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Change of U Solubility by Mole Ratios of UO_2 Crucible/Zircaloy-4 Melt

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Abstract

The U solubility in the Zircaloy melt including the other investigators' result was investigated in a range of reaction temperatures from 2223K to 2473K and for the mole ratios of UO_2 crucible/Zircaloy-4 melt(subsequently abbreviated as UO_2/Zry) from 2.4 to 18.2. The U solubility in the melt increased with increasing reaction temperature and with decreasing the mole ratio of UO_2/Zry. An empirical correlation was obtained as functions of UO_2/Zry mole ratio and reaction temperature including other investigators' results. The experimental results with use of internally heated fuel element simulators were analyzed by the empirical correlation from UO_2 crucible experiments.

1. Introduction

Results of out-of-pile integral rod and bundle tests under simulated severe fuel damage(SFD) accident conditions showed that relatively stable solid UO_2 fuel partially dissolves in the Zry melt [1]. Also, uncontrolled temperature escalation by coolant channel blockage and increase of fission gas release occurs due to Zry melt in SFD accidents. If the amount of fission gas release is considered to be proportional to the volume fraction of UO_2 fuel dissolved, the release source term can be derived from the U content in the Zry melt under simulated accident

conditions.

However, the U solubility in the Zry melt was greatly influenced by the mole ratio of UO_2/Zry in the integral fuel rod and crucible experiments [2~5]. It is important to correlate the U solubility with the mole ratio of UO_2/Zry for estimating the volume fraction of UO_2 fuel dissolved because the UO_2/Zry mole ratios of typical reactor fuel geometry would change greatly depending on the relocation of the melt. Therefore, the experimental results with use of UO_2 crucibles containing Zry melt was analyzed together with the literature data in the range of reaction temperatures from 2223K to 2473K and mole ratios of UO_2/Zry from 2.4 to 18.2 for obtaining the empirical correlation between U solubility and mole ratio of UO_2/Zry.

2. Equilibrium of U solubility in the Zry melt

The U contents in the Zry melt at various reaction temperatures and the mole ratios of UO_2/Zry were plotted against the square root of the reaction time in Fig. 1.The dissolution of U by the melt occurred rapidly during initial reaction time and the U content in the Zry melt approached a saturated value which changes with not only reaction temperature but also mole ratio of UO_2/Zry. The U content and solubility in the melt increased with increasing reaction temperature and decreasing mole ratio of UO_2/Zry.

There have been several studies on the solubility of U in the Zry melt [3-5]. However, these results are not well cosistent with each other. One possible explanation for the discrepancies is that the mole ratios of UO_2/Zry used are not the same. Figure 2 shows the relation between U solubility for various reaction temperature and mole ratios of UO_2/O-free Zry. The open symbols show the U solubility in the Zry melt obtained by other investigators [3,4]. As shown in this Fig., there is a great increase in the U solubility as the temperature increases and the mole ratio of UO_2/Zry decreases. The following empirical correlation for U solubility is obtained for the reaction temperatures from 2223 to 2473K and for the mole ratios of UO_2/Zry from 2.4 to 18.2 by statistical analysis,

$$C_s = 1791 \cdot \exp\left(-4.77\times10^{-2} \cdot \frac{M_{UO_2}}{M_Z} \right) \cdot \exp\left(-\frac{156}{RT} \right) \qquad (1)$$

where C_s : U solubility on the basis of an O-free Zry state

R : gas constant, 8.314×10^{-3} kJ/mol·K

T : reaction temperature, K.

The best-fit lines from Eq. (1) are also shown in Fig. 2. The U solubility in the Zry melt at 2273K approaches the maximum U solubility, about 51wt.% on O-free basis, calculated from the ternary U-Zr-O phase diagram as the mole ratio of UO_2/Zry decreases. The activation energy for dissolution of U in the Zry melt was 156kJ/mol, and it agrees well with that previously obtained.

