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# Effect of CO<sub>2</sub> on hydrogen absorption in Ti-Zr-Mn-Cr based AB<sub>2</sub> type alloys

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#### Abstract

The effect of CO<sub>2</sub> on hydrogen absorption has been investigated for AB<sub>2</sub> type alloys of  $Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}$  (Ti-Zr-Mn-Cr) and  $Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}M_{0.1}$  (Ti-Zr-Mn-Cr-M, M = Fe, Co, or Ni) in order to develop metal hydrides for a hydrogen purification and storage system. A magnitude of CO<sub>2</sub> poisoning tolerance was evaluated by comparing hydrogen absorption properties before and after CO<sub>2</sub> exposure. As the results, an order of CO<sub>2</sub> tolerance was Ti-Zr-Mn-Cr-Ni < Ti-Zr-Mn-Cr < Ti-Zr-Mn-Cr-Co < Ti-Zr-Mn-Cr-Fe. It suggests that the AB<sub>2</sub> alloys have dependence of additive 3d-transition elements on CO<sub>2</sub> tolerance.

Ti-Zr-Mn-Cr-Fe has the highest  $CO_2$  tolerance among them. The additive of Fe and Co improves tolerance of  $CO_2$  poisoning for hydrogen absorption properties. On the other hand, Ni element in AB<sub>2</sub> alloy decreases  $CO_2$  tolerance. The estimated enthalpy change between  $CO_2$  and the alloys surface was comparable to the formation of metal oxide. And the  $CO_2$ -exposed AB<sub>2</sub> alloys after reacting with hydrogen desorbed methane gas. Therefore,  $CO_2$ would dissociate to CO and O on the surface of alloys, and then oxygen atom reacts with the alloys.

Keywords: hydrogen absorbing materials, carbon dioxide, gas-solid reactions, poisoning tolerance, kinetics

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#### 1. Introduction

Polymer electrolyte fuel cells (PEFC) have advantages like high efficiency, low operating temperature, e.g. 80 °C, and quick response for electric load demand. It is important for PEFCs to provide pure hydrogen since the cell voltage drops when impurities exist in hydrogen gas [1]. When hydrogen is produced by steam reforming and following water-gas shift reaction [2], it involves 20-25% CO<sub>2</sub> and 0.5-1% CO as by-products. A CO Adsorbent and Metal hydride Intermediate-Buffer (COA-MIB) system has been proposed to purify from methane reforming gas and store hydrogen [3-9]. This system can supply pure hydrogen to PEFCs corresponding to electric load demand. The CO adsorbent used in this system decreases CO less than 1 ppm. The metal hydride stores hydrogen from the CO<sub>2</sub>-mixed gas, and it desorbs pure hydrogen when required. The metal hydride used currently is LaNi<sub>5</sub>-based AB<sub>5</sub> type alloy which contains Misch Metal in A site and mainly Ni in B site because of excellent tolerance of  $CO_2$  poisoning [8]. Here,  $CO_2$  poisoning is defined as the decrease of hydrogen absorption kinetics and hydrogen absorption amount. It is important for practical application of the COA-MIB system to reduce cost and volume of the metal hydride tank by replacing with one of low-cost and large hydrogen capacity. For designing the high functional metal hydrides with high tolerance of  $CO_2$  poisoning, we investigated the  $CO_2$  poisoning factors of constituent elements in AB<sub>5</sub> type alloys of LaNi<sub>5</sub>, CaNi<sub>5</sub>, and LaCo<sub>5</sub> [10]. As the result, CaNi<sub>5</sub> showed the best tolerance of  $CO_2$  poisoning among them. This means that Ni in B site has more important role to maintain high CO<sub>2</sub> tolerance rather than Co in LaCo<sub>5</sub> and the rare-earth metal of La in LaNi<sub>5</sub>. It has been reported that surface modified AB<sub>5</sub>-type alloys have higher poisoning tolerance and separates hydrogen from CO<sub>2</sub> and CO containing gas mixtures [11-13]. For other type of metal hydrides, TiFe alloys have been investigated the effects of CO<sub>2</sub> as the impurity gas on hydrogen sorption properties [14-16]. The hydrogen

absorption rate and capacity decreased even under 0.1% CO<sub>2</sub> concentration [15].

We focused on  $AB_2$  type laves phase alloys because of higher hydrogen capacity than  $AB_5$ , rare earth free, and easy activation [17]. There have been a number of publications reporting hydrogen sorption properties for  $AB_2$  type alloys [17-19]. We chose C14 laves phase alloys of Ti-Zr-Mn-Cr [18] as possible candidate for COA-MIB system because it is composed of low cost elements such as Zr and Mn.

In this study, an effect of CO<sub>2</sub> on hydrogen absorption has been investigated for  $Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}$  which has a moderate equilibrium pressure of 0.1 MPa at 25 °C for the COA-MIB system. In order to improve tolerance of CO<sub>2</sub> poisoning, 3d-transition elements of Fe, Co, or Ni, which potentially have a catalytic effect on hydrogen molecule dissociation, have been added as  $Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}M_{0.1}$  (*M* = Fe, Co, or Ni) and investigated the effect of CO<sub>2</sub> on hydrogen absorption. Furthermore, mechanism of the reaction between CO<sub>2</sub> and the alloys was discussed.

