

Hydrogenation of Body-Centered-Cubic Titanium-Chromium Alloys Prepared by Mechanical Grinding

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The C15 and C14 intermetallic TiCr_{2-x} ($x = 0, 0.2$ and 0.5) compounds were subjected to grinding in a high-energy ball mill. The X-ray diffraction profiles showed that the crystal structure transformed from C15 and C14 to bcc after mechanical grinding for 57.6 ks. The hydrogenation properties of the TiCr_{2-x} ($x = 0, 0.2$ and 0.5) samples were examined by differential thermal analysis and pressure-composition isotherm measurements. The sample reacted with hydrogen at 5 MPa and 523 K by maintaining the bcc structure. An higher hydrogen content was observed for the sample with the higher Ti content. The maximum hydrogen content of $\text{TiCr}_{2.0}$, $\text{TiCr}_{1.8}$ and $\text{TiCr}_{1.5}$ was found to be about 0.32, 0.36 and 0.47 H/M at 313 K, respectively, at 8 MPa.

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1. Introduction

Recently, it has been reported that certain alloys with bcc structure can absorb a large amount of hydrogen.¹⁻⁵⁾ Iba and Akiba reported that Ti-V-Mn and Ti-V-Cr alloys exhibited large hydrogen capacities¹⁻³⁾ of over 2 mass%. Okada *et al.* reported that a bcc phase, which is metastable at ambient temperatures in the Ti-Cr binary system, can be stabilized by the addition of third element such as V. The Ti-Cr-V ternary alloys have high hydrogen capacity at room temperature. Especially, the Ti-5V-57.5Cr alloy with bcc structure reversibly absorbed and desorbed 2.8 mass% hydrogen at 313 K.⁶⁾

The bcc solid solution phase in the Ti-Cr binary system is a metastable phase at room temperature in the range from 63 mol%Cr to 66 mol%.⁷⁾ Heat treatment followed by quenching is required to prepare a single phase sample of the bcc phase. However, it is difficult to obtain the single phase sample without addition of other elements, because Laves phases are simultaneously formed during quenching.

Both mechanical alloying (MA)⁸⁻¹⁰⁾ and mechanical grinding (MG)^{11,12)} are convenient and simple methods to prepare metastable materials. It has been reported that for intermetallic compounds such as Ti_3Ir , V_3Ga and Nb_3Au , the original Cr_3Si type structure can be transformed into the bcc structure that is stable at high-temperature by MG.¹³⁻¹⁶⁾ Based on this analogy, we expected to obtain a high-temperature phase in Ti-Cr system by MG. It is quite important to show an alternative technique to obtain such metastable phase for the preparation of hydrogen storage.

In this paper, we report that the C15 and C14 Laves structures transformed into bcc structure by MG. We also report on hydrogenation of bcc solid solution alloys prepared by MG.

2. Experimental

TiCr_{2-x} ($x = 0, 0.2$ and 0.5) alloy ingots were prepared by arc melting, and then crushed into a powder which passed through a 0.105 mm screen. The powder of each alloy was sealed in a stainless steel vial (SUS 304, inner volume: 250 ml) together with stainless steel balls (SUS 304, 4 mm in diameter) in a glove box under an Ar atmosphere in order to prevent alloys from oxidizing. The weight ratio of the balls to samples was maintained at 10:1. MG was performed using a high-energy planetary ball mill (BX254E Kurimoto, Ltd.) at a rotation speed of 12 rps (73.6 s^{-1}). The hydrogen occlusion samples were prepared by hydrogenation-dehydrogenation of the samples made by MG. The hydrogen content of the samples was calculated using a volumetric method.

The constituent phases in the sample were examined by the X-ray diffraction (XRD) analysis using a $2\theta-\theta$ powder diffractometer with Cu $K\alpha$ radiation. An analysis of the powder diffraction data collected between 10 and 120 degrees in 2θ at room temperature with 0.05 degree steps, was used in order to refine the crystal structures of the obtained alloys.

