Variation of PCT Isotherm in the Disproportionated ZrCo

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Abstract. The PCT isotherm of ZrCo hydride having fully disproportionated phase in it was studied to measure complex phase equilibrium and/or to compare a difference of deactivated metal hydride from normal hydride in temperature range of 100~300°C. A full portion of disproportionation in ZrCo hydride was measured and was estimated by Sievert PCT isotherm apparatus, XRD, EDX and so forth. As a result, a modification of H/ZrCo atomic ratio in the PCT diagram is necessary to depict a narrow range of PCT isotherm for fully disproportionated ZrCo metal hydride system, while some analytical methods indirectly supplement the effect of disproportionation on PCT isotherm of the ZrCo hydride.

1. Introduction

Disproportionation of zirconium cobalt (ZrCo), an intermetallic compound, has been reported on open literatures [1-5]. The critical point of the disproportionation in a hydride reaction is sometimes ambiguous, because the extent of disproportionation results from complexity in combination with temperature, pressure and residence time in irreversible reaction state, in addition to a hydride content ratio. Though the hydride reaction temperature is known as a main reason of the disproportionation, especially in ZrCo-H_2 system [1-4], the hydriding pressure is also one major reason for the ZrCo disproportionation [5]. Besserer reported that in thermal treatment of ZrCo at 340°C the ZrCo hydride brought 3.5% of disproportionation in the end of hydride reaction (residing more than 56 hours in a stagnant state) [1]. Shim et al. reported that the storage and the delivery of hydrogen into and from the ZrCo getter were available, without any disproportionation, maintaining fast hydrogen desorption at 350°C under high vacuum condition (at ~0.1 Pa) [2]. Konish et al. successfully showed the cyclic pathway of disproportionation and regeneration in ZrCo-H_2 system, such as ZrCo hydriding, disproportionation, dehydriding and regeneration at high temperature region (500°C) using apparent PCT isotherm (pressure-composition-temperature isotherm) diagram [3]. However, they did not suggest any correlation between disproportionation and PCT isotherm in ZrCo-H_2 system. Here, one question might be arrived how to match the state of ZrCo hydride in terms of hydride content and system pressure with the disproportionated ZrCo getter.

The phase equilibrium of ZrCo-H_2 system is of importance to estimate the state of hydrogen getter and the hydrogen accountancy. In normal operation of cyclic absorption and desorption process under moderate temperature and pressure conditions, the PCT isotherm value of the ZrCo hydride (ZrCo-H_2 or ZrCoH$_x$) system is well defined, but the real performance of ZrCo is apt to deteriorate at high temperature region and/or in pressurized system [1,3-5]. When a getter is deactivated caused by disproportionation, the effect of disproportionation on normal getter is so complex that it is not easy to predict each component's contribution to the whole system. In the early study the ZrCo hydride having some amount of disproportionation may show different equilibrium tendency, because of complex composition including zirconium hydride (ZrH$_2$) and zirconium dicobalt (ZrCo$_2$), which come from a new crystalline

rearrangement and become stable materials at higher temperature and higher pressure conditions, thermodynamically [1,3-5].

In this study a static equilibrium of ZrCo hydride in various hydride contents, especially in large portion of disproportionated ZrCo, was investigated. This static equilibrium in the PCT isotherms composes absorption and desorption profiles. The equilibrium data for the disproportionated ZrCo having high deterioration in getter performance is substantially no meaning in the ZrCo-H_2 system. However, it will be helpful to understand and restructure the state of getter performance for the purpose of; how to and when to recover its performance.

2.   Experimental Apparatus and Preparations

Two main chemicals were used for the metal hydride disproportionation study and its PCT isotherm measurement: One was chunk type, high purity ZrCo getter (SAES Getters, 2~4 mm size) and the other was high purity, H_2 gas (99.999% purity). The PCT isotherm of ZrCo-H_2 system was depicted by measuring hydrogen content outside the getter with Sievert apparatus (a volumetric gas absorption apparatus) (see Fig. 1.) The Sievert apparatus consists of a reactor (chamber) containing getter material (ZrCo) with an electric heater (maximum operation temperature~500°C), a manifold (a certain hydrogen volume), a vacuum pump (full capacity~0.01 Pa), and gas feed lines (hydrogen and helium gas).
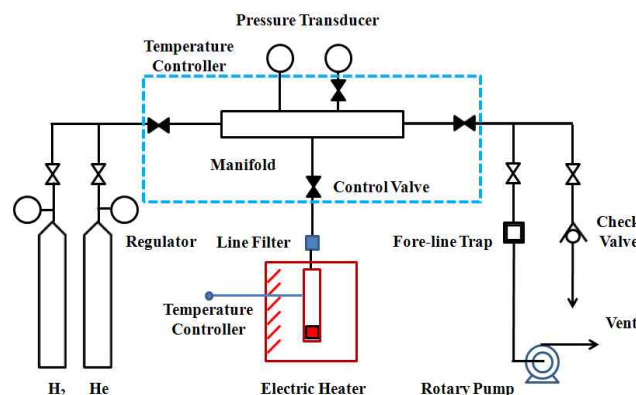