#### 2. Experimental

Alloy samples of AB<sub>2</sub> (Ti<sub>0.515</sub>Zr<sub>0.485</sub>Mn<sub>1.2</sub>Cr<sub>0.8</sub>) and AB<sub>2</sub>-M (Ti<sub>0.515</sub>Zr<sub>0.485</sub>Mn<sub>1.2</sub>Cr<sub>0.8</sub>M<sub>0.1</sub>; M = Fe, Co, Ni) were synthesized by arc melting (NEV-AD 03, Nisshin Giken Co.) in an argon atmosphere. Starting materials of Zr (99.7%), Mn (99.99%), Cr (99.99%), Fe (99.9%), Co (99.9%), and Ni (99.9%) were purchased from Furuuchi Chemical Co. Titanium (99.5%) was purchased from The Nilaco Corporation. As-prepared ingots of alloys were annealed at 1100 °C for 24 h in the argon atmosphere for homogenization. The cross sections of the annealed ingots were polished and observed by Scanning Electron Microscope (SEM, S-3400N, High-Technologies). Elemental Hitachi analysis was performed by Energy-Dispersive X-ray Spectroscopy (EDX, APOLLO XP, AMETEK) equipped with SEM. The ingots powders 150-500 diameters. were ground into of μm

Pressure-Composition-Temperature (PCT) curves were measured by using Sieverts-type apparatus. Measurement conditions were at pressure of  $0.05 \sim 1.0$  MPa H<sub>2</sub> and temperatures of 20, 30, 40, and 50 °C. The waiting time for each hydrogen absorption/desorption step was at least 20 min. Equilibrium pressures were determined as a point that pressure change during the waiting time became smaller than 0.002 MPa. A van't Hoff plot was obtained using the average of absorption and desorption pressures at a half of maximum amount of hydrogen in PCT curves at each temperature. Powder X-ray diffraction (XRD) with Cu-K $\alpha$  radiation (RINT-2100, Rigaku) was performed to obtain crystallographic information. The powders less than 150 µm diameter was used for the measurements. The lattice constants of the samples were calculated from peak positions.

Measurements for hydrogenation and dehydrogenation, and  $CO_2$  exposure were conducted using semi-continuous flow-type reactor. Each sample of 1 g was loaded into a stainless steel vessel of 14 ml volume with 4.6 mm in inner diameter. The sample vessel was covered with a coolant tube for water cooling, a ribbon heater for electric heating, and a heat insulating material on those. The sample temperature was monitored by a thermocouple located inside the vessel in good contact with the sample powder. The flow rate gas inlet was controlled using a needle valve and measured using a mass flow meter placed in the flow path of gas inlet. More details of the apparatus were reported in our previous paper [10]. For an initial activation process, the sample was heated up to 150 °C under vacuum by a rotary pump. Then H<sub>2</sub> of 0.9 MPa was introduced and kept flowing through the vessel for 1 h with 500 scc/min at 150 °C. After that, the sample was cooled down to 80 °C and vacuumed at 80 °C as a hydrogen desorption. Hydrogen of 0.9 MPa was introduced again at 80 °C as a hydrogen absorption. The hydrogen absorption and desorption was repeated 3 times. Finally, the sample was evacuated (~10 Pa) at 80 °C and then cooled to 20 °C.

For the hydrogenation test, H<sub>2</sub> was introduced into the vessel up to 0.9 MPa at 20 °C with

flow rate of approximately 5 scc/min (1 scc/min is flow rate at 20 °C under 0.1013 MPa). The test was stopped after 80 min or when the flow rate decreased to 0.1 scc/min. A hydrogen absorption rate  $R_{hy}$  was calculated by  $R_{hy} = R_{in} - R_{cell}$ , where  $R_{in}$  is a hydrogen flow rate, and  $R_{cell}$  is rate of remained gas amount in the cell calculated by PV/RT. The amount of hydrogen absorption was calculated by the integration of  $R_{hy}$ . More details were reported in Ref. [10]. For the dehydrogenation test, the sample after hydrogenation was simply evacuated for 30 min at 80 °C.

The CO<sub>2</sub> exposure was performed by the following procedures. First, CO<sub>2</sub> was introduced into the vessel up to 0.9 MPa after the dehydrogenation process. Second, this pressurized condition was kept for 30 min at 20 °C and then CO<sub>2</sub> was evacuated for 30 min. After CO<sub>2</sub> exposure, the hydrogenation and dehydrogenation was cycled for 3 times. The observed properties were discussed comparing to the properties before the CO<sub>2</sub> exposure.

After the  $CO_2$  exposure and hydrogenation property measurement, hydrogenation under  $CO_2$  partial pressure was performed,  $CO_2$  of 0.1 MPa was firstly supplied to the dehydrogenated state of alloys. Then H<sub>2</sub> was supplied with flow rate of approximately 5 scc/min at 20 °C to increase the pressure from 0.1 to 0.9 MPa. This test was stopped after 600 min or when the gas flow rate decreases to 0.01 scc/min. Hydrogen of 7N purity and  $CO_2$  of 99.97% purity were used for all experiments.

