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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	35
number	1
page range	84-91
year	1990-03-23
URL	http://hdl.handle.net/10097/28329

**Hydrogen-Induced Amorphization in Zr_3Al Compound
with $L1_2$ Structure***

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(Received February 5, 1990)

Synopsis

The process of hydrogen-induced amorphization in the $L1_2$ type intermetallic compound Zr_3Al has been investigated by x-ray diffraction and transmission electron microscopy. Then, it has been compared with that of the isomorphous Zr_3In . Zr_3Al amorphizes below about 500 K where the decomposition of it into ZrH_2 and Al is substantially suppressed in contrast to Zr_3In . Almost complete disordering precedes the onset of amorphization in the same way as irradiation-induced amorphization of this compound. The DSC result suggests that hydrogen atoms in α - Zr_3AlH_4 are trapped tightly in comparison with those in α - RM_2H_x (R = a rare earth metal, M = Fe, Co, Ni) prepared by hydrogenation.

I. Introduction

Amorphous alloys have usually been prepared either from the vapor or the liquid state via appropriate quenching techniques. However, amorphous alloys have also been successfully synthesized from initially crystalline alloys by the solid-state, nonequilibrium processing techniques including reaction of intermetallic compounds with gaseous hydrogen(1). The present authors have shown that hydrogenation of the intermetallic compounds with the $C15$, $C23$, $B8_2$,

* The 1849th report of Institute for Materials Research

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$D0_{19}$, and $L1_2$ structures gives rise to hydrogen-induced amorphization (HIA)(2), although its mechanism is still uncertain. In order to clarify the mechanism of HIA, it is essential to know the process and the conditions of HIA in intermetallic compounds with the different crystal structure. It has been reported that HIA in RM_x compounds (R is a rare earth metal, $M = Fe, Co, Ni, Al, In$ and so on) occurs at the temperature range where the decomposition of it into RH_2 and M (or RM_x) is substantially suppressed because of low diffusion rates of metal atoms (2). On the contrary, it has been reported that Zr_3In amorphizes below the temperature where it becomes $c-Zr_3InH_x$ (fcc)(3). Thus, there is an apparent difference in the HIA behavior between Zr_3In and the other intermetallic compounds. It is known that Zr_3Al with the $L1_2$ structure amorphizes by hydrogenation (4), although the conditions and the process of HIA in it are still unknown. In the present work, the process of HIA in the $L1_2$ type intermetallic compound Zr_3Al is investigated by x-ray diffraction and transmission electron microscopy, and compared with that of the isomorphous Zr_3In .

II. Experimental

The Zr_3Al compound was prepared from high purity metals (99.6% zirconium and 99.99 % aluminum) by arc melting in an argon atmosphere. The ingot was homogenized at 1123 K for 605 ks in an evacuated quartz tube, and then cut into small blocks. These blocks were slowly reacted with high purity hydrogen (7N) of 5 MPa pressure between 300 and 773 K for 178.2 ks after the activation treatment at 673 K for 3.6 ks in a vacuum. The amount of hydrogen absorbed was determined from the change in hydrogen pressure in a constant volume reactor. The crystallographic structure of the samples before and after hydrogenation was examined by powder x-ray diffraction (XRD) using monochromated $Cu K_\alpha$ radiation. Some samples were further examined by transmission electron microscopy (TEM) using a 200 kV JEOL 2000 EX microscope. Crystallization of the amorphous $a-Zr_3AlH_x$ prepared by hydrogenation was studied in a flow of pure argon gas at a heating rate of 40 K/min using a differential scanning calorimeter (DSC) in combination with TEM.

III. Results and discussion

Figure 1 shows powder XRD patterns of Zr_3Al before and after hydrogenation. Most Bragg peaks in the pattern of the homogenized sample can be indexed to the $L1_2$ structure of the Zr_3Al compound. The presence of all superlattice peaks with mixed even and odd Miller indices indicates a high degree of long-range order in this compound. Zr_3Al does not substantially absorb hydrogen at 300 K. On the other hand, XRD patterns of the samples hydrogenated at 373 and 473 K do not show any sharp Bragg peaks and are replaced by a broad maximum. Such sample was further examined by TEM.