Fig.1. Flow diagram of the Sievert apparatus for PCT Isotherm.

The followings show how to prepare a disproportionated ZrCo and how to get PCT isotherm data and chemical analysis data:

(1) Initial activation and powdering of ZrCo [2]

- Vacuum annealing of ZrCo at 500°C for more than 6 hours; to remove out or dissipate all of remaining gases into the getter inside; thereafter, to activate the getter surface.
- Running hydride (absorption) and dehydride reaction (desorption) cycles for four/five times at 100°C and 350°C, respectively.

(2) Preparation of disproportionated ZrCo [1]

- Heating of ZrCo hydride using sample (1) in a closed system for 2~4 hours at 500°C.

(3) Measurement of ZrCo PCT isotherm [3,4]

- Measuring PCT isotherm using sample (2).

(4) Analysis of physical and chemical properties of ZrCo and ZrCo hydride

- Physical and chemical analysis of ZrCo hydride using SEM, EDX, XRD, DSC, and TG.

3. Theoretical Considerations in ZrCo Disproportionation

The elementary reaction of disproportionation in the ZrCo-H_2 system is represented by the following chemical sequence [1,3-5]. Reaction (1) shows a normal and a reversible hydride and dehydride reaction of ZrCo. Reaction (2) means a real deactivation process of the ZrCo-H_2 system. Reaction (3) reveals another hydriding and dehydriding capability of $ZrCo_2$, even though a hydriding scale is rather small. Therefore, for a new PCT isotherm of ZrCo hydride having a large phase disproportionation a modification of PCT isotherm is inevitable to take into account a real application.

$$ZrCo + 0.5xH_2 \longleftrightarrow ZrCoH_x, \ \ 0 \leq x \leq 3 \tag{1}$$

$$2ZrCo + H_2 \longleftrightarrow ZrH_2 + ZrCo_2 \tag{2}$$

$$ZrCo_2 + 0.1H_2 \longleftrightarrow ZrCo_2H_{0.2} \tag{3}$$

Where *ZrCo* is the zirconium cobalt, intermetallic compound, H_x is the hydride (in x ratio), and *ZrH_2* and *$ZrCo_2$* are the zirconium hydride and the zirconium dicobalt (deactivated form), respectively. The followings are the detailed description in aspects of phase equilibrium in accordance with the above numbering of three elementary reactions:

(1) Normal and reversible hydride and dehydride reaction process:
- Theoretically maximum hydride amount (x, an atomic ratio of hydrogen to zirconium cobalt) is 3 for $ZrCoH_x$. However, the actual value of x is around 2.6.
- Forward reaction occurs at room temperature in an exothermic reaction scheme. Backward reaction occurs at higher temperature region. Besides, disproportionation is generally accompanied.
(2) Deactivation process:
- Since ZrH_2 is a strong hydrogen capture unless the system temperature is less than 500°C, it is assumed that ZrH_2 does not have any breathing capability in hydriding and dehydriding of the remaining ZrCo (or $ZrCoH_x$) during disproportionation propagation.
- This process also shows a reversible pathway while the system is under regeneration step. The reverse reaction shows a very slow kinetics so that it needs a long time treatment under severe temperature and pressure conditions.
(3) New hydrogen breathing capability:
- $ZrCo_2$ shows a little capability of hydrogen breathing.
- Comparing breathing capability between ZrCo and $ZrCo_2$ the theoretical ratio becomes 3:0.2. Thus, the breathing capability of $ZrCo_2$ is expected to be a one-fifteenth than that of ZrCo.