Gas chromatography-Flame Ionization Detector (GC-FID; GC-2014, Shimadzu Co.) analysis was performed in order to detect hydrocarbon in the sample gas which was prepared by following procedures: (1) after the initial activation, three times of hydrogenation at RT (~25 °C) and 0.9 MPa H<sub>2</sub> for 80 min and dehydrogenation at 80 °C under vacuum condition for 30 min; (2) CO<sub>2</sub> was introduced at RT from vacuum condition to 0.9 MPa within 5 min and then kept for 30 min; (3) after removing CO<sub>2</sub> by evacuation at RT for 30 min, hydrogen was pressurized to be 0.9 MPa; and finally (4) the sample was heated up to 200 °C for 3 days.

The gas in the sample vessel was measured by GC-FID. All sample scale was 1 g and vessel volume was  $\sim$ 55 mL. Blank data of the gas without CO<sub>2</sub> exposure (procedure 2) were also measured. Amount of detected gas was calculated by subtracting blank data from sample data.

#### 3. Results and discussion

### 3.1. Composition and crystal structure

Figure 1 and Table 1 show back scattering electron (BSE) images and the elements compositions EDX analysis  $Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}$  (AB<sub>2</sub>), by SEM and for  $Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}Fe_{0.1}$  $(AB_2-Fe),$  $Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}Co_{0.1}$  $(AB_2-Co),$ and Ti<sub>0.515</sub>Zr<sub>0.485</sub>Mn<sub>1.2</sub>Cr<sub>0.8</sub>Ni<sub>0.1</sub> (AB<sub>2</sub>-Ni), respectively. The observed compositions in all area of the samples almost corresponded to the target compositions. Since a vapor pressure at melting point of Mn is the lowest among contained elements, the Mn ratio in all samples is slightly less than the target one due to evaporation during arc melting. The spot 1 in AB<sub>2</sub> was a Zr-rich part, which was higher Zr concentration and lower Ti concentration than the target, while the spot 2 was a Ti-rich part. The spots 3-8 in AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni were also similar tendency with regard to Ti and Zr ratio. In particular, the BSE image of AB<sub>2</sub>-Co in Fig. 1 showed light gray (the Zr-rich part) and dark gray (the Ti-rich part) area in spot 5 and 6, respectively. These results indicate that the AB<sub>2</sub> alloys (AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni) contain Ti-rich and Zr-rich components.

Figure 2 shows XRD profiles of the  $AB_2$  alloys. All samples were determined as single phase of C14 Laves phase. No reflections from impurity phase was observed. Therefore, all of Ti-rich and Zr-rich parts in BSE images are corresponding to C14 Laves structure. All peaks were broad, and it can be explained by the variation of compositions as observed by BSE and EDX. Lattice constants and lattice volumes of the  $AB_2$  phases were evaluated using

XRD peaks as shown in Table 2. For the samples added the transition element, lattice constants *a* and *c*, and lattice volumes increased ( $AB_2$ -Ni <  $AB_2$ -Co <  $AB_2$ -Fe) with the atom radius of additive metal (Ni < Co < Fe).

#### 3.2 Hydrogen absorption properties

PCT curves of AB<sub>2</sub> alloys at 20, 30, 40, and 50 °C for hydrogen absorption and desorption are shown in Figure 3. The plateau regions for all samples leaned possibly due to the composition gradient. The equilibrium pressures of AB<sub>2</sub>-M (M = Fe, Co, and Ni) were slightly larger than that of AB<sub>2</sub>. Table 3 shows maximum hydrogen absorption amounts at 20 °C and 1 MPa of all samples, which were 0.92-0.99 H/M(1.6-1.7 mass%). Their van't Hoff plots are shown in Figure 4. The enthalpy and entropy of hydride formation are shown in Table 3. The absolute value of enthalpy -33 kJ/mol H<sub>2</sub> of AB<sub>2</sub> was slightly larger than that of AB<sub>2</sub>-Fe (-30 kJ/mol H<sub>2</sub>), AB<sub>2</sub>-Co (-29), and AB<sub>2</sub>-Ni (-31). The entropies of all AB<sub>2</sub> alloys were almost similar value of -100 J/mol·K H<sub>2</sub>.

Figure 5 shows hydrogen absorption properties for all AB<sub>2</sub> alloys at 20 °C. The maximum amounts of hydrogen absorption H/M were 1.02, 0.93, 0.92 and 1.02 for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni, respectively. These values were slightly larger than PCT results shown in Table 3. The deviations were probably caused due to measurement error of the mass flow meter, which was nominally  $\pm 1\%$  of full scale. The hydrogen absorption rates of samples were almost constant at 5–6 scc/min during initial 5 to 20 min, which corresponds to the controlled hydrogen flow rate. After 20 min, these rates gradually decreased and then their hydrogen absorption finished within 60 min. The vessel pressure gradually increased until 60 min for all AB<sub>2</sub> alloys according to the plateau region of hydrogen equilibrium pressure.

