

The activation process of ZrCo by an adsorption-desorption cycle of H₂

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1. Introduction

Along with uranium, a zirconium-cobalt intermetallic compound has been extensively studied and widely used due to its attractive properties as a tritium getter for a handling, transport, and storage of tritium. The zirconium-cobalt has two strong advantages compared with uranium. While uranium is restricted for a handling due to its radioactive characteristics, zirconium-cobalt is easy to handle. Also, from the point of view of a safety, zirconium-cobalt and its hydrides have proven to be much less pyrophoric than uranium and its hydrides are the most widely used as a tritium getter. However, the zirconium-cobalt has one shortcoming in that it brings about a disproportionation at above 673 K.

In the current study, before the experiment for the pressure-composition isotherm of zirconium-cobalt at room temperature, the activation process of the zirconium-cobalt intermetallic compound was dealt with and its result was discussed.

2. Experimental, results and discussion

In this section, the experimental apparatus and process for the preparation of a 255.4g ZrCo (1.7 mol, M.W = 150.15 g/mol) fine powder are described and discussed.

2.1. The experimental apparatus

A 255.4g ZrCo intermetallic compound supplied by SAES Getters (Milano, Italy) was used in the experiment. The experimental apparatus is shown in figure 1.

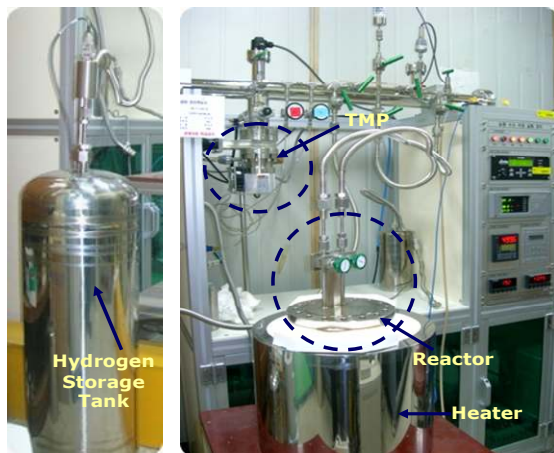


Figure 1. Experimental apparatus

2.2. Preparation procedure of the ZrCo fine powder and the disproportionation of ZrCo

A 255.4g ZrCo intermetallic compound was weighed and taken into the reaction vessel. Then, the activation of the ZrCo compound was carried out at 773 K for 5h. In addition, we previously anticipated the heat of the reaction for the ZrCo with hydrogen gas before powdering the ZrCo for the safety aspects. The heat of the reaction for the ZrCo with hydrogen gas was calculated by two equations.

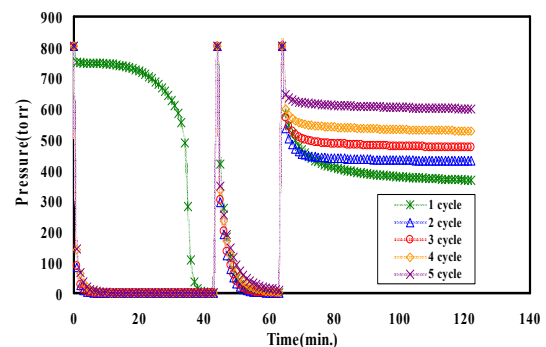
$$\text{Heat capacity}(C) = \text{Mass}(m) \times \text{Specific heat}(c)$$

$$\text{The amount of heat}(Q) = \text{Heat capacity}(C)$$

$$\times \text{Variation of temperature}(\Delta t)$$

In the calculation for the heat capacity, the value of a specific heat was used at about 645 J/Kg·K. This value was extracted from ref. 1. And the average enthalpy change for the adsorption of hydrogen was known to be -81.5 ± 1.6 KJ/mol for the plateau region ($0.8 < x < 2.0$). [2] This value was substituted for the amount of heat as most reaction of the ZrCo with hydrogen occurs at the plateau region. Consequently, the anticipated variation of the temperature was about 873 K when the reaction of the ZrCo with hydrogen becomes ZrCoH₃ at the maximum value.

