

Influence of additive elements on the terminal solid solubility of hydrogen for Zirconium alloy

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Abstract

The terminal solid solubility of hydrogen for pure Zr, Zircaloy-2, Zr–M (M = Fe, Sn, Cr, Ni) was measured, whose dependency on additive element was elucidated in relation to the integrity of fuel cladding. The present experimental method was in good accordance with the previous reports. The terminal hydrogen solid solubility for Zircaloy-2 was larger than that for pure Zr, the reason for which was considered that the solute Sn leads to decrease the free energy of α Zr phase.

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1. Introduction

Zirconium alloys such as Zircaloy and Zr–Nb have been widely used as the nuclear materials of light water and heavy water reactors. It has been reported that a part of hydrogen produced by the corrosion reaction between Zr alloy and cooling water is absorbed into the alloy. If the total hydrogen isotope concentration in the alloy exceeds the solubility limit, brittle zirconium hydride platelets are formed as precipitates in the alloy, which deteriorates the strength of fuel cladding. In recent years, the influence of zirconium hydride on the integrity of fuel cladding is observed with keen interest

because of longer extended burnup of nuclear fuel. Therefore, it is important to elucidate the thermodynamic properties of the Zr–H system such as terminal solid solubility of hydrogen (TSS). It is considered that the TSS is determined by fabrication history, irradiation, and additive elements. Although several effects have been studied [1–14], there have been few reports on the effect of additive elements. Therefore in the present study, the effect of additive elements such as Sn, Cr, Fe and Ni was examined separately and the influence of the additives on TSS was formulated.

2. Experimental procedure

The sheet samples of pure Zr, Zr–M (M = Sn, Fe, Cr, or Ni) binary alloys, and Zircaloy-2 alloys with different Fe content were tested. The composition for these alloys

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Table 1
Composition of the evaluated Zr alloys

Sample name	Cr	Ni	Fe	Sn	Si	O	Zr
Pure Zr	<0.005	<0.0035	0.0083	<0.0010	<0.0040	<0.0050	Balance
High Fe Zry(0.18Fe)	0.1	0.07	0.18	1.3	0.009	0.120	Balance
High Fe Zry(0.25Fe)	0.1	0.07	0.25	1.3	0.009	0.12	Balance
High Fe Zry(0.40Fe)	0.1	0.07	0.40	1.3	0.009	0.12	Balance
Zr–0.08Fe	–	–	0.079	<0.01	–	–	Balance
Zr–0.22Fe	–	–	0.22	<0.01	–	–	Balance
Zr–0.49Fe	–	–	0.49	<0.01	–	–	Balance
Zr–1.00Sn	–	–	0.036	1.00	–	–	Balance
Zr–1.25Sn	–	–	0.027	1.25	–	–	Balance
Zr–1.49Sn	–	–	0.059	1.49	–	–	Balance
Zr–0.10Ni	<0.001	0.098	0.025	<0.001	0.001	0.136	Balance
Zr–0.25Ni	<0.001	0.240	0.042	<0.001	0.001	0.186	Balance
Zr–0.50Ni	<0.001	0.480	0.061	<0.001	0.001	0.239	Balance
Zr–0.10Cr	0.086	<0.001	0.041	<0.001	0.001	0.110	Balance
Zr–0.25Cr	0.220	<0.001	0.030	<0.001	0.001	0.132	Balance
Zr–0.50Cr	0.460	<0.001	0.035	<0.001	0.001	0.134	Balance

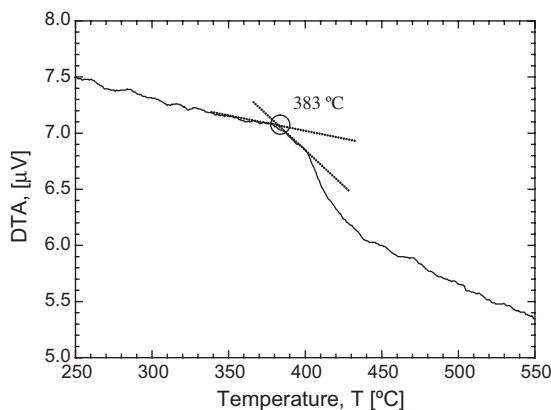


Fig. 1. Typical DSC curve for pure Zr.

was tabulated in Table 1. The hydrogenation was executed using a modified UHV Sieverts' apparatus. Details of the apparatus is described elsewhere [15]. The absorbed hydrogen contents in the specimens were measured with a hydrogen analyser (HORIBA, EMGA-621). The $\alpha/\alpha + \delta$ phase transition temperature was evaluated with a differential scanning calorimeter (ULVAC-RIKO, Triple-cell DSC) in Ar-flow atmosphere. The transition temperature is obtained experimentally from $\alpha + \delta$ to α (heating) or α to $\alpha + \delta$ (cooling) [8,9]. These temperatures are summarized as TSSD (TSS-dissolving) and TSSP (TSS-precipitating), respectively. Khatamian [8,9] mentioned that the TSSD was the more reproducible result than the TSSP. Therefore the TSSD was adopted as TSS in the present study. The typical DSC curve is exhibited in Fig. 1.

