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Effect of Nb addition on the terminal solid solubility of hydrogen for Zr and Zircaloy-4

Masato Ito*, Kazuhira Ko, Hiroaki Muta, Masayoshi Uno, Shinsuke Yamanaka

Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University,
2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

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Abstract

The terminal solid solubility of hydrogen (TSS) for pure Zr, Zr–Nb binary alloys with different Nb concentrations, and Nb added Zircaloy-4 was examined from the view point of the integrity of new-type nuclear fuel cladding. These alloys were hydrogenated by a modified UHV Sieverts' apparatus at 973 K. The hydrogen concentration and the hydride dissolution temperature of specimen were measured by using a hydrogen analyzer and a differential scanning calorimeter (DSC), respectively, and then the terminal solid solubility of hydrogen was determined. The TSS of the α single-phase Zr–0.3Nb (Zr–0.3 wt.% Nb) specimen appeared to be almost same as that of pure Zr. On the contrary, the TSS of the Zr–1.0Nb and Zr–2.5Nb alloys, which were α + β biphasic specimens, were larger than that of pure Zr and slightly increased with Nb concentration. The increment of TSS by Nb addition was slightly larger than that by the traditional additive elements of Sn, Ni, and Cr in Zircaloys. The Nb added Zircaloy-4 had higher TSS than the Zircaloy-2 and -4, which was attributed to the further additive effect by βZr precipitation in Zircaloy besides the traditional additive element effects.

Keywords: Metal hydrides; Nuclear reactor materials; Precipitation; Phase transitions; Thermodynamic properties

1. Introduction

The integrity of Zr based alloys for fuel cladding materials has become more important because of high burnup of nuclear fuel. Hence, Nb containing Zr alloys viz., NDA, MDA, and ZIRLO have been newly introduced to improve corrosion resistance and mechanical strength. However, it was reported that Zr alloys absorb a part of evolved hydrogen during operation by the corrosion reaction between Zr alloy and cooling water. If the total hydrogen concentration in the alloy exceeds the solubility limit, brittle Zr hydrides are formed as precipitates in the alloy, which markedly deteriorates the material strength. 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 terminal solid solubility of hydrogen (TSS) for the Zr alloys. It is considered that the TSS depends on fabrication history, irradiation, and additive elements. Although several effects have been studied [1–15], there have been few reports on the effect of additive elements. Therefore, 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 in our previous study [16].

In the Nb modified fuel cladding, the concentration of added Nb ranges from 1 to 5 wt.% contrary to the small amount of concentration of the other traditional additive element. Most of the added Nb dissolves into the matrix α phase (hcp), but a small amount of Nb-rich β Zr phase (bcc) precipitates in the alloys. Several studies on the TSS of Zr–Nb alloys have been carried out [3–9,11,14–15]. However, the effect of Nb dissolution into the matrix α phase on TSS has scarcely been investigated, although the volume fraction of α phase is dominant in the alloys. Moreover, the effect of Nb addition on the TSS for the commercial fuel cladding such as Zircaloy is still unknown. Therefore, the TSS of Zr–Nb binary alloys with different Nb contents, which were α single phase or α + β biphasic specimens, and Nb added Zircaloy-4 were evaluated in the present study, and the effects of Nb addition on the TSS were discussed.

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* Corresponding author. Tel.: +81 6 6879 7905; fax: +81 6 6879 7889.
E-mail address: ito@ms.see.eng.osaka-u.ac.jp (M. Ito).