3. Application of the U solubility results in SFD Modelling

It is known, in connection with the analysis of SFD accident, that the amount of fission gas release is closely related to the volume of UO_2 fuel dissolved in the Zry melt and that this can be determined by measuring the U content in the melt. Also, the use of U solubility to model the SFD accidents allows upper limits to be placed on possible release of volatile fission products at any one temperature, and may have more conservative result than the use of U content in kinetic data for modelling fuel dissolution.

Rosinger et al. [2] measured the maximum UO_2 volume fraction dissolved in the Zry melt at 2273K to be 6 and 0.5vol.% under an inert and steam atmospheres, respectively, using internally heated fuel element simulators with about 3.7 mole ratio UO_2/Zry. Eq. (1) predicts that the maximum fractional volume decrease of the UO_2 pellet is about 7 vol.% under inert atmosphere. Also, if the fuel rod is assumed to be saturated with O under steam atmosphere and if the exterior ZrO_2 of the fuel element simulator is neglected for the calculation of the UO_2/Zry mole ratio, the volume fraction of the dissolved UO_2 is calculated to be about 2vol.% at 2273K under steam atmosphere. These calculated values are well in agreement with the obtained experimental results.

In out-of-pile integral rod and bundle tests, it was found that the Zry cladding had been

severely oxidized before melting [1] and the U solubility was shown to decrease as the O content of the melt increased. Therefore, the amount of UO_2 dissolved in O-free Zry with non-oxidized condition represents the worst-case scenario in terms of fission product release. In SFD accidents, the steam generation rate was relatively low, which leads to hydrogen blanketing or steam starvation of the Zry cladding [6]. Hence, if it is assumed that the relocation of the melt and the oxidation of Zry by steam is not considered for the worst core melt accidents, the solid lines in Fig. 3 show the maximum fractional volume decrease of the UO_2 pellet in the cladding melt for the three different typical reactor fuel geometries. It can be seen that for such a fuel rod having higher mole ratio of UO_2/Zry as CANDU-PHWR type fuel, much less solid UO_2 is dissolved in the cladding melt than for PWR and BWR type fuels having lower mole ratios of UO_2/Zry.

For the deficiency of experimental data of pre-charged Zry(O) reactant, the U solubility for the UO_2/Zry mole ratios of BWR, PWR, and CANDU-PHWR fuel geometries at 2273K is calculated by the intersection of the lower phase boundary of two phase region and material balance line [5]. If a further assumption is given to the same dependence of U solubility on temperature for the reactant of O-free Zry and pre-charged Zry(O), the dashed lines in Fig. 3 show the volume decrease of UO_2 pellet in the pre-charged Zry(O) melt for the three different typical reactor fuel geometries calculated by Eq. (1). The dissolved volumes of UO_2 pellet in the pre-charged Zry(O) melt are largely decreased compared with those in O-free Zry melt as cladding temperature increased.

4. Conclusions

The U content in the Zry melt rapidly approached to a saturated value which varied depending on reaction temperature and mole ratio of UO_2/Zry. The U solubility in the Zry melt was inversely proportional to the mole ratio of UO_2/Zry. An empirical correlation of the U solubility in the Zry melt was obtained for a range of reaction temperatures from 2223 to 2473K and mole ratios of UO_2/Zry from 2.4 to 18.2 including other investigators' results. This empirical correlation obtained from UO_2 crucible experiments could be applicable to estimate the UO_2

dissolution in cladding melt provided that candling of the melt is absent.

References

[1] S. Hagen, OECD-NEA-CSNI/IAEA Specialists Meeting on Water Reactor Fuel Safety and Fission Products Release in Off - Normal and Accident Conditions, Riso National Laboratory, Denmark (1983).

[2] H.E. Rosinger et al. , Proc. of 6th CNS Conf., Ottawa (1985).

[3] K.T. Kim and D.R. Olander, J. Nucl. Mater., 154 (1988).

[4] P.J. Hayward and I.M. George, J. Nucl. Mater., 208 (1994).

[5] Y.K. Mok, Y.K. Yoon, J. Nucl. Sci. & Tech., 31 (1994).

[6] C.M. Allison et al., Proc. of 5th Int. Meeting on Thermal Nuclear Reactor Safety, Karlsruhe, (1984).