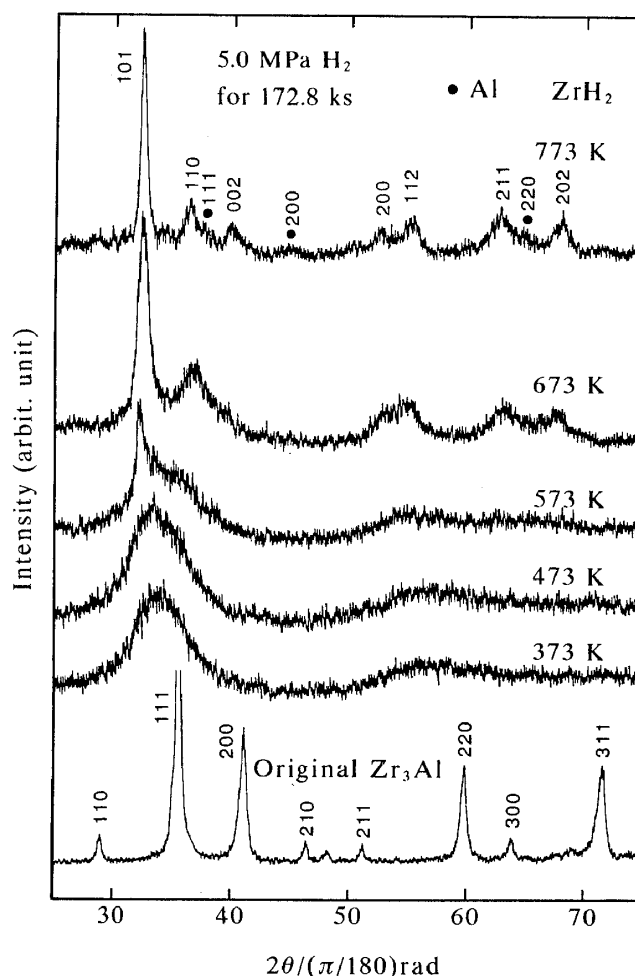


Figure 1 The x-ray diffraction patterns of Zr_3Al hydrogenated at various temperatures for 172.8 ks.

Figure 2 shows a bright-field image and the corresponding diffraction pattern of the sample (hydrogenated at 473 K) showing a broad maximum in the XRD pattern. The microstructure is featureless and the diffraction pattern shows a diffuse halo. These indicate that the alloy has amorphized by hydrogen absorption. The hydrogen to metal ratio in this sample was determined to be 1.0. This corresponds to 4.0 absorbed hydrogen per formula, so that the alloy can be written as $a-Zr_3AlH_4$. The structure of hydrogen-induced amorphous $a-Zr_3AlH_4$ investigated by the x-ray structural analysis is described in other paper(5).

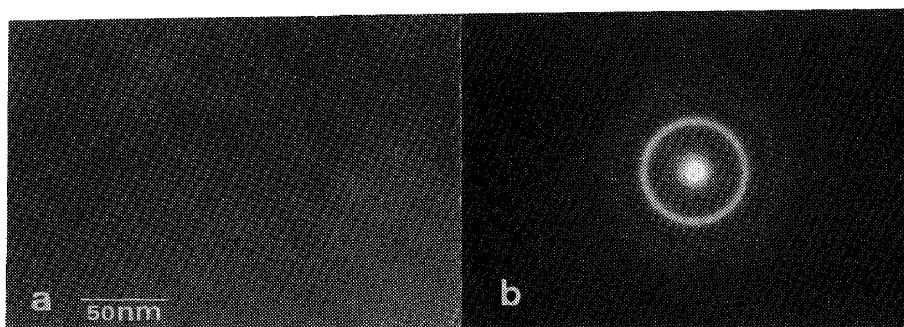


Figure 2 A transmission electron micrograph (a) and the diffraction pattern of Zr_3Al hydrogenated at 473 K for 178.2 ks.