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Table 1
Composition of the evaluated Zr alloys (wt.%)

Sample name	Fe	Sn	Cr	Nb	H	C	N	O	Zr
Zr–1.0Nb	0.038	0.002	0.002	1.00	0.0025	0.006	0.0047	0.100	Balance
Zr–2.5Nb	0.038	0.001	0.004	2.56	0.0032	0.008	0.0031	0.181	Balance
Nb modified Zircaloy-4	0.260	1.310	0.100	1.01	0.0030	0.008	0.0037	0.201	Balance

2. Experimental procedure

The specimens of Zr–1.0 wt.% Nb, Zr–2.5Nb, and 1.0 wt.% Nb added Zircaloy-4 fuel cladding alloys were produced by Sumitomo Metal Industry Ltd. The preparation process of these alloys is the same as that for the commercially supplied stress relieved Zircaloy-4. The composition of these alloys was tabulated in Table 1. In addition to those specimens, pure Zr and Zr–0.3Nb alloy were also examined in order to evaluate the variation of TSS in the matrix α phase due to Nb dissolution. This concentration is near the Nb solubility limit at room temperature. The principal impurities of the pure Zr specimen included 0.001 wt.% Sn, 0.0083 wt.% Fe, 0.005 wt.% Cr, 0.0035 wt.% Ni, 0.004 wt.% Si, and 0.005 wt.% O. For preparing the Zr–0.3Nb alloys, pure Nb of 99.95 wt.% and pure Zr were used as precursor. The source materials were melted in an arc furnace under Ar atmosphere at 0.05 MPa. For homogeneity, the specimen was turned over and melted more than five times, and then annealed in vacuum at 1273 K for 12 h. The hydrogenation was executed using a modified UHV Sieverts' apparatus under a highly pure (7N) hydrogen gas atmosphere. Details of the apparatus are described elsewhere [17]. After the hydrogenation at 973 K, the specimens were retained at the temperature to homogenize hydrogen distribution for 3 h and then were furnace cooled with an average cooling rate of 5 K/min.

X-ray diffraction measurements were performed at room temperature using Cu Kα radiation (RINT-2000/PC, Rigaku Corp.) to analyze the existing phases in the specimens. The absorbed hydrogen content in the specimens was measured with a hydrogen analyser (HORIBA, EMGA-621). Their hydrogen contents range from 26 to 770 ppm, and the statistical errors were within 2%. The hydride dissolution temperature of specimen was evaluated with a differential scanning calorimeter (ULVAC-RIKO, Triple-cell DSC) in the temperature range from 50 to 873 K. The apparatus has a "triple-cell" system and an adiabatic temperature control system, which was originally developed by Takahashi and Asou [18]. The measurement was made in high-purity Ar (6N) atmosphere with a flow rate of 100 ml/min. The accuracy of the apparatus was checked to be ±3% using an α-Al_2O_3 standard. The transition temperature is obtained experimentally from heating or cooling [8,9]. These temperatures are summarized as TSSD (TSS-dissolving) and TSSP (TSS-precipitating), respectively. Khatamian and Ling [8,9] mentioned that the TSSD temperature provided more reproducible results than the TSSP. Therefore the TSSD was adopted as TSS in the present study.

3. Results and discussion

Based on the X-ray diffraction analysis at room temperature, it is observed that there are two αZr and δZrH_{2-X} phases in the hydrogenated pure Zr and Zr–0.3Nb alloy. On the other hand, there exist αZr, βZr, and δZrH_{2-X} phases in the hydrogenated Zr–1.0Nb, Zr–2.5Nb, and Nb added Zircaloy-4. β-Nb, γZrH, and εZrH_{2-X} phases were not detected in all the specimens. Since the Nb is a stabilizer element for βZr, the metastable βZr phase can exist in the specimens below the eutectic temperature of 893 K [19].

A typical DSC curve and heat capacity C_P for pure Zr are exhibited in Fig. 1(a) and (b), respectively. From this figure, it is found that there is an inflection point in the DSC curve at 655 K, which may be related to the complete dissolution temperature of the hydride. It is also found that the C_P increases with temperature up to 655 K due to the endothermic reaction of hydride dissolution and this termination temperature agrees with the temperature obtained from the DSC curve. The temperature is considered to signal the end of hydride dissolution. Une and Ishimoto [20] reported that heat capacities C_P of hydrogenated zirconium alloys increase with temperature to a certain temperature, which was attributed to the hydride dissolution effect, and the end temperature agreed with the complete dissolution temperature of hydride obtained from the TSSD data. Therefore, the maximum C_P point is chosen as the complete dissolution temperature of hydride in the present study because the peak is clearer than that of DSC curve. 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 agreement with the previous reports. Therefore the measuring method in the present study is consistent with previous studies. The TSS shows the linear relation of ln C_H versus $1/T$ and can