The hydrogenation properties of the samples were evaluated by differential thermal analysis (DTA) and pressure-composition isotherm (PC-isotherm) measurement. In the DTA measurement of the samples, the temperature was increased from room temperature to 773 K, and the temperature scanning rate upon heating and cooling was kept at 0.167 K/s. The PC-isotherms were measured with an automatic Sieverts'-type apparatus. The sample was put into a vessel, and then evacuated at 573 K for 7.2 ks using a rotary vacuum pump. Hydrogen was gradually introduced into the vessel up to a pressure of 10 MPa, and then degassed at 623 K under vacuum for 1.8 ks. This process was repeated twice for the initial hydrogenation. Each equilibrium pressure at the respective hydrogen contents was determined at least 3 h after adding or removing hydrogen. The hydrogen absorption-desorption properties were defined by the 3rd cycle of the PC-

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isotherms.

3. Results and Discussion

Figure 1 shows the XRD profiles of the as-melt TiCr_{2-x} ($x = 0, 0.2$ and 0.5) alloys. The profile of the TiCr_2 alloy indicated the existence of the phases with the cubic C15-type structure and the hexagonal C14-type structure besides Si mixed into the sample for correction of diffraction angles. It was found that the constituent phases of the $\text{TiCr}_{1.8}$ and $\text{TiCr}_{1.5}$ samples were the C15 and C14 Laves phases as well as TiCr_2 . Therefore, these as-melt samples were composed of two Laves phases within the detection ability of our XRD instrument.

Figure 2 shows the XRD profile of the $\text{TiCr}_{1.8}$ sample ground for 57.6 ks and the profile of $\text{TiCr}_{1.8}$ with bcc structure simulated by Rietveld method. The diffraction peaks from the C15 and C14 Laves phases disappeared and only the peaks from the new phase were observed after MG. The sets of the new peaks agreed well with those corresponding to the interplanar spacing of the bcc structure. Since a solid solution region with bcc structure exists in the Ti–Cr phase diagram,⁷⁾ we propose that this new phase is a solid solution phase with a

bcc structure. Figure 3 shows the XRD profiles of the TiCr_{2-x} ($x = 0$ and 0.5) samples ground for 57.6 ks together with the profile of the $\text{TiCr}_{1.8}$ sample ground for 57.6 ks. As well as the MG $\text{TiCr}_{1.8}$ sample, the XRD diffraction peaks observed for the two alloys were identified as those from the bcc phase. The results showed that MG also caused a phase transformation from the Laves phases to the bcc phase for these two samples. The X-ray diffraction peaks shifted to lower angles with increasing the Ti concentration in the sample, which indicates enlargement of the lattice constant of the bcc phase due to the substitution of the smaller atoms (Cr) by larger atoms (Ti).

Figures 4 and 5 show the DTA profiles measured under a hydrogen atmosphere for the samples prepared by MG and the XRD profiles for the samples after the DTA measurements, respectively. An exothermic peak was observed at 500–550 K for the 1st cycle and no other peak appeared after repeating the heating and cooling in the range from room temperature to 773 K. The XRD profile of the sample after the DTA measurement indicated that existence of the phase with bcc structure. Since the diffraction peaks shifted to lower angles compared with those of the original sample after the DTA measurement, the lattice constant was enlarged with respect to that of the original samples. These results indicate that hydrogenation occurred in the MG sample at 500–550 K during the 1st cycle.

