the increase of the plateau pressure is related to the decrease of the lattice constants [8,9]. However for the present alloys the increase in plateau pressure cannot be explained by a change in

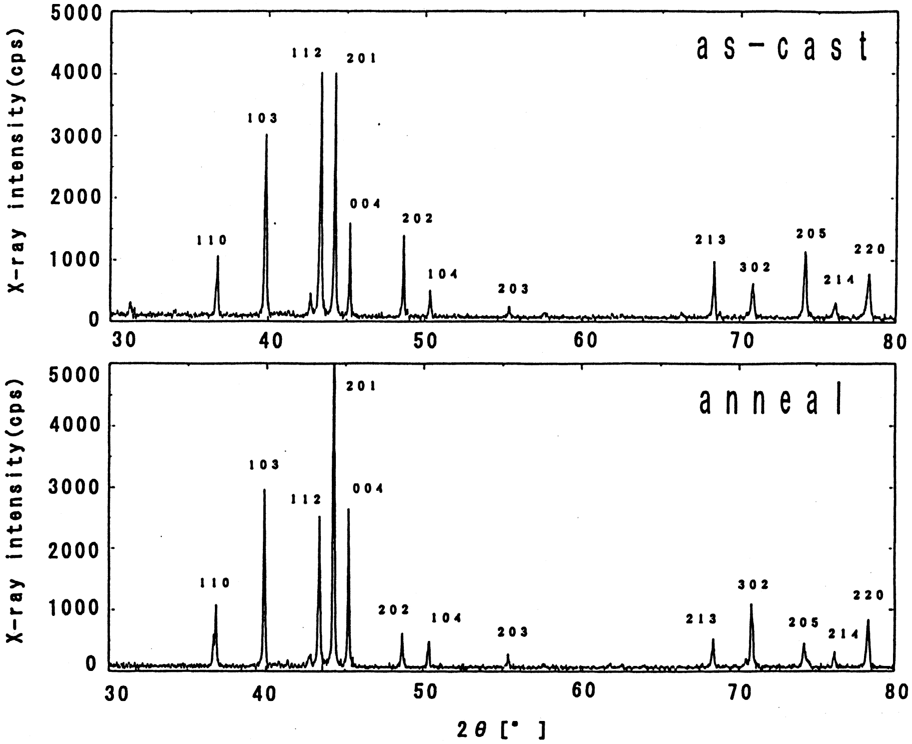


Fig. 2. X-ray diffraction patterns of as-cast and annealed $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}S_{0.03}$ alloys.

lattice constants because those of the annealed samples have almost the same values, see Table 1. In order to explain these phenomena we have investigated the microstructures by use of SEM. Although we have found no difference between the nonmetal free and nonmetal added alloys on a macroscopic scale, we could observe many minute particles on the alloy-powder surface by using SEM. As an example, Fig. 6 shows the SEM image of as-cast $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ alloy-powder after hydrogenation of hydrogen absorbing/desorbing 6 cycles. Many minute particles with the diameter of 20~30 nm appear on the alloy-powder surface. Transmission electron microscopy experiments revealed the composition of the particles to be rich in Mn, the detailed results of which will be

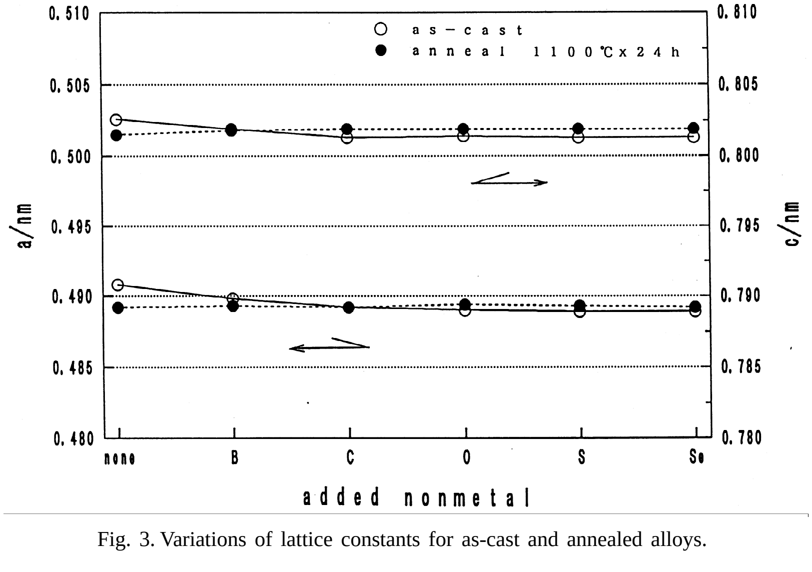


Fig. 3. Variations of lattice constants for as-cast and annealed alloys.