4. Results and Discussion

Fig. 2, Fig. 3, and Fig. 4 show the microscopic morphology (SEM) and the image mapping result (EDS) on the ZrCo surface treated by hydrogen absorption. Fig. 2(a) and Fig. 2(b) show SEM morphology and EDX result of the $ZrCoH_x$ sample, respectively, having a particle cleavage caused by volume expansion from hydriding & dehydriding cycles. In whole surface area, Zr and Co phases are uniformly distributed. Near cleavage, however, relatively Co-rich zone where Co atoms are concentrated is present. Otherwise, it is assumed that the zirconium hydride may exist in this area.
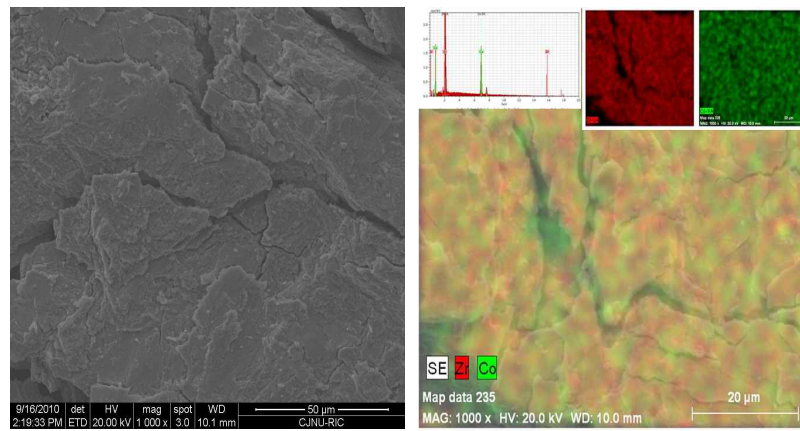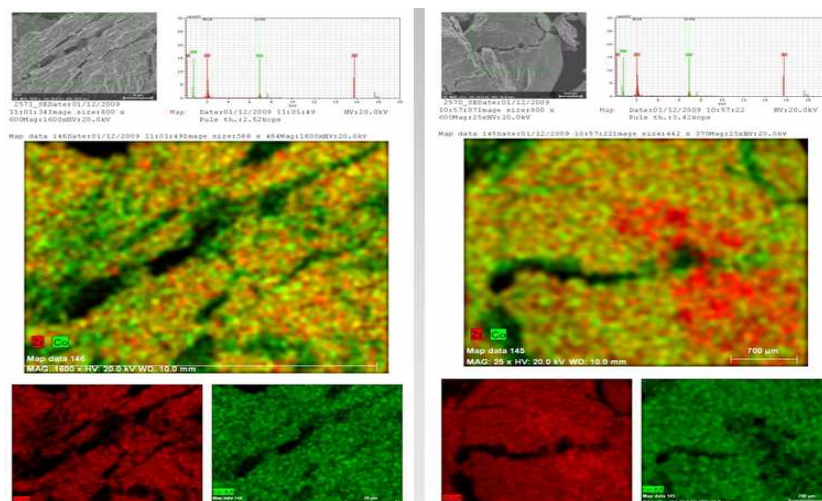
(a) SEM (×20,000)   (b) EDX

Fig. 2. SEM morphology (a) and results of image mapping (b) on ZrCoH$_x$.
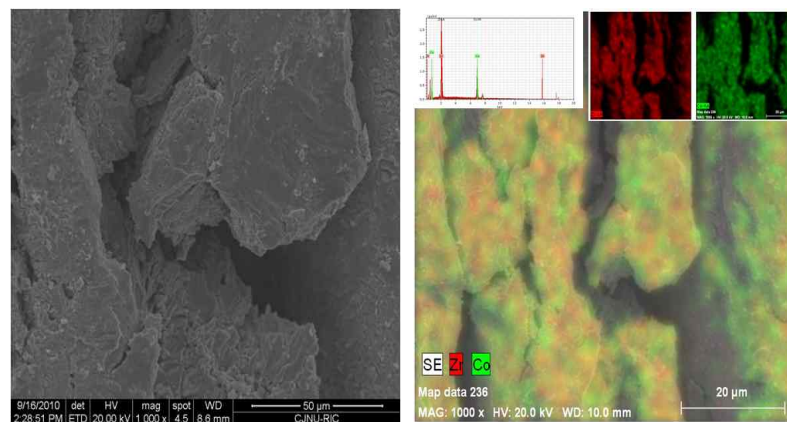
(a) SEM (×20,000)   (b) EDX

Fig. 3. SEM morphology (a) and results of image mapping (b) after activation of ZrCo.