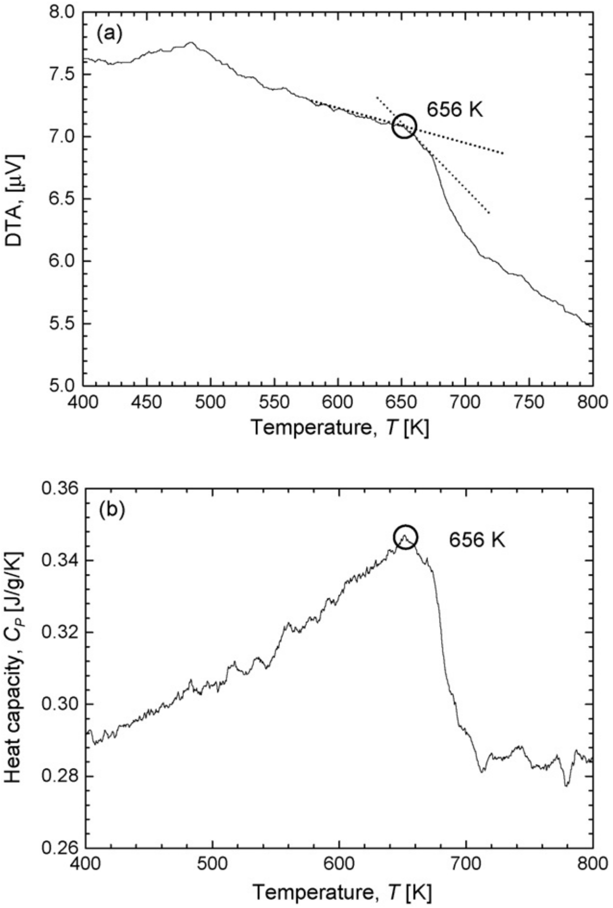

Fig. 1. Typical DSC (a) and C_P (b) curves of pure Zr with 186 wt ppm hydrogen.

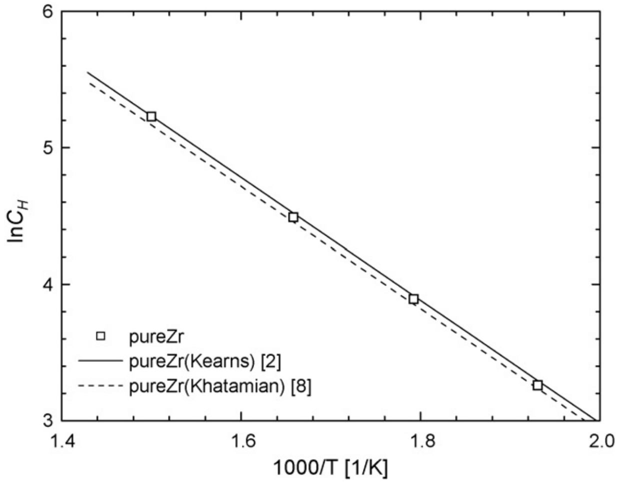

Fig. 2. The terminal solid solubility of hydrogen for pure Zr.

Table 2
The van't Hoff's fit parameters of the terminal solid solubility

Sample name	*A* (wt ppm)	*Q* (kJ/mol)
Pure Zr	1.42×10^5	37.1
Zr–0.3Nb	2.89×10^5	40.4
Zr–1.0Nb	4.30×10^5	41.5
Zr–2.5Nb	3.98×10^5	40.6
Nb modified Zircaloy-4	4.27×10^5	40.1

be fitted using the van't Hoff's equation [21]:

$$C_{\mathrm{H}}\,(\mathrm{wt\,ppm}) = A \exp\left(-\frac{Q}{RT}\right) \tag{1}$$

where $C_{\mathrm{H}}, A, Q, R, T$ are the hydrogen content, a constant related to the dissolution entropy, the dissolution enthalpy, the ideal gas constant, and the absolute temperature, respectively. The *A* and *Q* values for pure Zr are listed with those for the other alloys in Table 2.

