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A Study on Optimum Operating Conditions for ITER ZrCo SDS bed

Myung-Hwa Shim,a·b Hongsuk Chung†,d Hiroshi Yoshida,c Seungwoo Paek,d Chang-Shuk Kim,b
Minsoo Lee,d Kwang-Rag Kim,d Sung-Paal Yim,d Do-Hee Ahn,d
a University of Science & Technology,52 Eoeun-dong, Yuseong-gu, Daejeon,305-333 Korea
b ITER Project TFT,52 Eoeun-dong, Yuseong-gu, Daejeon,305-333 Korea
c ITER Tritium Plant Consultant, 3288-10, Sakado-cyo, Mito-shi, Ibakaki-ken, Japan
d Korea Atomic Energy Research Institute,150 Deokjin-dong, Yuseong-gu, Daejeon,305-353 Korea
† hschung1@kaeri.re.kr

1. Introduction

ZrCo has been selected as the reference material for the metal hydride beds in the ITER fuel storage and delivery system (SDS). The disproportionation reaction of ZrCoHx expressed by equation (1) has been known to occur at high temperature(~673-923K) and hydrogen pressure higher than equilibrium pressure [1-3]

$$2ZrCoH_x \rightarrow ZrH_2 + ZrCo_2 + (x-1)H_2 \qquad (1)$$

In the present study, disproportionation rate at expected operating conditions of SDS hydride beds are calculated using preceding study on the ZrCo disproportionation kinetics and mechanism [2, 3], and discuss optimum operating conditions to avoid and/or minimize disproportionation during delivery operation for ITER plasma experiments.

2. Methods and Results

2.1 Mechanism and kinetics of ZrCo disproportionation

The disproportionation is caused by the formation of a thermodynamically more stable species such as ZrH_2 and $ZrCo_2$**.** Konishi et al have applied Avrami-Erofeev equation (2) to analyze the disproportionation kinetics [2]

$$б = 1- \exp\{-(t/\tau)^n\} \qquad (2)$$

Where, б represents the ratio of disproportionation estimated from the pressure change caused by reaction (1), τ means the time of ~~a~~ 63.2% disproportionation and t is the elapsed time. The reaction time of 63.3% disproprotination occurred under 132 kPa of hydrogen at 673-773K is shown in Fig. 1.

Hara et al have analyzed the pressure and temperature dependence of disproportionation rate by developing a nucleation and nuclei growth model expressed by equations (3) and (4) [3]. Overall rate constant with temperature and disproportionation time course with pressure at 773K are shown in Figs. 2 and Fig. 3.

$$-\ln(1-x)=k_{OV}K_{SQ}P(t)^{(m+0.5)}t^{3n+1} \qquad (3)$$

x : Extent of reaction

$$k_{OV} = 4\pi / 3 / (3n+1) * k_{nnc} * k_{net}^3 \qquad (4)$$

k_{nnc} : Proportionality constant

K_{SQ} : Sievert's constant

$k_{net} = (k_{cg} - k_{reg})/n$

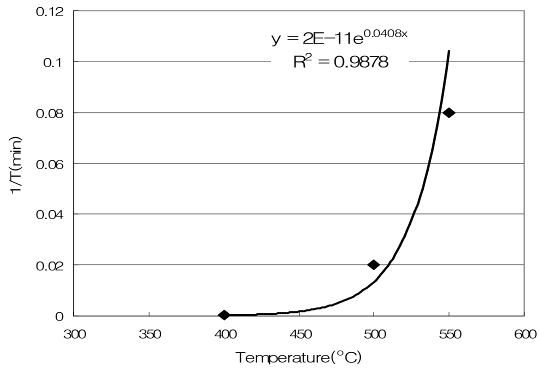

Figure 1. Time of a 63.2% disproportionation with temperature

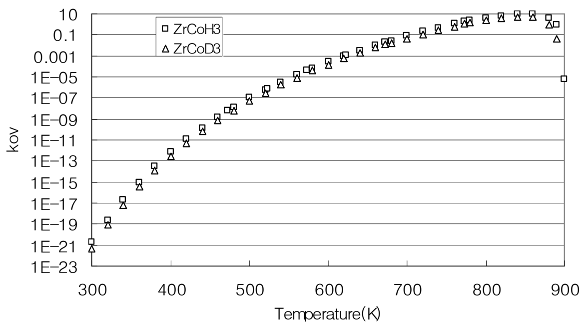

Figure 2. Overall rate constant (k_{OV}) with temperature

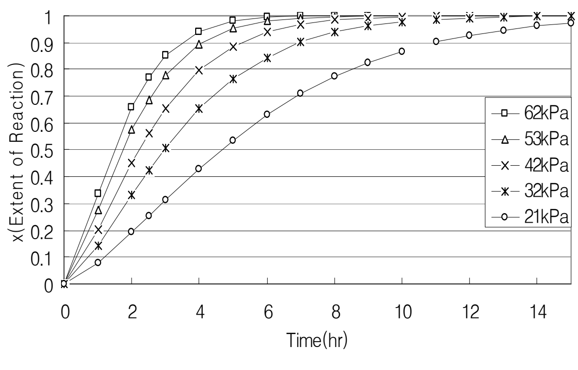

Figure 3. Disproportionation time course with pressure at 773K

$k_{cg} = A_{cg} * \exp(-E_{cg}/RT)$, Disproportionation rate

$k_{reg} = A_{reg} * \exp(-E_{reg}/R/T)$, Redisproportionation rate

P(t) : Over-pressure at a giventime

$P(t)^m$: Correction term for the deviation of Sievert's law with increasing solubility(m=1 from experiment)