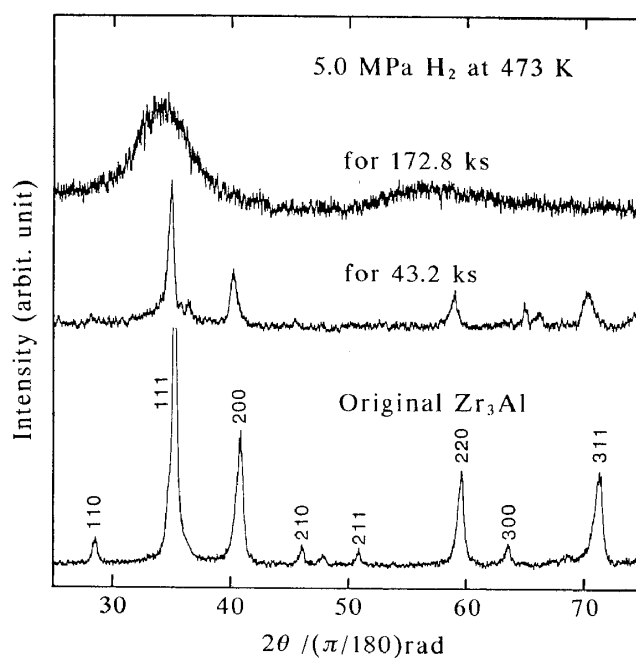


Figure 3 The x-ray diffraction pattern of Zr_3Al hydrogenated at 473 K for for 43.2 and 172.8 ks.

Figure 3 shows XRD patterns of Zr_3Al hydrogenated at 473 K for 43.2 and 172.8 ks. The appearance of the broad diffraction peak in the sample hydrogenated for 43.2 ks, which exhibits an intensity maximum close to the (111) fundamental peak, implies that the hydrogenated alloy has been partially amorphized. The remaining Bragg peaks can be indexed to the fcc structure as seen in this figure and in the electron diffraction pattern (Fig. 4). The disappearance of the superlattice peaks suggests that chemical disordering plays a dominant role in HIA in this compound in the same way as irradiation - induced amorphization (6). However, it has recently been reported

that hydrogenation of Zr_3Al causes no appreciable change in long-range order prior to amorphization(7). The reason for this discrepancy is uncertain at the present time.

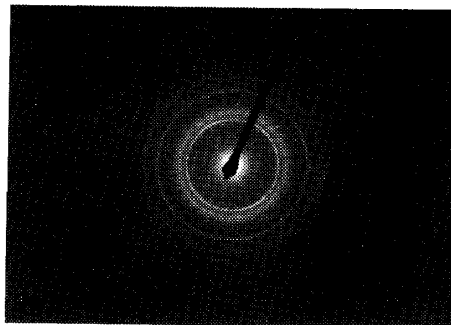


Figure 4 An electron diffraction pattern of Zr_3Al hydrogenated at 473 K for 43.2 ks.

On hydrogenation at 573 and 673 K, Bragg peaks are overlapped with the broad maximum. The XRD pattern of the sample hydrogenated at 773 K can be satisfactorily indexed on the basis of a phase mixture which consists of the tetragonal ZrH_2 with a lattice parameter $a = 0.352$ nm and $c = 0.445$ nm and Al with a lattice parameter of $a = 0.406$ nm.

Figure 5 shows a bright-field image and the corresponding diffraction pattern of the sample hydrogenated at 773 K. A set of Debye-Scherrer rings is observed and can be indexed in terms of ZrH_2 and Al phases. Thus, HIA in Zr_3Al occurs at the temperature where the decomposition of the compound into the metal hydride and the intermetallic compound is suppressed in contrast to Zr_3In . Therefore, we can say that HIA behavior of Zr_3In is an exceptional one.

A differential scanning calorimetry (DSC) curve of hydrogen induced $a-Zr_3AlH_4$ heated in an argon atmosphere is shown in Figure 6.

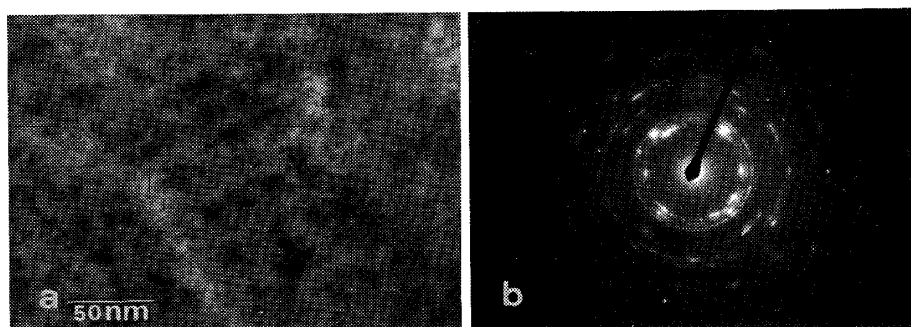


Figure 5 A bright-field image and the corresponding diffraction pattern of Zr_3Al hydrogenated at 773 K.