(a) Normal   (b) Disproportionated

Fig. 4. Comparison of SEM morphology and image mapping on

(a) the normal sample and (b) the disproportaionated sample of ZrCoH$_x$.

Fig. 3 shows similar result to that of Fig. 2's. Fig. 3(a) and Fig. 3(b) show SEM morphology and EDX result, respectively. After activation and powdering through several cycles of hydriding and dehydriding, ZrCo hydride sample shows a sort of lack in both of Zr and Co atoms in the cleavage area (see Fig. 3(b)). Therefore, Fig. 3(b) gives a little difference comparing with Fig. 2(b). It is assumed that there is no hydride form in the cleavage zone in Fig. 3 sample. In the same way, Fig. 4 shows same analysis results to that of Fig. 2's and Fig. 3's. On the contrary, Fig. 4(b) sample is a typical ZrCo hydride which has a certain amount of disproportionation. Highly segregated Co zone (see red dots in Fig. 4(b)) is present on the ZrCo hydride surface comparing with that of normal ZrCo hydride (see Fig. 4(a)).

Fig. 5 shows the results of DSC and TG of $ZrCoH_x$, having a part of disproportionation. This sample shows three endothermic peaks (see Fig. 5). The enthalpy value is 40.94, 68.72, and 83.16 J/g, by turns. The dehydrogenation temperature is 393, 523, 653 K, respectively. The larger peak is shown at higher temperature region. In general, $ZrCoH_x$ has two endothermic peaks in DSC analysis. Thus, it is assumed that the last peak in DSC corresponds to the enthalpy for dehydrogenation of ZrH_2. In TG analysis there is a part of mass reduction, thereafter a small increase. This means that the dehydrogenation and oxidation on $ZrCoH_x$ occurs at the last peak temperature, simultaneously.
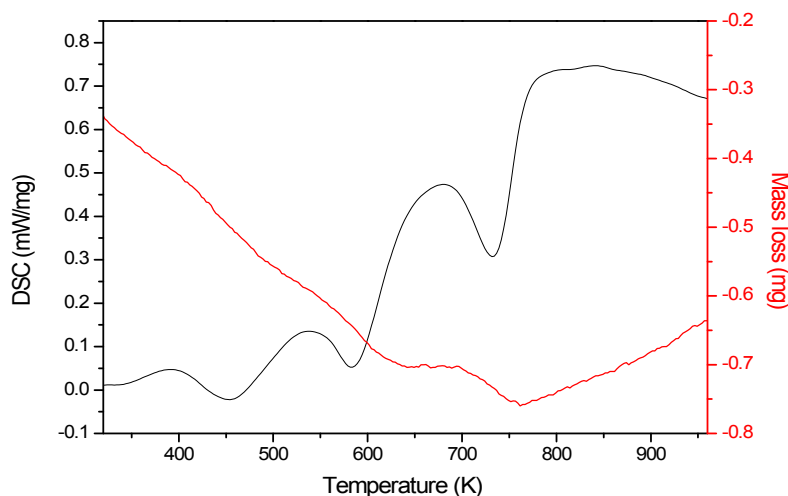

Fig. 5. Results of TG/DSC on disproportionated $ZrCoH_x$.

Fig. 6 shows XRD results of three different ZrCo samples. In Fig. 6 one is a sample of ZrCo after activation and powdering, another is a sample of ZrCo hydride having tens of hydriding and dehydriding cycles without any disproportionation, and the other is a ZrCo sample having a part of disproportionation in it. The activated ZrCo shows that it has no armporphous type compound such as $ZrCoH_3$ in XRD patterns, even though it was activated by hydrogen and powdered into nano particles. The normal $ZrCoH_x$ shows an armorphous $ZrCoH_3$ peak caused by the micron size powdering. The partially disproportionated ZrCo shows ZrH_2 and $ZrCoH_x$ peak in XRD patterns. There is a strict distinction between samples having disproportionation and no disproportionation in XRD pattern analysis [4,5]. Though there is no $ZrCo_2$ peak in Fig. 6, it can be assumed that there must be some portion of ZrH_2 by considering ZrH_2 compound.