# 3.3. Hydrogen absorption properties after CO<sub>2</sub> exposure

Figure 6 shows hydrogen absorption properties of the AB<sub>2</sub> alloys at 20 °C after CO<sub>2</sub> exposure. The hydrogen absorption properties before  $CO_2$  exposure were also shown for comparison. Amount of hydrogen absorption was normalized using maximum amount of hydrogen absorption before CO<sub>2</sub> exposure. The hydrogenated fraction at 80 min for AB<sub>2</sub> and AB<sub>2</sub>-Co gradually decreased to approximately 0.9 within 3 cycles after CO<sub>2</sub> exposure. In the case of AB<sub>2</sub>-Ni, the hydrogenated fraction decreased to 0.83 even at the 1<sup>st</sup> cycle and to 0.77 at the 3<sup>rd</sup> cycle. On the other hand, the fraction of AB<sub>2</sub>-Fe in all 3 cycles were almost identical. The hydrogen absorption rates of AB<sub>2</sub>, AB<sub>2</sub>-Fe, and AB<sub>2</sub>-Co at the 1<sup>st</sup> cycle were slower than those before  $CO_2$  exposure in the measurement beginning. When the pressure increased more than 0.3 MPa at about 10 min, the rates suddenly increased up to 15–20 scc/min at maximum. It indicates that those AB<sub>2</sub> alloys require hydrogen pressure higher than equilibrium pressure probably due to kinetic barrier by  $CO_2$  chemisorption. In the 2<sup>nd</sup> and 3<sup>rd</sup> cycles, the hydrogen absorption rates from 5 to 20 min were almost constant at ~5 scc/min and then gradually decreased. This behavior was almost same to that before  $CO_2$  exposure. In the case of AB<sub>2</sub>-Ni, the hydrogen absorption rate in the 1<sup>st</sup> cycle suddenly increased at 20 min, where the maximum absorption rate was 23 scc/min at 0.6 MPa hydrogen. In the 2<sup>nd</sup> cycle, a similar peak to 1<sup>st</sup> cycle appeared at 10 min. In the 3<sup>rd</sup> cycle, that peak finally disappeared. The chemisorbed CO<sub>2</sub> would remain on AB<sub>2</sub>-Ni even after the hydrogen desorption at 80 °C. These results suggest that the  $CO_2$  bonding with  $AB_2$ -Ni is stronger than that with the other AB<sub>2</sub> alloys.

The hydrogen absorption properties of  $AB_2$  alloys in the 3<sup>rd</sup> cycle are summarized in Figure 7. Weak  $CO_2$ -metal bonding was supposed to be removed at 3<sup>rd</sup> dehydrogenation treatment, the strong  $CO_2$ -metal bonding, which causes irreversible poisoning such as strong chemisorption or surface reaction, would degrade hydrogen absorption properties of  $AB_2$ -M. The order of total hydrogenated fraction in 3<sup>rd</sup> cycle was:

$$AB_2$$
-Ni <  $AB_2 \approx AB_2$ -Co <  $AB_2$ -Fe.

On the other hand, the order of hydrogen absorption rate at 5-20 min was AB<sub>2</sub>-Ni  $\approx$  AB<sub>2</sub>-Co < AB<sub>2</sub>-Fe < AB<sub>2</sub>. It is difficult to directly compare their hydrogen absorption rate regarding to CO<sub>2</sub> poisoning tolerance with each other, because the hydrogen equilibrium pressure effects the hydrogen absorption rate. Therefore, a magnitude of CO<sub>2</sub> poisoning tolerance regarding kinetics was defined by the ratio of the reaction rate constant after CO<sub>2</sub> exposure to that before CO<sub>2</sub> exposure. The following equation for the reaction rate of hydrogen absorption was employed [20],

$$v = \frac{dC}{dt} = \frac{P(C) - P_{eq}(C,T)}{P_0} k f(C),$$
(1)

where v is the reaction rate, *C* is the amount of absorbed hydrogen (H/*M*), *P*(*C*) is hydrogen pressure (MPa),  $P_{eq}(C,T)$  is hydrogen equilibrium pressure (MPa),  $P_0$  is atmospheric pressure (MPa), *k* is reaction rate constant (s<sup>-1</sup>) corresponding to temperature *T* (°C), and *f*(*C*) is function of *C* regarding to reaction process (H/M). The reaction rate before and after CO<sub>2</sub> exposure with elimination of the effect of hydrogen equilibrium pressure are defined as:

$$v'_{\text{bef}} = \left(\frac{dC}{dt}\right)_{\text{bef}} \left/ \frac{P_{\text{bef}}(C) - P_{\text{eq}}(C,T)}{P_0} = k_{bef} f(C),$$
(2)

$$v'_{\text{aft}} = \left(\frac{dC}{dt}\right)_{\text{aft}} / \frac{P_{\text{aft}}(C) - P_{\text{eq}}(C,T)}{P_0} = k_{aft} f(C).$$
(3)

The reaction rate (dC/dt) and P(C) was obtained by hydrogen absorption properties before CO<sub>2</sub> exposure and 3<sup>rd</sup> cycle, respectively.  $P_{eq}(C,T)$  was chosen from a fitting curve of the PCT plots in Fig. 3. If f(C) do not change before and after CO<sub>2</sub> exposure, a ratio of reaction rate constant regarding magnitude of CO<sub>2</sub> poisoning tolerance  $\chi$  is estimated as:

$$\frac{v'_{\text{aft}}}{v'_{\text{bef}}} = \frac{k_{aft}}{k_{bef}} = \mathcal{X}.$$
(4)

Figure 8(a) shows magnitude of CO<sub>2</sub> poisoning tolerance ( $\chi$ ) at *C* = 0.3, 0.4, 0.5, 0.6, and 0.7 for all samples. The values of  $\chi$  were less than 0.5 and decreased with increasing amount of

hydrogen absorption. It indicates that effect of CO<sub>2</sub> poisoning becomes strong at higher hydrogen absorption amount. Average values of  $\chi$  for 0.3-0.7 H/M (Fig. 8(b)) were described in the following order:

$$AB_2$$
-Ni <  $AB_2$  <  $AB_2$ -Co <  $AB_2$ -Fe.

