Determination of hydrogen concentration in Zircaloy cladding using hot vacuum extraction method with two-step heating

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ABSTRACT

The amount of hydrogen absorbed in the fuel cladding increases due to extended burnup fuel. The absorbed hydrogen which exceeds the solid solubility limit of the fuel cladding precipitates in the cladding as the hydride phase. And the high concentration of hydride causes the embrittlement of fuel cladding which might become the cause of fractures of the cladding. Therefore, it is very important to measure the hydrogen content in the cladding to estimate the safety margin of the irradiated cladding. Hydrogen is absorbed not only into the cladding metal phase, but into the oxide layer. To evaluate the embrittlement of the cladding, it is necessary to measure the hydrogen content in the cladding metal phase and the oxide layer separately. The usual method based on the hot vacuum extraction, the method heats the whole cladding at a time, cannot measure the hydrogen in the cladding metal phase and in the oxide layer separately. Then, the new device which can control the heating temperature was adopted to measure the amount of hydrogen in the cladding metal phase and the oxide layer separately by using the two-step heating method.[1] This present report is concerned with the technical review of the measuring method including the technique for the determination of extraction temperature.

Keywords: Concentration of hydrogen, Oxide layer, Fuel cladding, Extended burnup

1. Introduction

The amount of hydrogen absorbed in the fuel cladding increases due to extended the burnup of commercial reactor fuel. The absorbed hydrogen which exceeds the solid solubility limit of the fuel cladding precipitates in the cladding as the hydride phase.

And the high concentration of hydride causes the embrittlement of fuel cladding which might become the cause of fractures of the cladding. Therefore, it is very important to measure the hydrogen content in the cladding to estimate the safety margin of the irradiated cladding. Hydrogen is absorbed not only into the cladding metal phase, but into the oxide layer. To evaluate the embrittlement of the cladding, it is necessary to measure the hydrogen content in the cladding metal phase and oxide layer separately. The usual method based on the hot vacuum extraction, the method heats the whole cladding at a time, cannot measured the hydrogen in the cladding metal phase and in the oxide layer separately. Then, the new method has been developed by Paul Scherrer Institute. The controlled heat temperature was adopted to measure the amount of hydrogen in the metal phase and the oxide layer separately by the two-step heating method. However, it is difficult to determine the heating temperature of the first step in the two-step heating method. The temperature is strongly related for the property of the oxide layer. Several examinations were performed in Japan Atomic Energy Agency to optimize the two-step heating method for irradiated cladding.

2. Improvement of measurement techniques

Hydrogen content is determined by the ratio of the cladding weight to the amount of hydrogen in the cladding. It is possible to measure the hydrogen content by the hot vacuum extraction with controlled heating temperature condition. The previous method based on the hot vacuum extraction is measured the amount of hydrogen from the completely melted sample. In this method, the heating temperature is set above the melting point of the cladding. All amount of hydrogen in the cladding including the oxide layer is released in this temperature condition. Therefore, it is impossible to confirm the only amount of hydrogen in the metal phase of the cladding.

The two-step heating method has the benefit to measure the amount of hydrogen in the metal phase and oxide layer separately which is based on the characteristic of hydrogen release behavior of the oxide layer. The hydrogen in the oxide layer is released at lower temperature than the melting point of cladding.

In the first step, the cladding is heated to a temperature lower than the melting point of cladding and hydrogen in the oxide layer is released. The next step, the cladding is heated over the melting point of cladding and hydrogen in the metal phase is released. The hydrogen content in the metal phase and the oxide layer can be determined separately by this method. However, the released temperature of hydrogen is infected by the density and thickness of the oxide phase. So, the first step temperature should be determined with considering the oxide condition by each cladding.

3. Considering of hydrogen release form cladding

To confirm the hydrogen release behavior due to heating temperature, continuous heating examinations were performed using unirradiated claddings on several heating conditions. Fig.1 shows the most suitable release curve to separate the released hydrogen from metal and oxide phase. As a result, it's obtained hydrogen release peak from oxide layer and metal phase by taking measurement in continuous heating at over 1000 seconds up to 2500 ℃ from room temperature.

It can be estimated, the first peak at the temperature of 500℃ shows the released hydrogen from the oxide layer and the second peak at the temperature of 1300℃ shows the released hydrogen from the metal phase.