According to the above DTA measurement, we selected the

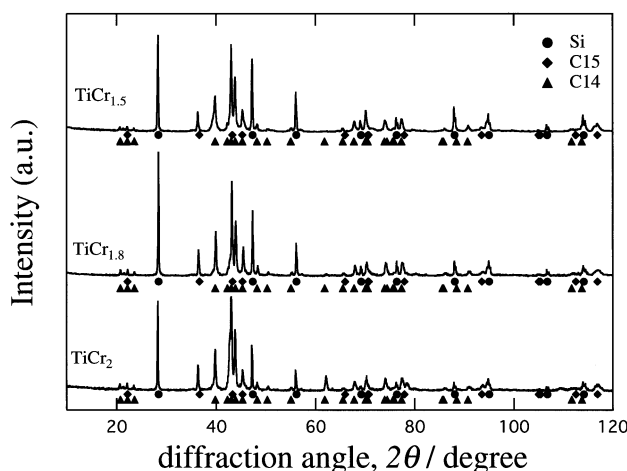


Fig. 1 The X-ray diffraction profiles of TiCr_{2-x} ($x = 0, 0.2$ and 0.5) alloys prepared by arc melting.

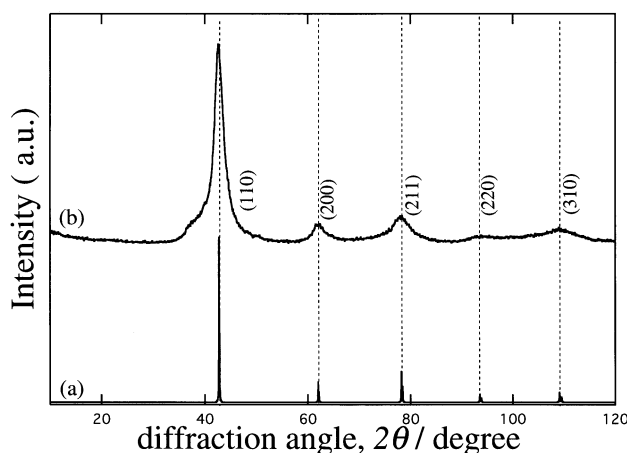


Fig. 2 A comparison of the X-ray diffraction profiles of (a) bcc structure simulated by Rietveld method with (b) the $\text{TiCr}_{1.8}$ alloy prepared by MG for 57.6 ks.

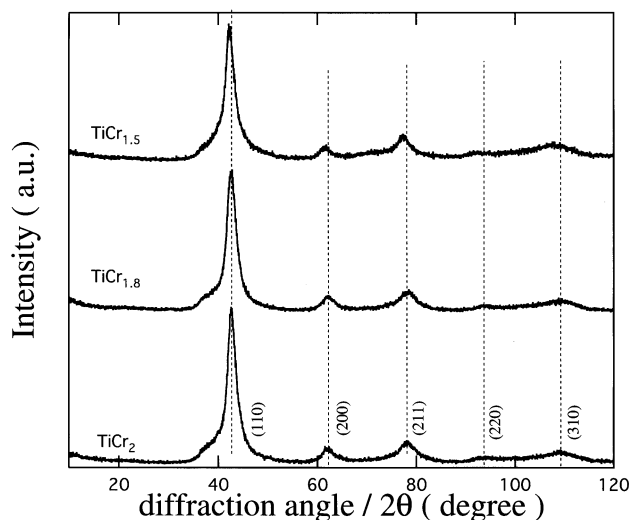


Fig. 3 The X-ray diffraction profiles of the TiCr_{2-x} ($x = 0, 0.2$ and 0.5) alloys prepared by MG.

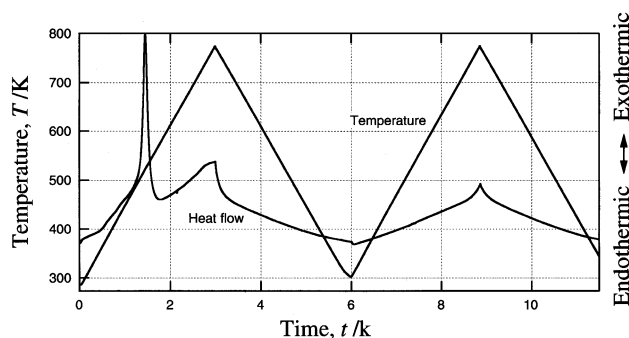


Fig. 4 Heat flow profile obtained by differential thermal analysis in 5 MPa H_2 atmosphere for the $\text{TiCr}_{1.8}$ sample prepared by MG.