This order was the almost same as the total hydrogenated fraction. From above results, AB<sub>2</sub>-Fe has the highest CO<sub>2</sub> tolerance among them. The fact which AB<sub>2</sub>-Fe and AB<sub>2</sub>-Co have larger  $\chi$  than that of AB<sub>2</sub> indicates that Fe and Co additive improve tolerance of CO<sub>2</sub> poisoning for hydrogen absorption properties. In contrast, because AB<sub>2</sub>-Ni has smaller  $\chi$  than that of AB<sub>2</sub>, Ni additive degrades CO<sub>2</sub> tolerance.

#### 3.4. Hydrogen absorption properties under CO<sub>2</sub> partial pressure

The hydrogen absorption properties of AB<sub>2</sub> alloys under CO<sub>2</sub> partial pressure at 0.1 MPa were evaluated after the CO<sub>2</sub> exposure test as shown in Figure 9. In this condition there are possible effects of both weak CO<sub>2</sub> bonding such as physisorption and strong CO<sub>2</sub> bonding, which is irreversible poisoning, such as chemisorption and surface reaction with alloys. The amount of hydrogenated fractions at 80 min became 0.074, 0.22, 0.14, and 0.066 for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co and AB<sub>2</sub>-Ni, respectively. These values are smaller than the results of hydrogen absorption after CO<sub>2</sub> exposure tests. It indicates that CO<sub>2</sub> adsorption on the surface such as physisorption hinders further the hydrogen absorption kinetics of the AB<sub>2</sub> alloys. The order of hydrogenated fractions at 600 min (not shown) was AB<sub>2</sub>-Ni (0.48) < AB<sub>2</sub> (0.55) < AB<sub>2</sub>-Co (0.75) < AB<sub>2</sub>-Fe (0.86). Moreover, the order of hydrogen absorption rate in Fig. 9 was AB<sub>2</sub>-Ni  $\approx$  AB<sub>2</sub> < AB<sub>2</sub>-Co < AB<sub>2</sub>-Fe. From these results, the order of magnitude of CO<sub>2</sub> tolerance under CO<sub>2</sub> partial pressure can be described as

$$AB_2$$
-Ni <  $AB_2$  <  $AB_2$ -Co <  $AB_2$ -Fe.

The dependency of the additive element is the same order as the CO<sub>2</sub> exposure test.

#### 3.5. Analysis of bonding state between CO<sub>2</sub> and alloy

The hydrogen absorption properties of all samples were not recovered from  $CO_2$  exposure test even after 3 cycles as mentioned in section 3.3. The possible bonding types between  $CO_2$ and  $AB_2$  are strong chemical adsorption, chemical dissociation, surface reaction, and bulk reaction with the alloys. Here, we investigated the bonding state by analyzing the structure and surface condition.

Firstly, in order to investigate the bonding state between the bulk and  $CO_2$ , the samples after hydrogen absorption under 0.1 MPa of  $CO_2$  and subsequently hydrogen desorption were measured by XRD for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni as shown in Fig. 10. All samples showed peaks of C14 laves phase. There were also hydride peaks of C14 laves phase in AB<sub>2</sub>, AB<sub>2</sub>-Fe, and AB<sub>2</sub>-Co. Since hydrogen desorption was performed at the atmospheric pressure, not vacuum condition, the hydride phase remained in the samples. The peaks of C14 laves phase and the hydride phase were relatively broad comparing to those just after heat treatment as shown in Fig. 2. It is indicated that the hydrogen absorption and desorption cause the pulverization accompanying by the decrease of crystalline size and induction of lattice strain. Other peaks that indicates the reaction between  $CO_2$  and  $AB_2$  alloys were not observed. It is concluded that the reaction between  $CO_2$  and the  $AB_2$  alloys occurs only on the surface.

Secondly, to investigate the CO<sub>2</sub> bonding state on the surface, a reaction heat between CO<sub>2</sub> gas and the surface was estimated. Figure 11(a) shows temperature changes for all samples during the CO<sub>2</sub> exposure. Just after CO<sub>2</sub> introduction, the temperatures increased around 15 °C in 10-20 sec. The blank data in empty vessel was also shown in Fig. 11. Since the temperature increased only 0.8 °C, the adiabatic effect by the pressure increase was enough negligible. A reaction heat Q(J) of the sample based on the temperature change is estimated

as:

$$Q = \sum_{t} \Delta Q(t) = \sum_{t} \Delta Q_{s}(t) + \sum_{t} \Delta Q_{v}(t).$$
<sup>(5)</sup>

A heat flow rate into and out of the sample  $\Delta Q_s(t)$  is deduced as:

$$\Delta Q_s(t) = c_s m_s \frac{T_s(t + \Delta t) - T_s(t)}{\Delta t},$$
(6)

where *t* is time,  $c_s$  is specific heat capacity of the sample (J/K·g), which is determined by the Neumann-Kopp rule that molar heat capacity is approximately equal to the total piece of the atomic heat capacity [21],  $m_s$  is sample weight (g),  $T_s(t)$  is sample temperature (°C), and  $\Delta t$  is interval of measurement (sec). The conductive heat transfer rate from inside to outside of the sample vessel  $\Delta Q_v(t)$  is defined as follow.