3n+1 = 1.4 from experimental results

2.2 ZrCo disproportionation at 623-673K

Figs. 4 and 5 show the disproportionation time courses with pressure at 623 and 673K extrapolated from Konishi's and Hara's studies. From these Figures, it can be seen that disproportionation rate decreases exponentially with temperature decrease and 1.5 times power with pressure. The elapsed time of 20% disproportionation can be identified as about 1-2days at 673K and 10-100 days at 623K. At 350^{o}C considered to be delivery temperature from ZrCo SDS bed, disproportionation reaction occurred, but the rate is slow at low equilibrium pressure.

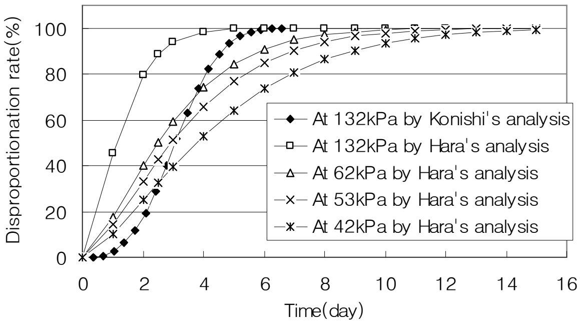

Figure 4. Disproportionation time course with pressure at 673K

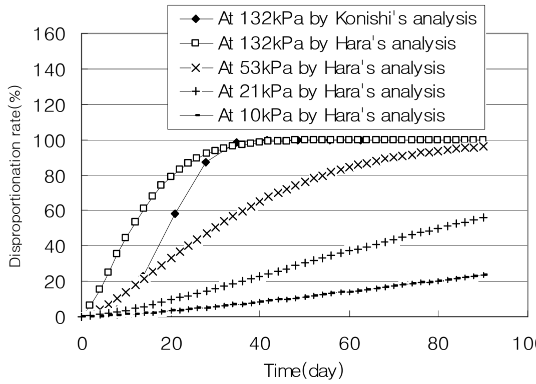

Figure 5. Disproportionation time course with pressure at 623K

2-3 Operation window of ITER ZrCo SDS bed

In order to define optimum operation conditions, the disproportionation rate under different hydrogen pressures at lower temperature (< 673K) were investigated. The equilibrium pressure was calculated by the next formula [1].

$$\text{Log P (Pa)} = -2856/T(K) + 9.075 \qquad (5)$$

At 548-623K under equilibrium pressure, disproportionation occurs ~~ed~~ over 20 years as shown in Fig. 6. Under lower hydrogen pressures (<< equilibrium pressure), disproportionation rate is much lower as shown in Fig. 7.

In the ITER SDS operation, In case the disproportionation reaches to unacceptable level (~ 10% of D-T gas storage capacity), the deteriorated hydride beds will be regenerated by heating at ~770K with vacuum pumping for several hours. Frequency of the regeneration can be minimized ~~by~~ developing optimum operating conditions for D-T gas delivery through the present analysis and on going experimental work of disproportionation implemented at KAERI

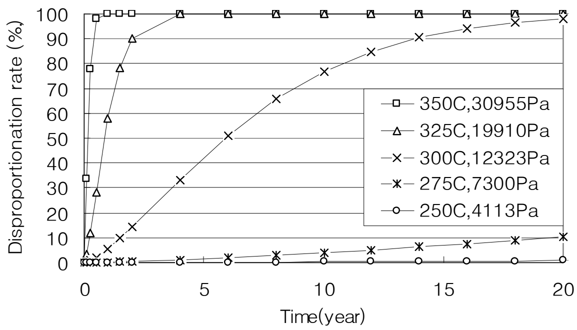

Figure 6. Disproportionation time courses under equilibrium pressure at each temperature

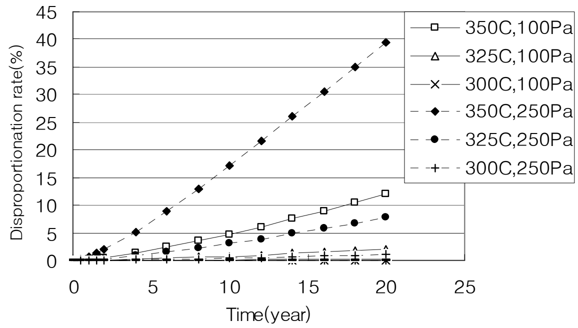

Figure 7. Disproportionation time courses under 100Pa or 250Pa at each temperature

3. Conclusion

Disproportination rates at lower temperatures (<673K) and different hydrogen pressures were analyised based on Konishi's and Hara's studies and experimental results. From the present study, the following indications were obtained: (i) ZrCo disproportionation rate decreases exponentially with temperature decrease and 1.5 times power with pressure decrease, and (ii) the disproportionation rate under equilibrium hydrogen pressure can be minimized lower than 1% over 20 years if operating temperature is kept at 523K.

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