Studies on Particle Behavior and Kinetics during Hydride Reaction of ZrCo

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1. Introduction

The rapid change phenomena of the superficial characteristics and the crystalline structure for the hydride material during hydride reaction between a hydrogen-getter material and the hydrogen reactant have not easily been observed by means of a visual cell (or a view cell) assembly system. Even in case of analyzing hydriding and dehydriding phenomenon using ZrCo, an intermetallic compound, a fastidious high temperature operation condition and/or a high vacuum condition are required to accomplish the whole range of the hydride reaction. Moreover, the well-known volume expansion and the micro-powder formation of the metal hydride system, including major concerns such as this ZrCo-H_x material system, have not been measured, but been estimated indirect method. Recently the authors have established a set of visual cell equipment so that it is able to see the hydride phenomena during hydride and dehydride reaction steps by means of using a video camera outside the reaction chamber. Comparing the hydrogen absorption amount with the initial state of the getter material, and the shape change of the micron size of the fragmented getter material, the hydriding phenomenon in superficial state and the reaction kinetics at initial state can be measured and the results are presented in this study.

2. Optical View of Hydride Reaction and Results

The hydride reaction of the ZrCo-H_2 system was measured in a small scale reactor that the reaction phenomena could be well observed through a visual cell device having two transparent sapphire windows at both ends and a video camera. The followings are the results of the hydride reaction scheme and the initial reaction kinetics of the ZrCo and hydrogen reaction system.

2.1 View Cell Reactor

The visual cell (or view cell) was adopted to observe a hydride reaction system of the ZrCo-H_2 system so that at every time the reaction status can be monitored and superficially analyzed by means of using video camera. The volume of the view cell reactor is approximately 12 ml and the operating temperature was maintained less than 300℃, because of the packing material made by an elastomer for the flexible tightness of the sapphire window to the metal main body. The overall configuration of the view cell is shown in Fig 1. For the hydride reaction the temperature was maintained about 100℃ after 8 g of the ZrCo (true density ~ 7.624 g/cm^3) was inserted into the reactor.

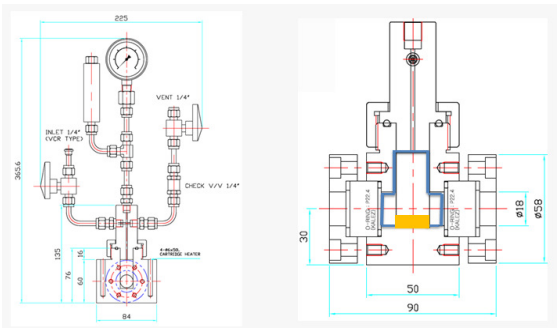
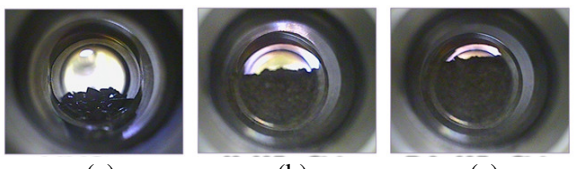


Fig. 1. Drawing and dimension of the visual cell for the hydride and dehydride reaction of the ZrCo getter material, while the reaction system is maintained at 100℃ in hydriding step, and less than 300℃ in dehydriding step .

2.2 Volume Expansion during Hydride Reaction

The initial activation process is necessary to make the ZrCo (initially chunk type, SAES Getter, Italy) to the activated state. One of the important phenomena in hydriding of getter material including initiation and/or activation of the hydrogen absorption is to understand the volume expansion of the getter material itself [1]. This special step could be available to monitor the particle behavior by video camera as shown in Fig. 2 . In Fig. 2 a stepwise status of the volume expansion in the hydriding of ZrCo was illustrated.



(a) (b) (c)

Fig. 2. Hydriding status in the visual cell reactor: Stepwise volume expansion of the ZrCo during hydriding. (a) Initial state, (b) Intermediate volume expansion state, (c) Final expanded state. [ZrCo: SAES Getters (Italy)]

After four to five times of hydriding cycles the particle size of the ZrCo (or $ZrCoH_x$) becomes rather micro-sized particle as shown in Fig. 3. Superficial differences between the initial getter material, ZrCo, and the hydride material, $ZrCoH_x$, are apparently shown (using optical microscope). The fragmented particle sizes are around tens of micro in average after tens of hydriding cycles [2].