$$\Delta Q_{\nu}(t) = A\lambda \frac{T_{s}(t) - T_{\nu}}{L}.$$
(7)

where *t* is time,  $\lambda$  is a thermal conductivity of sample vessel (J/s·m·K), *A* is heat transfer area (m<sup>2</sup>), and L is a thickness of vessel wall (m). *T*<sub>v</sub> is regarded as the temperature of outside the vessel, which is kept approximately at 20 °C by water cooling. Here, the temperature distribution of the sample in the vessel was assumed to be homogenous because the sample amount of 1g is enough small. Heat transfer by convection and thermal radiation was negligible in this case. The constant value of  $A\lambda/L$  in Eq. (7) was optimized to 0.035 for all samples which the reaction heat rate  $\Delta Q(t)$  did not be negative value in all measured time. Fig. 11 (b) shows the estimated  $\Delta Q(t)$ ,  $\Delta Q_s(t)$ , and  $\Delta Q_v(t)$  for AB<sub>2</sub> sample. The reaction heat *Q* of AB<sub>2</sub> was calculated to 9.7 J. When it is assumed that CO<sub>2</sub> gas adsorbs on the surface, enthalpy change for CO<sub>2</sub> adsorption  $\Delta H_{CO_2}$  (J/mol CO<sub>2</sub>) is estimated by dividing the reaction heat *Q* by adsorbed CO<sub>2</sub> amount of  $n_{CO_2}$  (mol),

$$\Delta H_{co_2} = \frac{Q}{n_{co_2}} \quad . \tag{8}$$

It is difficult to quantify adsorbed CO<sub>2</sub> amount, because the amount is too little to detect as a

pressure change. Therefore, adsorbed CO<sub>2</sub> amount of  $n_{CO_2}$  was calculated by using specific surface area *S* (m<sup>2</sup>/g) of the sample.

$$n_{\rm CO_2} = \frac{Sm_{\rm s}}{N_{\rm A}A_{\rm CO_2}} \quad , \tag{9}$$

where  $A_{CO2}$  is occupation area (m<sup>2</sup>) of one CO<sub>2</sub> molecule on the surface and  $N_A$  is Avogadro constant. The *S* was estimated by SEM image of AB<sub>2</sub> after all the experiments. Particle boundary was separated by the lines indicated in Fig. S1. The large particles were agglomerates of small particles. The average diameter of the particles was 1.3 µm. The calculated specific surface area was 0.68 m<sup>2</sup>/g when the particles were assumed sphere shape. The enthalpy change for CO<sub>2</sub> adsorption was estimated to be 1800 kJ/mol CO<sub>2</sub> by assigning the values to Eq. (8) and (9). The enthalpy of other alloys were also evaluated using the same method as shown in Table 4. The estimated  $\Delta Q$  (*t*),  $\Delta Q_s(t)$ , and  $\Delta Q_v(t)$  and SEM images are also shown in Fig. S2 and S1, respectively for AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni. The enthalpy values were much larger than the CO<sub>2</sub> adsorption enthalpy of titanium or zirconium metal oxide [25]. It indicates that oxidation of AB<sub>2</sub> alloys surface occurs via CO<sub>2</sub> dissociation to CO and O. Therefore, the surface reaction is assumed as follows:

$$\operatorname{CO}_2 + M_{\operatorname{surf}} \to \operatorname{CO}_{\operatorname{ads}} + M_{\operatorname{surf}} \operatorname{O},$$
 (10)

where  $M_{surf}$  is surface atom of AB<sub>2</sub> alloys, CO<sub>ads</sub> is CO molecule adsorbed on the alloys,  $M_{surf}$ O is metal oxide of surface atom. In order to prove CO adsorption, methanation (CO<sub>ads</sub> +  $3H_2 \rightarrow CH_4 + H_2O$ ) was tested. AB<sub>2</sub>-Fe and AB<sub>2</sub>-Ni after CO<sub>2</sub> exposure were kept under 0.9 MPa H<sub>2</sub> at 200 °C for 3 days. As a result, hydrocarbons especially methane were detected in the gas of the sample vessel by GC-FID analysis as shown in Fig. 12. Blank data without CO<sub>2</sub> exposure showed small hydrocarbon peaks, which could originate from unremoved CO<sub>2</sub> species on the surface of AB<sub>2</sub> alloys during activation. Table 5 showed amounts of hydrocarbons by GC-FID analysis. Heavier hydrocarbons than methane such as ethane,

propane, and butane were also detected, although their amounts were less than one tenth of methane. These hydrocarbons were probably generated by the reaction between adsorbed CO and hydrogen. The results are an evidence of CO adsorption on  $AB_2$  alloys. Moreover, the amount of hydrocarbons of  $AB_2$ -Fe was smaller than that of  $AB_2$ -Ni. It indicates that the amount of CO<sub>2</sub> dissociation correlates with magnitude of CO<sub>2</sub> tolerance.