3. Results and discussion

The measured TSS points for pure Zr are plotted in Fig. 2 with the data by Kearns [2] and Khatamian [8]. The results in the present study are in good accordance with the previous reports. Therefore the measuring method in the present study is comparable with the previous studies. The TSS, C_H , is expressed as the following equation:

$$C_H(\text{wt ppm}) = A \exp(-Q/RT) \quad (1)$$

where A and Q are the constants, R is the gas constant and T is the absolute temperature. The A and Q values for pure Zr are listed with those for the other alloys in Table 2.

The solid marks in Fig. 3 are the results for the Zircaloy-2 in the present study. The TSS for the Zircaloy-2 alloys is independent on Fe content, all of the plots are summarized in $A = 1.70 \times 10^5$ wt ppm and $Q = 38.0$ kJ/mol. The TSS for the Zircaloy-2 is larger than that for pure Zr. Since there is no difference on fabrication process between the Zircaloy-2 and pure Zr, it can be considered that the additive elements increase the TSS. In addition, the present results show that the iron may not affect the TSS. Therefore in order to evaluate the influence of each additive element in the Zircaloy-2 separately, the TSS for the Zr–M (M = Sn, Fe, Cr, Ni) binary alloys was measured, as shown in Figs. 4–7. In these figures, it is observed that the increasing of Sn or Cr leads to increase the TSS, whereas the Fe or Ni addition does not affect it. Since most of the added Fe atoms form Zr_2Fe intermetallic compounds, Fe may not affect the

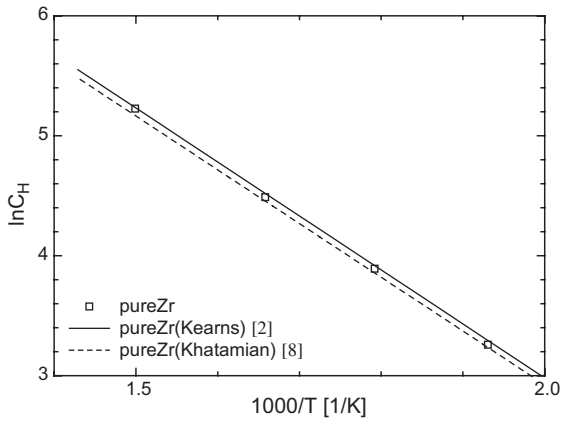


Fig. 2. The terminal solid solubility for pure Zr.

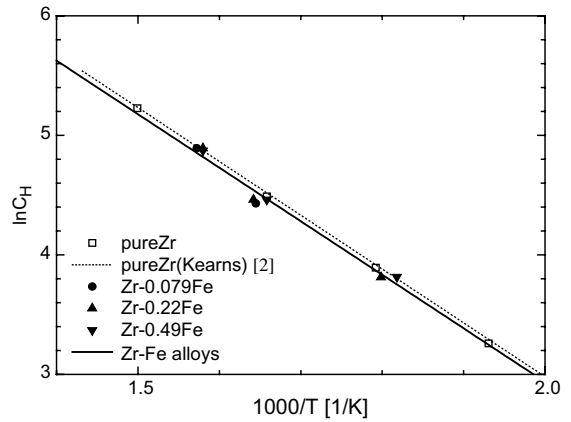


Fig. 4. The terminal solid solubility for Zr–Fe alloys.

Table 2
Fit parameters for the terminal solid solubility

Sample name	A (wt ppm)	Q (kJ/mol)
Pure Zr	1.42×10^5	37.1
High Fe Zry(0.18Fe)		
High Fe Zry(0.25Fe)	1.11×10^5	35.9
High Fe Zry(0.40Fe)		
Zr–0.08Fe		
Zr–0.22Fe	1.70×10^5	38.0
Zr–0.49Fe		
Zr–1.00Sn	4.53×10^4	42.3
Zr–1.25Sn	2.94×10^5	40.0
Zr–1.49Sn	1.97×10^5	37.8
Zr–0.10Ni		
Zr–0.25Ni	5.39×10^4	30.6
Zr–0.50Ni		
Zr–0.10Cr	1.98×10^5	38.1
Zr–0.25Cr	1.50×10^5	36.0
Zr–0.50Cr	9.89×10^4	33.5

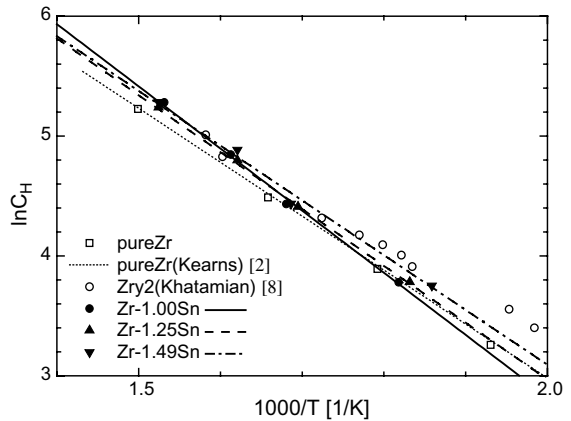


Fig. 5. The terminal solid solubility for Zr–Sn alloys.