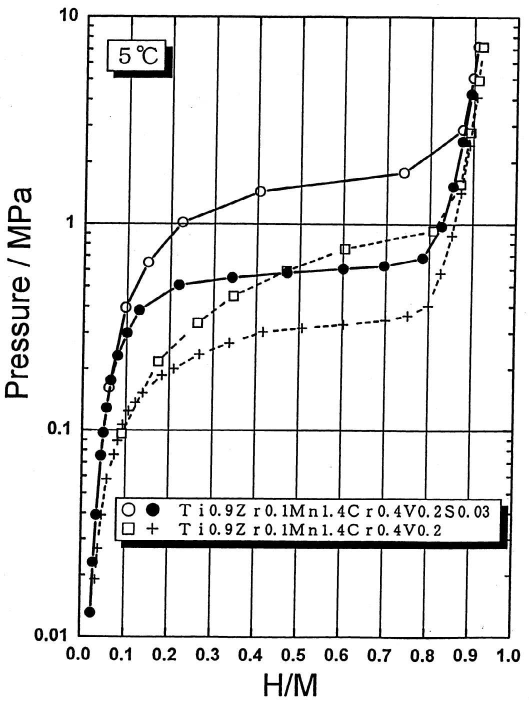


Fig. 4. Pressure–composition (PCT) diagrams measured at 5°C for as-cast non-additional and S-added alloys.

reported later. For Ti–Mn based Laves phase alloys it is known that a increase of the Mn content raises the plateau pressure and improves the plateau slope factor [1,8]. At present, we believe that the effects of the nonmetal addition are related to the appearance of small Mn-rich particles.

4. Conclusions

$Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ Laves phase alloys containing about 1 at% nonmetal element such as B, C, O, S and Se were characterized with regard to their hydriding properties.

The following conclusions can be drawn:

1. Additions of nonmetal elements such as S, Se and C greatly increase the plateau pressure, improve the plateau slope factor, and expand the hysteresis.
2. These effects suggest the possibility of increasing the hydrogen storage capacity of Ti–Mn alloys.
3. The plateau slope factor of Ti–Mn based Laves phase alloys which is commonly improved by heat treatments, can be improved without heat treatment by nonmetal addition.

Acknowledgments

This study was conducted as one of the Eco-Energy City Projects supported by the government under consignment from NEDO (New Energy and Industrial Technology