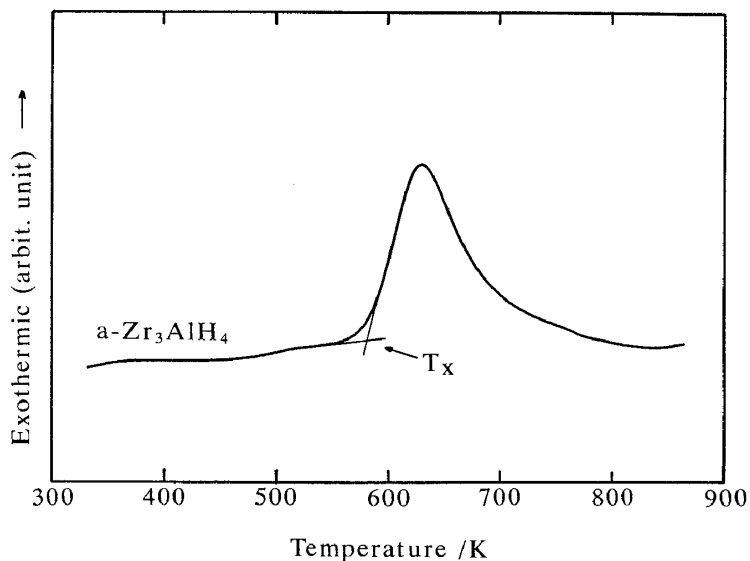


Figure 6 A differential scanning calorimetry (DSC) curve of a-Zr₃AlH₄ heated in an argon atmosphere.

The curve shows only one broad exothermic peak around 600 K similar to that of a-Zr₃InH_x(3). No endothermic peak resulting from hydrogen desorption is observed in contrast to a-RM₂H_x (8). This result suggest that hydrogen atoms in the present amorphous alloy are more tightly trapped. To clarify the nature of the exothermic peak, structures of the samples heated below and above the exothermic peak were examined. Since the diffraction pattern of the sample heated to 550 K shows only a diffuse halo, we can conclude that the amorphous structure is retained up to this temperature.

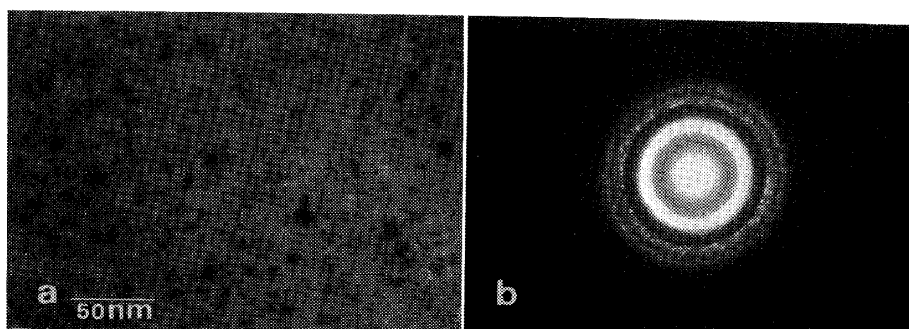


Figure 7 A bright field image of the sample heated to 873 K and (b) the corresponding diffraction pattern.

Figure 7(a) shows a bright field image of the sample heated to 873 K and (b) the corresponding diffraction pattern. The bright field image shows homogeneous precipitates and the diffraction pattern shows the overlapping with the amorphous halo and a set of Debye-Scherrer rings, although they are not indexed. This result shows that the α - Zr_3AlH_4 prepared by hydrogenation is thermally stable. The crystallization temperature, T_x , defined as the cross point of the extrapolated base line and the steepest tangent of the peak is 580 K. The authors have proposed that HIA in intermetallic compounds occurs where the decomposition of RM_2 into the hydride RH_2 and a pure metal M is suppressed by low diffusion rates of metallic atoms. The present work supports our proposal for the conditions of HIA in intermetallic compounds.

IV. Summary and conclusions

Hydrogen-induced amorphization in the intermetallic compound Zr_3Al with the $L1_2$ structure has been demonstrated by hydrogenation below 473 K where the decomposition of the compound into ZrH_2 and Al is suppressed in contrast to Zr_3In . Almost complete disordering precedes prior to HIA in the same way as irradiation-induced amorphization. It is suggested that hydrogen atoms in the amorphous Zr_3AlH_4 prepared by hydrogen absorption are more tightly trapped.

Acknowledgments

The present work was supported in part by a Grant-In-Aid for the Scientific Research on Priority Areas, New Functionality Materials-Design, Preparation and Control, The Ministry of Education, Science and Culture (01604509), Japan.

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