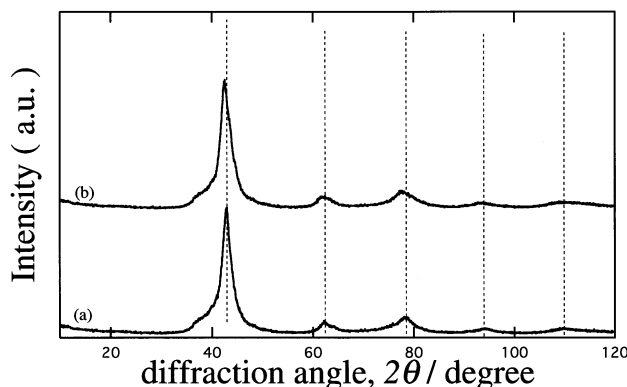


Fig. 5 The X-ray diffraction profiles of (a) the $\text{TiCr}_{1.8}$ sample prepared by MG with (b) the $\text{TiCr}_{1.8}$ sample prepared by MG after differential thermal analysis from room temperature to 773 K under H_2 atmosphere.

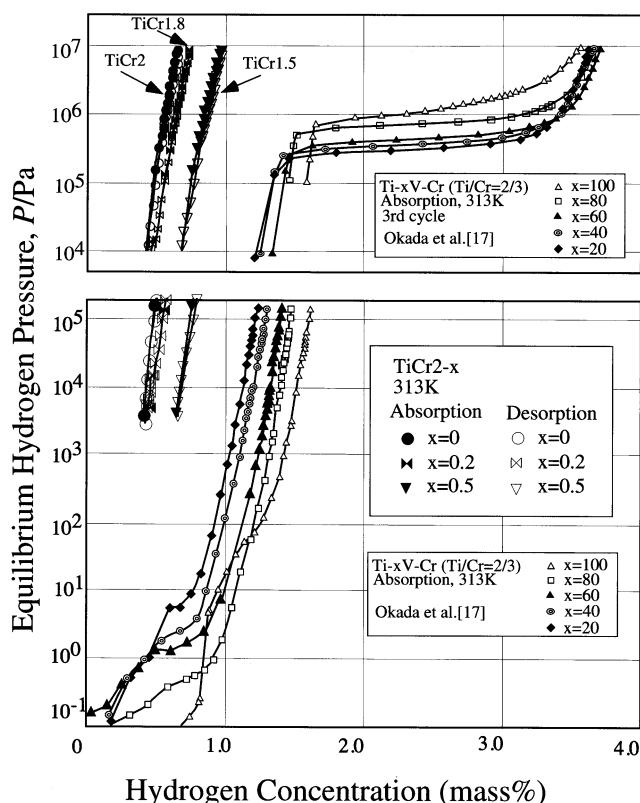


Fig. 6 The hydrogen pressure-composition-isotherms of the TiCr_{2-x} ($x = 0, 0.2$ and 0.5) samples prepared by MG at 313 K, together with the data reported by Okada *et al.*¹⁷⁾

condition of the activation treatment in this study; 573 K for the reaction temperature and 5 MPa for the hydrogen pressure. After the activation treatments, the PC-isotherms were measured at 313 K. Figure 6 shows the PC-isotherms in the absorption-desorption process of the TiCr_{2-x} ($x = 0, 0.2$ and 0.5) samples prepared by MG, together with the data of Ti-V-Cr with bcc structure prepared by melting and heat treatment.¹⁷⁾ It is characteristic that all the PC-isotherms of the samples were significantly sloped. The equilibrium pressure of the samples increased with increasing Cr content at a given hydrogen content, and the hydrogen content increased with decreasing Cr content. The maximum hydrogen contents of $\text{TiCr}_{2.0}$, $\text{TiCr}_{1.8}$ and $\text{TiCr}_{1.5}$ at 8 MPa were 0.32, 0.36 and 0.47 H/M at 313 K, respectively, where H/M means the