From these results,  $CO_2$  would dissociate to CO and O on the surface of AB<sub>2</sub> alloys, and then oxygen atom reacts with AB<sub>2</sub> alloys. The CO adsorption and generation of metal oxide on the surface might decrease their hydrogen absorption kinetics. Therefore, additive element in AB<sub>2</sub> alloys, which effects on magnitude of CO<sub>2</sub> tolerance, probably controls the amount of CO<sub>2</sub> dissociation.

#### 4. Conclusion

The effect of  $CO_2$  on hydrogen absorption has been investigated for  $AB_2$  and  $AB_2$ - $M_{0.1}$  (M = Fe, Co, or Ni). All samples were single phase of C14 laves structure and had no impurity phase. The ratio of reaction rate constant of hydrogen absorption after  $CO_2$  exposure to that before  $CO_2$  exposure was evaluated as the magnitude of  $CO_2$  poisoning tolerance. An order of  $CO_2$  tolerance was obtained as,

$$AB_2$$
-Ni <  $AB_2$  <  $AB_2$ -Co <  $AB_2$ -Fe.

Moreover, the hydrogen absorption properties under  $CO_2$  partial pressure at 0.1 MPa showed the same order of  $CO_2$  tolerance. The results suggest that  $AB_2$  alloy has dependence of additive elements on  $CO_2$  tolerance.  $AB_2$ -Fe has the highest  $CO_2$  tolerance among them. The additive of Fe and Co improves tolerance of  $CO_2$  poisoning for hydrogen absorption properties. On the other hand, Ni element in  $AB_2$  alloy decreases  $CO_2$  tolerance. The  $CO_2$ -exposed  $AB_2$  alloys after reacting with hydrogen desorbed methane gas. It is suggested that CO adsorbs on the surface via  $CO_2$  dissociation. Moreover, the estimated enthalpy

change between  $CO_2$  and the alloys surface was comparable to the formation of metal oxide. Therefore,  $CO_2$  would dissociate to CO and O on the surface of AB<sub>2</sub> alloys, and then oxygen atom reacts with AB<sub>2</sub> alloys. Additive element in AB<sub>2</sub> alloys probably controls the amount of  $CO_2$  dissociation corresponding to magnitude of  $CO_2$  tolerance.

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Fig. 1 Back scattering electron (BSE) images of Ti<sub>0.515</sub>Zr<sub>0.485</sub>Mn<sub>1.2</sub>Cr<sub>0.8</sub> (AB<sub>2</sub>),

Ti<sub>0.515</sub>Zr<sub>0.485</sub>Mn<sub>1.2</sub>Cr<sub>0.8</sub>Fe<sub>0.1</sub> (AB<sub>2</sub>-Fe), Ti<sub>0.515</sub>Zr<sub>0.485</sub>Mn<sub>1.2</sub>Cr<sub>0.8</sub>Co<sub>0.1</sub> (AB<sub>2</sub>-Co) and

Ti<sub>0.515</sub>Zr<sub>0.485</sub>Mn<sub>1.2</sub>Cr<sub>0.8</sub>Ni<sub>0.1</sub> (AB<sub>2</sub>-Ni). Cross marks in the images are the spots analyzed by

EDX.



Fig. 2 X-ray diffraction profiles of AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni.



Fig. 3 PCT curves of hydrogen absorption and desorption at 20, 30, 40 and 50 °C for AB<sub>2</sub>,

AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni.



Fig. 4 Van't Hoff plots for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni.



Fig. 5 Pure hydrogen absorption properties at 20 °C for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni.



Fig. 6 Hydrogen absorption properties of  $1^{st}$ ,  $2^{nd}$  and  $3^{rd}$  cycles at 20 °C for (a)AB<sub>2</sub>, (b)AB<sub>2</sub>-Fe, (c)AB<sub>2</sub>-Co, and (d)AB<sub>2</sub>-Ni after CO<sub>2</sub> exposure.



Fig. 7 Hydrogen absorption properties of 3<sup>rd</sup> cycle at 20 °C for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and

AB<sub>2</sub>-Ni after CO<sub>2</sub> exposure.



Fig. 8 Ratio of reaction rate constant after CO<sub>2</sub> exposure to that before CO<sub>2</sub> exposure ( $\chi$ ) regarding magnitude of CO<sub>2</sub> poisoning tolerance at (a) H/M= 0.3-0.7 and (b) average values

at H/M= 0.3-0.7 for  $AB_2$ ,  $AB_2$ -Fe,  $AB_2$ -Co, and  $AB_2$ -Ni.



Fig. 9 Hydrogen absorption properties at 20 °C for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni under

CO<sub>2</sub> partial pressure at 0.1 MPa.



Fig. 10 X-ray diffraction profiles of AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, and AB<sub>2</sub>-Ni after hydrogen absorption under CO<sub>2</sub> 0.1 MPa and subsequently hydrogen desorption.



Fig. 11 (a) Temperature during CO<sub>2</sub> induction from vacuum to 0.9 MPa for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co, AB<sub>2</sub>-Ni, and blank of empty vessel and (b) reaction heat rate ( $\Delta Q$ ), heat flow rate into and out of the sample vessel ( $\Delta Q_s$ ), and heat transfer rate from inside to outside of sample vessel ( $\Delta Q_v$ ) during CO<sub>2</sub> induction for AB<sub>2</sub>.