The TSS results of Zr–Nb binary alloys, Zr–0.3Nb, Zr–1.0Nb, and Zr–2.5Nb are shown in Fig. 3. The TSS of the α single-phase Zr–0.3Nb specimen appears to be almost same as that of pure Zr. Therefore, it is considered that the Nb dissolution into αZr does not affect the TSS. In general, the dissolved constituents lead to an entropy increase by mixing, and then the free energy decreases. Therefore the TSS increases by solute elements [16,21]. In the present case, the concentration of Nb is too small to bring obvious conspicuous increase in the TSS of αZr.

The literature results for Zr–1.0Nb and Zr–2.5Nb alloys are also included in Fig. 3. The present TSS of the Zr–1.0Nb and Zr–2.5Nb alloys are in good agreement with the data by Khatamian [13] in the temperature range from 580 to 670 K, but higher than the data by Pan [7]. This difference may be caused by the effect of βZr decomposition, which has been revealed to decrease the TSS of Zr–Nb alloy [9]. It is found from Fig. 3 that the TSS of the Zr–1.0Nb and Zr–2.5Nb alloys, which are α + β biphasic specimens, is higher than that of pure Zr. In addition, the TSS of Zr–2.5Nb alloy is slightly higher than that of Zr–1.0Nb alloy.

Since the TSS of the matrix α phase is unchanged by Nb addition, the precipitation of βZr must have a major part in increasing the TSS in Zr–Nb binary alloys. The TSS means the maximum hydrogen content of the hydrogen solid solution phase in equilibrium with the coexisting hydride phase; the concentration is determined at the point that provide a common tangent for the free energies of the solution phase and the hydride [21]. In the case of multiple systems in which three or more phases exist, the interactions between constituent elements in different phases must be taken into account in order to discuss the equilibrium. For example, the free energy of βZr phase in the Zr–Nb–H ternary system probably decreases below the common tangent line of free energies between αZr and hydride in the Zr–H binary system due to the Nb and H dissolution, which may result in the increase of TSS. Further experimental and theoretical investigations are required to address this question.

In Fig. 4, the present TSS results of Zr–Nb binary alloys are compared with the TSS results for Zr–M (M = Fe, Sn, Cr, and Ni) binary alloys obtained in our previous study [16]. The amounts

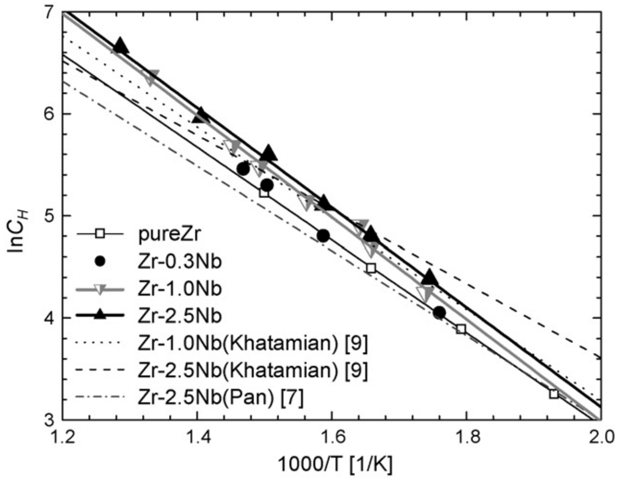

Fig. 3. The terminal solid solubility of hydrogen for Zr–Nb binary alloys.