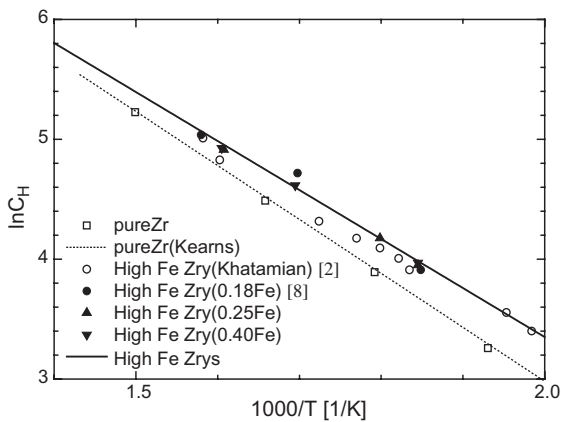


Fig. 3. The terminal solid solubility for Zircaloy-2 alloys.

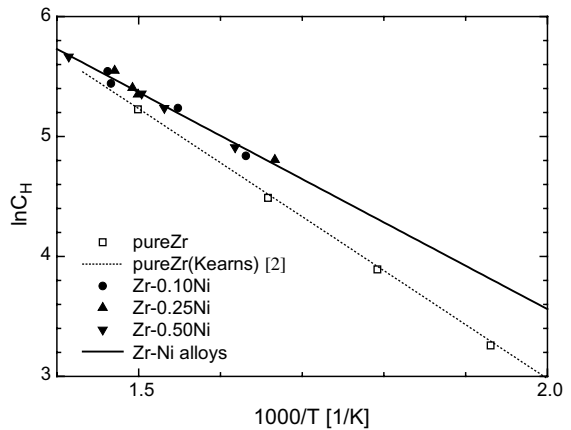


Fig. 6. The terminal solid solubility for Zr–Ni alloys.

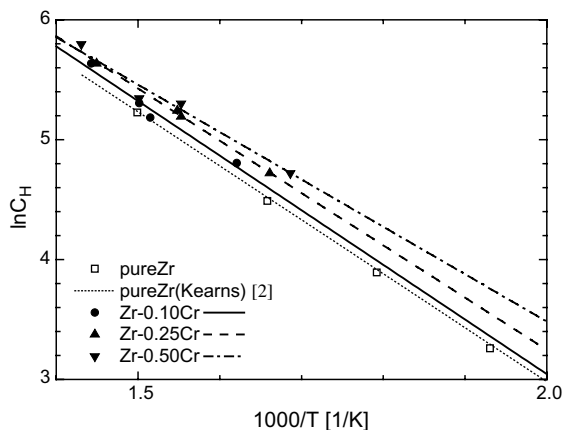


Fig. 7. The terminal solid solubility for Zr–Cr alloys.

thermodynamic properties of α Zr. On the other hand, the Sn is possible to dissolve in α Zr, and then the thermodynamic properties of the matrix changes by Sn addition. In general, increasing the dissolved constituents lead to increase the entropy by mixing, and then the free energy decreases. Therefore the Zr–Sn alloys have more stable α Zr than pure Zr, which promotes the TSS increasing.

Although both Cr and Ni also do not dissolve in α Zr, the Zr–Cr and Zr–Ni alloys show the different behaviour on the TSS from the Zr–Fe alloy. The reason may be the properties of the intermetallic compounds $ZrCr_2$, which are known as hydrogen storage materials, or be the effect of Ni as catalyst for dissociating H_2 molecule on the sample surface. For further quantitative discussion, investigating the hydrogen absorbing properties of such compounds will be required.

4. Conclusions

The terminal solid solubility of hydrogen for pure Zr, Zircaloy-2, Zr–M (M = Fe, Sn, Cr, Ni) was measured, by means of a differential scanning calorimeter, and the dependency of additive element was elucidated in order to supply fundamental data for the integrity of fuel cladding. The present experimental method was in good accordance with the previous reports. The terminal solid solubility for Zircaloy-2 was larger than that for pure Zr, the reason of which was considered that the solute Sn leads to decrease the free energy of α Zr phase.

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