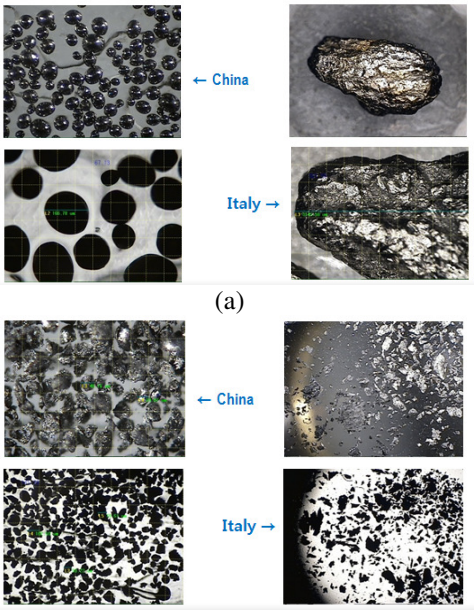


Fig. 3. Formation of micro-powder of the ZrCo getter material during hydriding at 100℃: (a) Initial status of ZrCo: Chunk type (Italy) and granule type (China), (b) After hydriding status of $ZrCoH_x$: Debris or fragments by cracking of ZrCo.

2.3 Hydrogen Absorption Kinetics of ZrCo

The initial hydriding rate of the ZrCo is shown during consecutive hydrogen loading reaction system in Fig. 3. The 2nd hydrogen loading is followed by the first loading of hydrogen to the powder ZrCo, and the third and fourth so forth to the same sample of ZrCo.

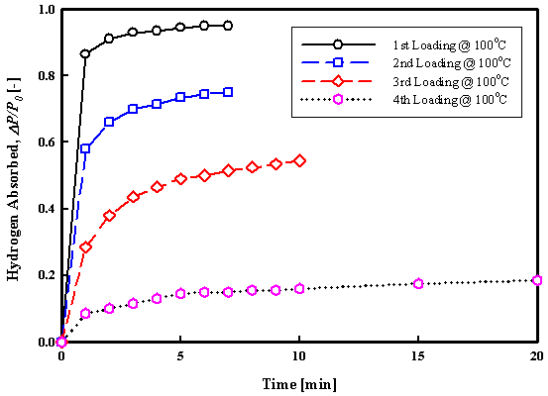


Fig. 4. Hydriding rate of ZrCo at 100℃: From the initial loading (1st Loading) to the additional loading (4th Loading at the final step) in consecutive hydrogen loading reaction.

The initial hydride reaction rate for the massive and the surface reaction in the bulk type of ZrCo plate at a very high temperature region was reported using microscopy technology [3,4], however, no reports in a powder type of ZrCo using visual reactor technology. In Fig. 3 the gradual decrease of the reaction rate was shown in accordance with the hydrogen saturation of the $ZrCoH_x$, where the x value of the hydride form of ZrCo is less than 3 [5].

2.4 Properties of ZrCo Hydride Material

In this study the physical properties of $ZrCoH_x$ were measured by SEM, XRD, and for the thermophysical properties DSC, EDX. A great difference between the reactant ZrCo and the product $ZrCoH_x$ was observed due to the intervention of the proton in the crystal lattice of the Zr and Co atom structure [2,6].

2.5 Hydrogen Desorption of ZrCo Hydride

The dehydriding of the ZrCo hydride was conducted at less than 300℃ as a reaction temperature under a vacuum condition in this study [5]. Here the expanded volume of the $ZrCoH_x$ is decreased in a little amount in a reverse way comparing to the hydriding system.

3. Conclusions

The superficial particle behavior and the initial reaction rate of the hydride reaction using a particulate ZrCo getter material were well observed by a visual reactor system. The volume expansion during hydriding, and vice versa in dehydriding, was monitored and the formation of the micro-powder in status of $ZrCoH_x$ was also observed as well as the initial hydriding rate.

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