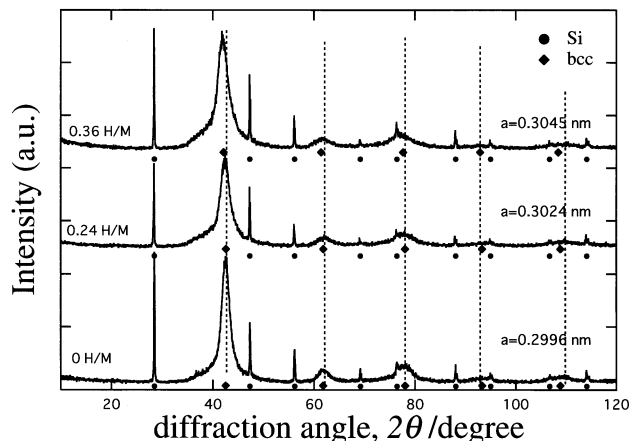


Fig. 7 The X-ray diffraction profiles of the hydrogen occlusion phase. These samples have hydrogen contents of 0, 0.24 and 0.36 H/M.

atomic ratio of hydrogen to metal.

Figure 7 shows the XRD profiles of the hydrogen occlusion phase with hydrogen contents of 0, 0.24 and 0.36 H/M. The XRD profiles indicated the existence of a phase with bcc structure along with Si mixed to the sample for correction of the diffraction angles, and the diffraction peaks shifted to lower angles compared with those of the original sample. The lattice constants calculated by the least square method for these samples were 0.2996, 0.3024 and 0.3045 nm, respectively. The value continuously changed with the hydrogen content. Therefore, it is concluded that the samples prepared by MG form a solid solution phase with hydrogen up to 10 MPa as determined in this study.

Okada *et al.*¹⁷⁾ reported that the stable vanadium monohydride became unstable by adding the other element. This PC-isotherm showed two hydrogen occlusion phases with low and high contents coexisted in the hydrogenated sample. One can find that behavior of the sample prepared by MG is quite different from that of the alloys prepared by melting followed by heat treatment. From the Fig. 6 and Fig. 7, the sample prepared by MG exhibited the hydrogenation behavior as a continuous hydrogen solid solution, but several orders of magnitude higher hydrogen pressures. Moreover, the sample prepared by MG did not show much hydrogen absorption such as 3 mass% with the phase transformation, which was observed in the previous paper.¹⁷⁾ At the present stage, it is difficult to give an appropriate explanation for the instability of the hydrogenation of the samples prepared by MG. However, it is interesting to examine the local atomic structure of the sample prepared by MG. We plan to measure the diffraction profile using transmission electron microscopy (TEM) and neutron diffraction. Further work is now in progress.

In conclusion, the structural change from C15 and C14 to bcc was found after mechanical grinding of the TiCr_{2-x} ($x = 0, 0.2$ and 0.5) alloys. As far as we know, this is the first example of a phase transition from the Laves phases to bcc structure phase by mechanical grinding. The samples with the bcc structure reacted with hydrogen at 573 K under 5 MPa of hydrogen atmosphere by maintaining bcc structure. This behavior is different from some bcc alloys with a high hydrogen storage capacity which indicate a 2 step hydride formation like the V-H system. The maximum hydrogen contents of

TiCr_{2.0}, TiCr_{1.8} and TiCr_{1.5} were estimated to be about 0.32, 0.36 and 0.47 H/M at 313 K, respectively, under an 8 MPa hydrogen atmosphere.

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