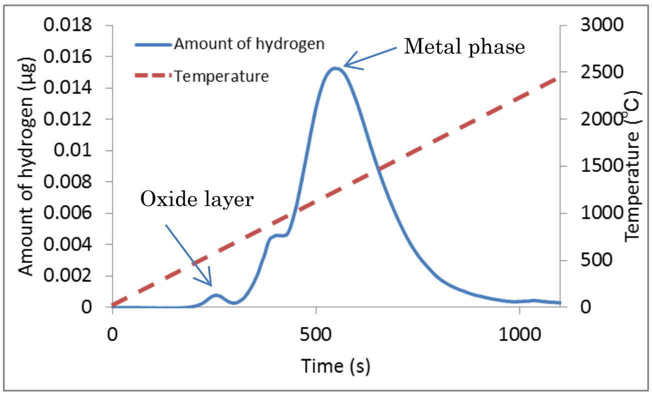
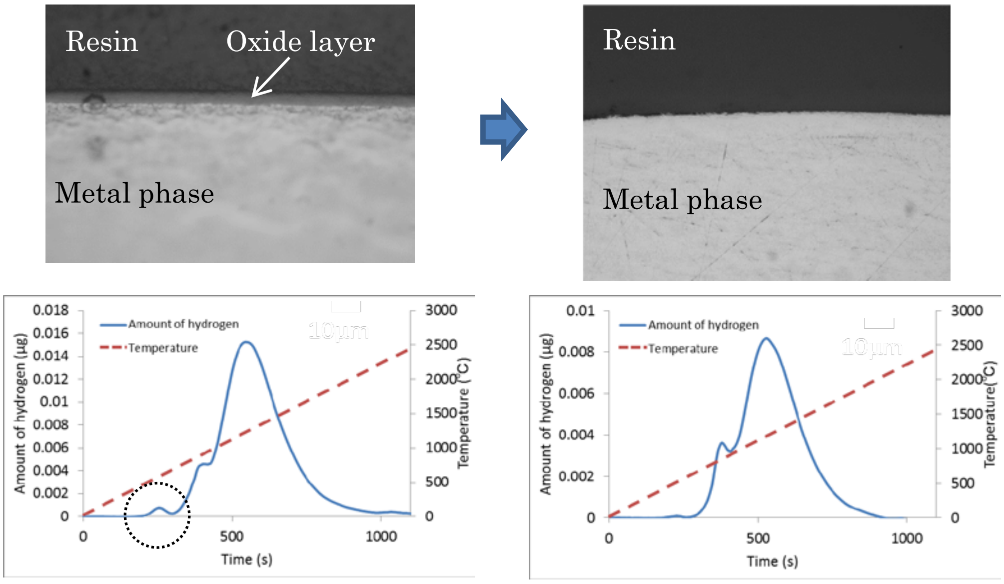


Fig.1 Result of continuous heating on unirradiated cladding

4. Confirmation test

In order to confirm the derivation of the lower side peak at the temperature of 500℃ on the continuous heating, the confirmation test was performed using the sample of which the oxide layer removed. The oxide layer was removed by the turning machine mechanically. Fig.2 shows the comparison photographs and results of hydrogen analysis on the cladding before and after the removing process. The peak of the lower temperature side disappeared on the removed oxide sample. It could be notice that the lower side peak shows the hydrogen release from the oxide layer. In the results of several examinations, the released temperature was moved depending on the thickness and density of the oxide layer. Therefore, the heating temperature of first step on the two-step heating method should be determined by the hydrogen release curve from the continuous heating.



Before removing After removing

Fig.2 Mechanical removing of oxide layer

The continuous heating examinations were performed to determine the optimum temperature of first step. Fig.3 shows the enlarged peak of hydrogen release from the oxide layer as Fig.1. Three samples were prepared from the unirradiated cladding with oxide layer and these were heated up at 400℃, 550℃ and 650℃ respectively. These temperature conditions were selected as the beginning, top and end of the lower side peak of hydrogen release. After the heating, all samples were heated again as the condition of continuous heating and confirmed presence of the peak at low temperature side. Fig.4 shows result of the cladding heated at each temperature and heated again as the condition of continuous heating. In the case of the heated the cladding at 400℃, the hydrogen peak was still observed at low temperature side in the result of continuous heating. It means the hydrogen in the oxide layer was not fully released at 400℃. The hydrogen was released continuously in the result of heating at 650℃. It means the hydrogen in the oxide layer was fully released and the hydrogen release in the metal phase was started at 650℃. In the case of the heated the cladding at 550℃, all of hydrogen in the oxide was released and there is no peak at the lower side temperature in the result of continuous heating.