So, previously to prevent the hazard of a high temperature and the possibility to a disproportionation of the ZrCo observed at above 673 K, a highly pure hydrogen gas at a pressure of about 800 torr was introduced into the reaction vessel three times. And this process of the adsorption and desorption of the hydrogen was repeated several times. Finally, the ZrCo compound was decrepitated into a powder upon a hydrogen sorption. Figure 2 shows the variation of the adsorption rate and the variation of the temperature according to an adsorption and desorption cycle of the hydrogen.



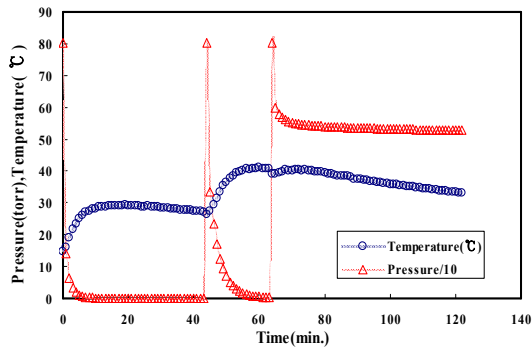


Figure 2. Above: the variation of adsorption rate according to the cycle of the adsorption and desorption of the hydrogen, Below: the variation of temperature during the adsorption and desorption of the hydrogen.

As shown in figure 2, the increment of an adsorption and desorption cycle of the hydrogen led to a more rapid rate of an adsorption of the hydrogen. It was confirmed that the reaction of the ZrCo with the hydrogen is exothermic. But, unlike a process to powder a 5g ZrCo compound, the remarkable point in a process to powder a 255.4g ZrCo compound is the definite reduction of the storage capability for the hydrogen when the number of adsorption and desorption cycles of the hydrogen was increased. Roughly, this appearance was shown to be responsible for the disproportionation of the ZrCo occurred in the process of a desorption at 673 K. Thus, the ZrCo was evacuated at 773 K for 18h, and the disproportionated product was completely returned to the ZrCo of the original storage capability for the hydrogen. Figure 3 shows the process of a desorption of hydrogen at 673 K and the reproduction of the ZrCo of the original storage capability for the hydrogen when evacuated at 773 K for 18h.

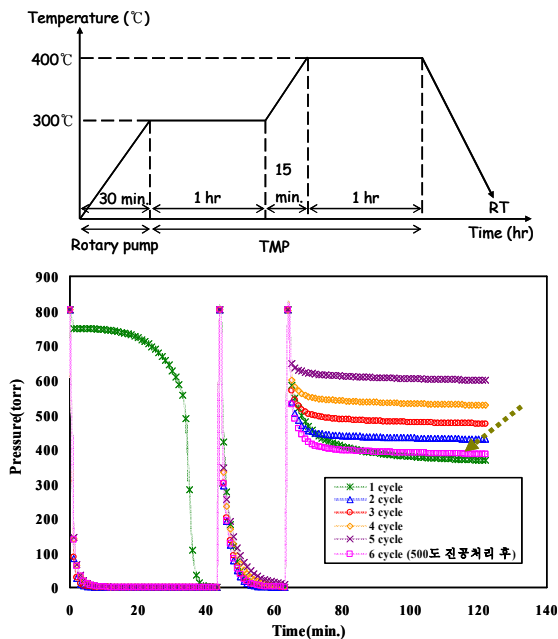


Figure 3. Above: the process of desorption of the hydrogen, Below: the reproduction of the ZrCo of the original storage capability for the hydrogen when evacuated at 773 K for 18h

3. Conclusion

Before the experiment for the pressure-composition isotherm of ZrCo at room temperature, a preceding treatment of the ZrCo intermetallic compound was carried out. The ZrCo was decrepitated into a fine powder upon an adsorption and desorption cycle of the hydrogen. In this process, unlike a process to powder a small scale ZrCo compound, the remarkable point in a process to powder a large scale ZrCo compound is the definite reduction of the storage capability for the hydrogen. Roughly, this appearance was shown to be responsible for a disproportionation of the ZrCo. Thus, the ZrCo was evacuated at 773 K for 18h. As a result, the disproportionated product was completely returned to the ZrCo of the original storage capability for the hydrogen.

REFERENCES

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- [2] R.-D. Penzhorn, M. Devillers and M. Sirch, Characterization of the ZrCo-Hydrogen system in view of its use for tritium storage, Chem. Mater., 2, 255-262 (1990)