Fig. 12 GC-FID profiles after  $CO_2$  exposure test and keeping under 0.9 MPa H<sub>2</sub> at 200 °C for 3 days for AB<sub>2</sub>-Fe, AB<sub>2</sub>-Ni. Blank was the measurement without  $CO_2$  exposure test.

Comple	Analyzed	Ti	Zr	Mn	Cr	Fe, Co, or Ni
Sample	place	(at%)	(at%)	(at%)	(at%)	(at%)
	Target	17.2	16.2	40.0	26.7	R- '
$Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}$	All area	18.5	17.1	37.4	27.1	-
(AB <sub>2</sub> )	Spot 1	13.0	21.9	35.9	29.1	-
	Spot 2	23.1	12.7	38.4	25.8	_
	Target	16.6	15.6	38.7	25.8	3.2
$Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}Fe_{0.1}$	All area	16.9	15.8	37.5	26.6	3.2
(AB <sub>2</sub> -Fe)	Spot 3	13.8	19.6	35.8	27.1	3.7
	Spot 4	21.7	10.9	38.2	25.9	3.3
	Target	16.6	15.6	38.7	25.8	3.2
$Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}Co_{0.1}$	All area	18.3	15.5	37.2	25.8	3.2
(AB <sub>2</sub> -Co)	Spot 5	14.5	18.6	35.5	28.1	3.3
	Spot 6	20.8	11.7	38.6	25.3	3.7
Q	Target	16.6	15.6	38.7	25.8	3.2
$Ti_{0.515}Zr_{0.485}Mn_{1.2}Cr_{0.8}Ni_{0.1}$	All area	17.1	15.9	36.5	26.7	3.7
(AB <sub>2</sub> -Ni)	Spot 7	13.9	18.7	36.6	26.9	3.9
	Spot 8	21.3	10.6	38.4	25.7	4.0

Table 1 Element c	ompositions	by EDX	analysis of all	area and spot 1-8 of	f BSE images
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corresponding to Fig. 1 for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co and AB<sub>2</sub>-Ni.

	Lattice constant	Lattice constant	Lattice volume	
sample	a [Å]	c [Å]	V [Å <sup>3</sup> ]	
$AB_2$	4.9518	8.1398	172.849	
AB <sub>2</sub> -Fe	4.9495	8.1365	172.619	
AB <sub>2</sub> -Co	4.9472	8.1284	172.291	
AB <sub>2</sub> -Ni	4.9425	8.1186	171.752	

Table 2 Lattice constants and lattice volumes of AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co and AB<sub>2</sub>-Ni.

Table 3 Maximum hydrogen absorption amount at 20 °C and 1 MPa, enthalpy and entropy of hydride formation for AB<sub>2</sub>, AB<sub>2</sub>-Fe, AB<sub>2</sub>-Co and AB<sub>2</sub>-Ni.

	Maximum hydrogen absorption		Enthalpy of hydride	Entropy of hydride	
sample	amount at 20 °C and 1 MPa		formation ( $\Delta H$ )	formation ( $\Delta S$ )	
	H/M	mass%	(kJ/mol H <sub>2</sub> )	(J/mol·K H <sub>2</sub> )	
$AB_2$	0.99	1.69	-33±2	-103±7	
AB <sub>2</sub> -Fe	0.92	1.58	-30±2	-99±7	
AB <sub>2</sub> -Co	0.92	1.57	-29±1	-97±5	
AB <sub>2</sub> -Ni	0.95	1.63	-31±3	-105±9	

Table 4 Reaction heat, specific surface area and CO<sub>2</sub> adsorption enthalpy for AB<sub>2</sub>, AB<sub>2</sub>-Fe,

	Reaction heat $(Q)$	Specific surface area (S)	$CO_2$ adsorption enthalpy ( $\Delta H$ )
sample	(J)	(m <sup>2</sup> /g)	(kJ/mol CO <sub>2</sub> )
AB <sub>2</sub>	9.7	0.68	1800
AB <sub>2</sub> -Fe	9.6	0.73	1650
AB <sub>2</sub> -Co	9.2	0.79	1485
AB <sub>2</sub> -Ni	8.2	0.61	1690

Table 5 Amount of hydrocarbon detected by GC-FID analysis after CO<sub>2</sub> exposure test and keeping under 0.9 MPa H<sub>2</sub> at 200 °C for 3 days for AB<sub>2</sub>-Fe and AB<sub>2</sub>-Ni.

G	AB <sub>2</sub> -Fe	AB <sub>2</sub> -Ni
Species	(mL/g alloy)	(mL/g alloy)
CH <sub>4</sub>	0.517	0.387
C <sub>2</sub> H <sub>6</sub>	0.037	0.025
C <sub>3</sub> H <sub>8</sub>	0.029	0.016
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.010	0.004
n-C <sub>4</sub> H <sub>10</sub>	0.015	0.005
	I	

- The effect of CO<sub>2</sub> on hydrogen absorption has been investigated for AB<sub>2</sub> type alloys.
- An order of CO<sub>2</sub> tolerance was Ti-Zr-Mn-Cr (AB<sub>2</sub>)-Ni < AB<sub>2</sub> < AB<sub>2</sub>-Co < AB<sub>2</sub>-Fe.
- Fe and Co improve CO<sub>2</sub> poisoning tolerance for hydrogen absorption properties.
- CO<sub>2</sub> would dissociate to CO and O on the surface of AB<sub>2</sub> alloys.

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