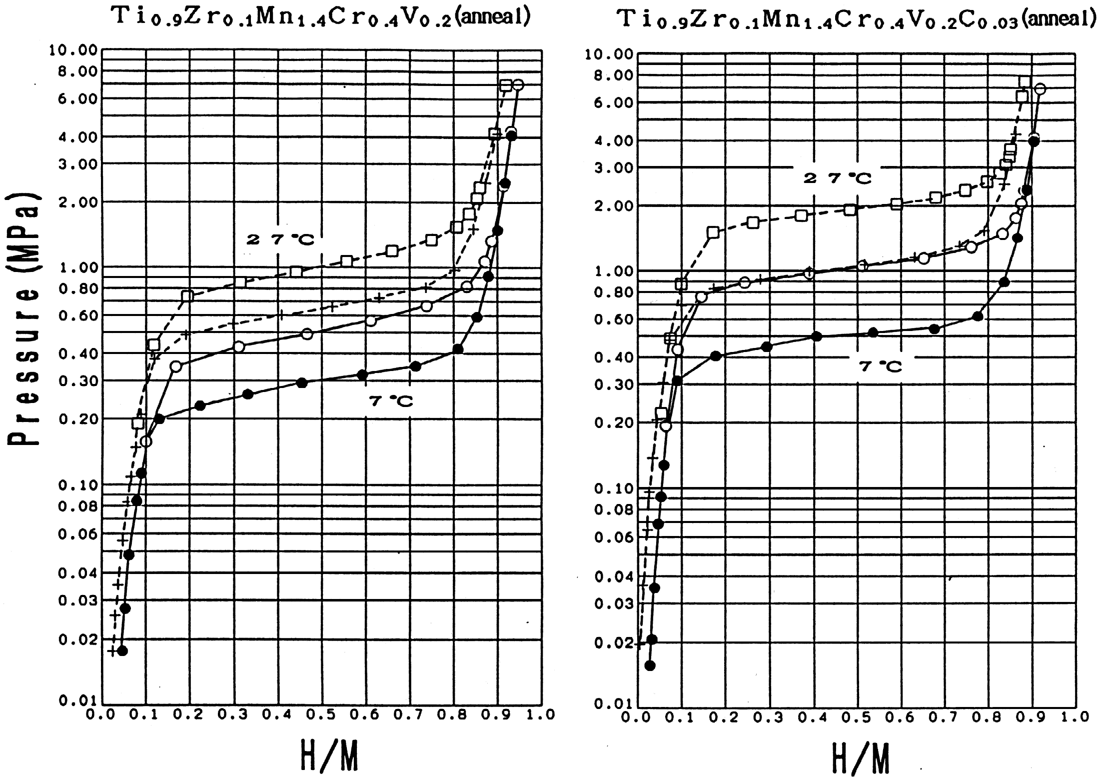


Fig. 5. Pressure–composition (PCT) diagrams measured at 7°C and 27°C for annealed non-additional and C-added alloys.

Table 1
Effects of nonmetal additions on plateau pressure, plateau slope factor and hysteresis factor

	As-cast						Annealed					
Plateau Pressure (MPa)	none	≤B	≤O	<C	<Se	<S	none	≤O	≤B	<C	<Se	<S
Absorption ($H/M=0.5$)	1.3	1.5	1.6	2.1	2.5	2.9	1.0	1.2	1.4	1.9	2.2	2.7
Desorption ($H/M=0.5$)	0.76	0.85	0.95	1.2	1.3	1.4	0.65	0.76	0.77	1.1	1.2	1.4
Plateau Slope Factor (Sf)	S	≤C	<Se	≤B	<none	<O	C	≤S	<Se	≤B	≤none	≤O
Absorption	0.52	0.57	0.72	0.81	1.0	1.2	0.30	0.37	0.42	0.49	0.52	0.59
Desorption	0.42	0.42	0.50	0.50	0.57	0.77	0.30	0.30	0.39	0.41	0.42	0.42
Hysteresis Factor (Hf)	O	<none	≤B	≤C	≤Se	<S	O	≤none	<B	≤C	≤Se	<S
	0.44	0.51	0.53	0.55	0.58	0.69	0.48	0.50	0.58	0.62	0.65	0.69

The values measured refer to at 27°C.

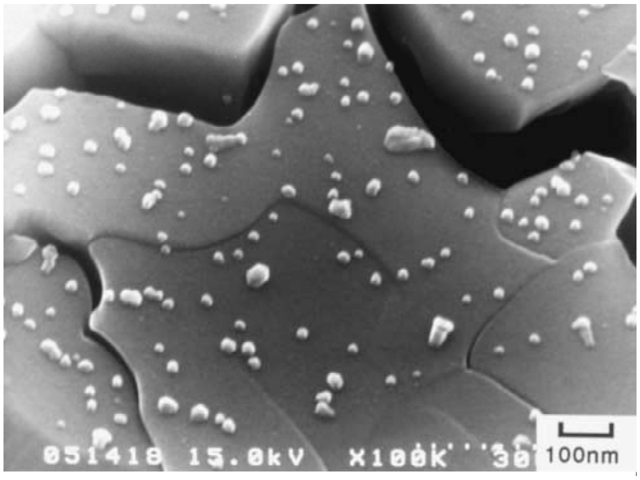


Fig. 6. SDEM image of as-cast $Ti_{0.9}Zr_{0.1}Mn_{1.4}Cr_{0.4}V_{0.2}$ alloy-powder after hydrogenation of hydrogen absorbing/desorbing 6 cycles.

Development Organization) and ECC (Energy Conservation Center).

References

[1] T. Gamo, Y. Moriwaki, N. Yanagihara, T. Yamashita and T. Iwaki, *Int. J. Hydrogen Energy, 10* (1985) 39.

[2] T. Gamo, Y. Tsuji and Y. Moriwaki, *Proc. Symp. Hydrogen and Metal Hydride Batteries*, 1994 (ECS, 94–27) p. 155.

[3] H. Nakano and S. Wakao, *J. Alloys Comp.,* 231 (1995) 587.

[4] Y. Morita and T. Gamo, *J. Japan Inst. Metals, 59* (1995) 1084.

[5] K. Morii and T. Shimizu, *J. Alloys Comp., 231* (1995) 524.

[6] D.G. Ivey and D.O. Northwood, *Z. Phys. Chem. N.F., 147* (1986) 191.

[7] J.M. Park, Y.G. Kim and J.Y. Lee, *J. Alloys Comp., 198* (1993) L19.

[8] Y. Moriwaki, T. Gamo and T. Iwaki, *J. Less-Common Met., 172–174* (1991) 1028.

[9] F. Pourarian, V.K. Sinha, W.E. Wallace and H.K. Smith, *J. Less-Common Met., 88* (1982) 451.