Fig. 7 shows a PCT isotherm of ZrCo hydride having extreme case of disproportionation. Fig. 7 also shows very low value in x-coordinate (hydrogen content in wt. %), since this sample has nearly full of disproportionation part in a ZrCo hydride form. Therefore, it is assumed that this sample remains only small breathing capability (see Fig. 7), for hydriding

(absorption) and dehydriding (desorption) by $ZrCo_2$. Moreover, this sample seems to have lots of ZrH_2 and $ZrCo_2$ compounds in it.
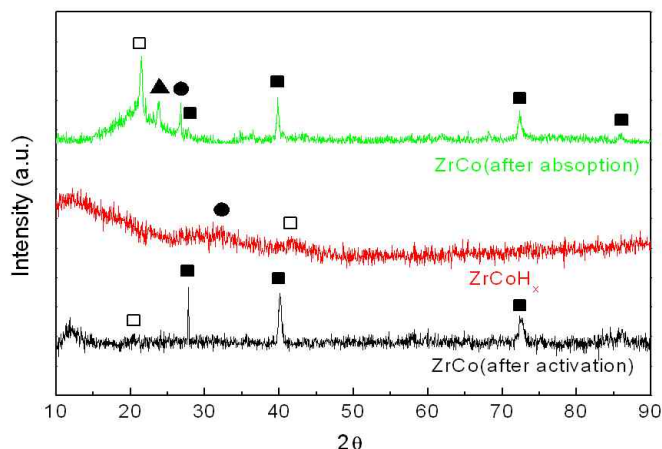

Fig. 6. Results of XRD patterns on ZrCo.

(■; ZrCo, □; ZrH_2, ●; $ZrCoH_3$, ▲; ZrO_2)

Fig. 7 shows a different manner of PCT isotherm, comparing with normal ZrCo hydride in temperature range of 100~300°C [3,4]. In normal PCT isotherm of ZrCo hydride the PCT isotherm curve has high system pressure value at high temperature range. Or, at lower temperature the hydrogen content absorbed in a metal getter is greater than that of higher temperature's. On the other hand, Fig. 7 shows that at higher temperature case the metal hydride contains more large hydrogen content, even though the hydrogen absorption value is very small. It is assumed that this result is due to a character of $ZrCo_2$.
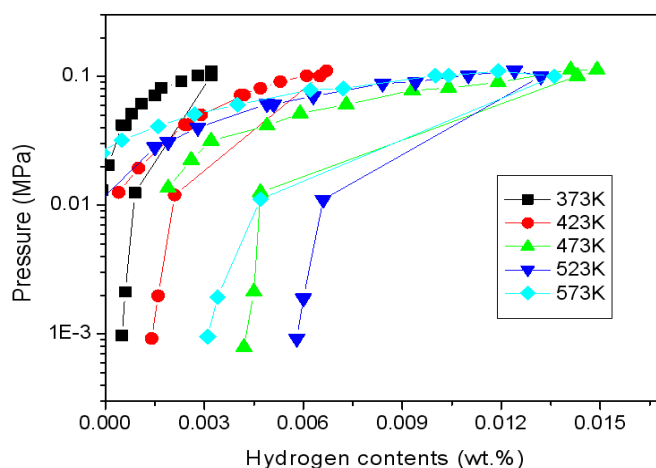

Fig. 7. Hydriding/dehydriding profiles of highly diproportionated ZrCo.

As a result, a new PCT isotherm could be established as shown in Fig. 7. In the PCT isotherm the absorption and the desorption plateaus in highly disproportionated ZrCo show similar isotherm curves to that of normal ZrCo hydride compound's, but the PCT isotherm of this material also shows very little breathing capability caused by $ZrCo_2$. Even in case of highly

disproportionated ZrCo, however, it is assumed that the hydrogen content can be estimated by considering hydrogen content in ZrH_2 using a modified PCT isotherm.

5. Conclusion

The PCT isotherm of ZrCo hydride having highly disproportionated part was studied to measure a complex correlation for phase equilibrium. In comparison of differences between a performance deteriorated ZrCo hydride with a normal ZrCo hydride the analyzing methods, SEM & EDX, DSC/TG, XRD, were helpful to understand the disproportionation phenomena of the ZrCo hydride. A full portion of disproportionation in the ZrCo hydride was estimated by Sievert PCT apparatus so that a modification of H/ZrCo atomic ratio in the PCT diagram could be applied, as an illustration, in a narrow range of H/ZrCo atomic ratio and in temperature range of 100~300°C. Even in case of highly disproportionated ZrCo it is assumed that the hydrogen content can be estimated by considering hydrogen content in ZrH_2.

Acknowledgments

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