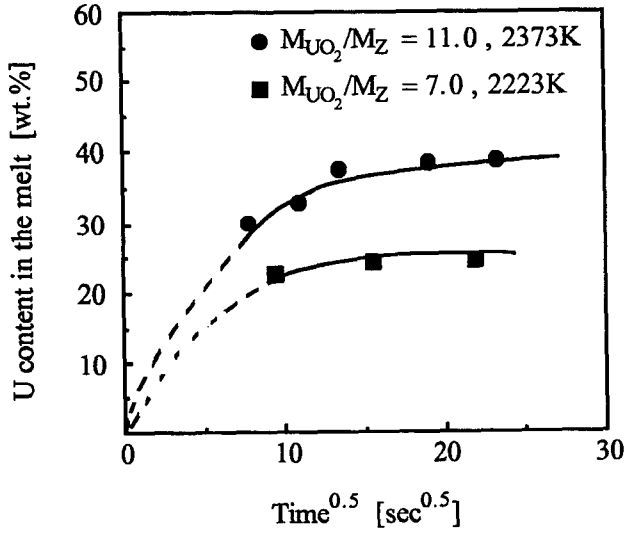

Figure 1. Change of U content in the Zry melt.

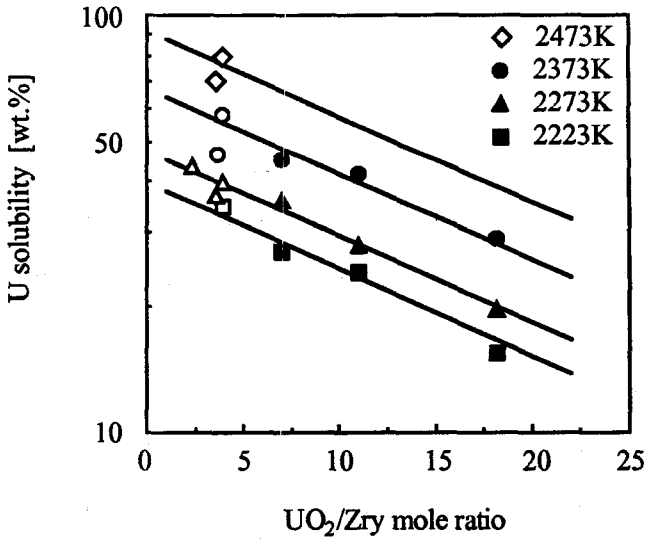

Figure 2. U solubility in the melt heated at various reaction temperatures as a function of the mole ratio of UO_2/Zry.

Open symbols represent the literature [3,4]. Solid lines show the correlation of Eq. (1)

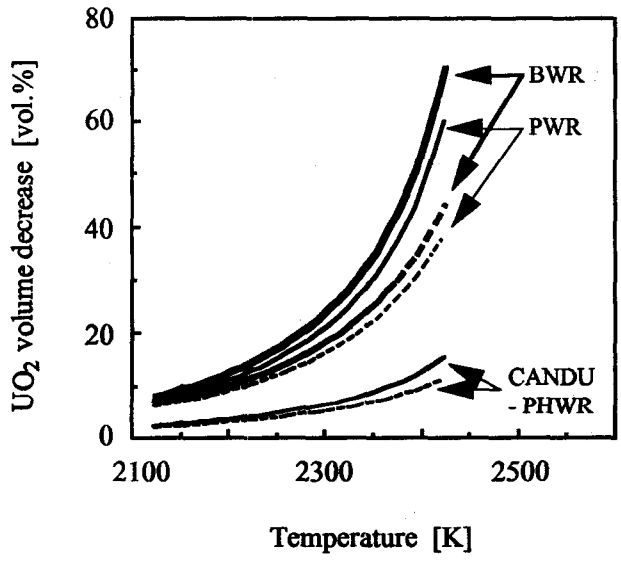

Figure 3. Decrease of UO_2 pellet volume for cases of three reactor type fuels (PWR, BWR and CANDU–PHWR).

The solid and dotted lines represent for the reactant of O–free and O–saturated Zry melt, repectively.