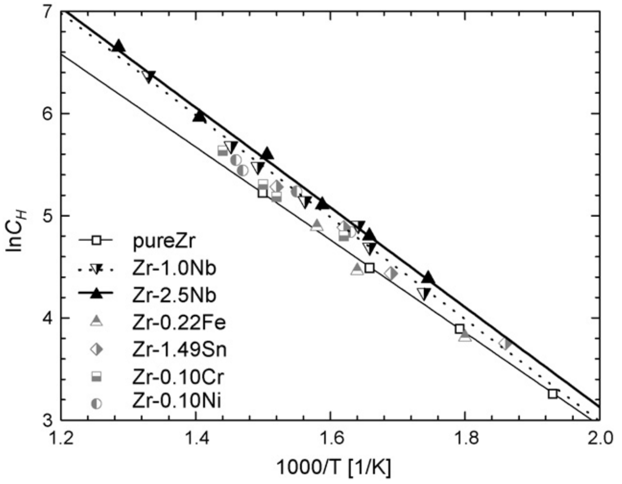

Fig. 4. The terminal solid solubility of hydrogen for Zr–Nb alloys, together with our previous data for Zr–M alloys (M = Fe, Sn, Cr, and Ni) [16].

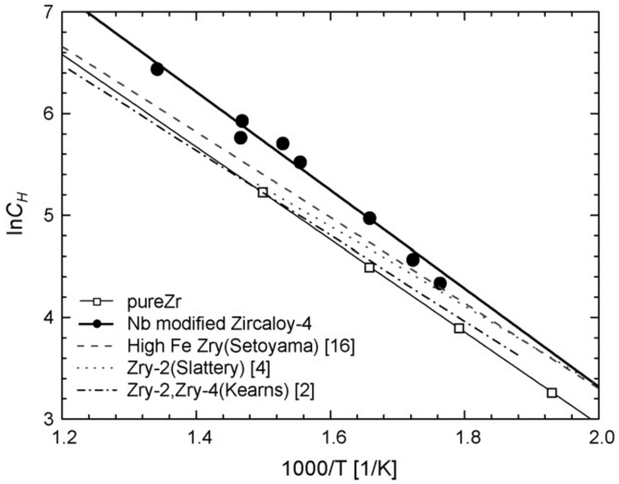

Fig. 5. The terminal solid solubility of hydrogen for 1.0 wt.% Nb added Zircaloy-4.

of the previous additive elements are chosen based on the specifications of the Zircaloys that are actually practically used in the present commercial light-water reactors. It is found from this figure that the increase of TSS by the addition of Nb is slightly larger than that by the addition of Sn, Cr, and Ni. Therefore, it is considered that Nb addition to the zirconium alloys can play an important role in terms of the TSS for increasing the life-time of cladding.

The TSS points of 1.0 wt.% Nb added Zircaloy-4 are plotted in Fig. 5, together with the literature data for Zircaloy-2 and -4. It is found from this figure that the Nb modified Zircaloy-4 has higher TSS than Zircaloy-2 and -4. The reason why the TSS of Zircaloy is larger than that of pure Zr have been revealed in our previous study [16] to be the effect of the Sn dissolution into αZr phase and the precipitation of intermetallic compounds of Zr–Cr and Zr–Ni alloys. The βZr phase does not exist in the normal Zircaloy, whereas this phase exists in the present Nb-modified Zircaloy specimens. Therefore, the increase of TSS for Zircaloy is attributed to the further effect of βZr precipitation by Nb addition besides the traditional additive element effects.

4. Conclusions

The terminal solid solubility of hydrogen (TSS) for pure Zr, Zr–Nb binary alloys with different Nb concentrations, and Nb additive Zircaloy-4 was measured, and the effect of Nb addition was determined in order to supply fundamental data for the integrity of new-type fuel cladding. It was found that the TSS of αZr was not affected by the solute Nb and that the βZr precipitant leads to increase the TSS in the Zr–Nb alloys. The change in TSS by Nb addition was slightly larger than that by the traditional additive elements. The TSS of Nb added Zircaloy-4 was found to be higher than that of Zircaloy-2 and -4 due to the further effect of βZr precipitation on top of the traditional additive element effects. Therefore, it is concluded that Nb addition to the zirconium alloys can play an important role in terms of the TSS for increasing the life-time of cladding.

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