Therefore, it’s guessed the hydrogen release from the metal phase and the oxide layer of the cladding can be controlled by the difference of the heating temperature. The optimized temperature is the peak top of lower side in the continuous heating. After performed the continuous heating, the two-step heating method was performed based on the result of the continuous heating. Fig.5 shows the result of the two-step heating method with the unirradiated cladding. In the Fig.5, the released hydrogen peak was observed from oxide layer at first step and metal phase at second step. Therefore, it's possible to measure hydrogen in the metal phase and oxide layer separately with unirradiated cladding. In addition, this method was suitable for the irradiated cladding. Fig.6 shows measurement result by the two-step heating method with the irradiated cladding. In the Fig.6, it's possible to measure hydrogen in the metal phase and oxide layer separately with irradiated cladding.

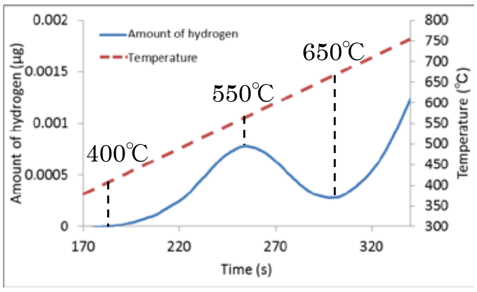


Fig.3 Enlarged peak of hydrogen release from oxide layer in Fig.1.

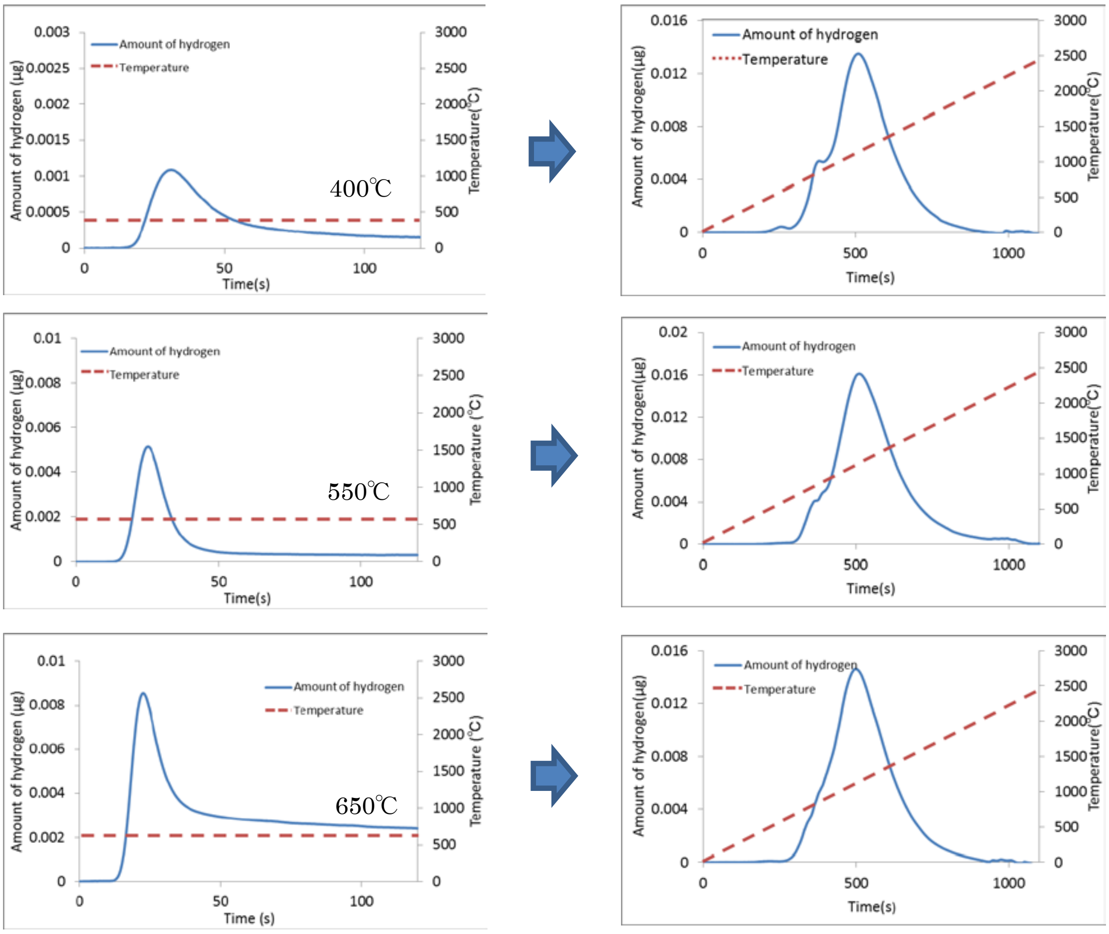


Fig.4 Result of the cladding heated at 400℃, 550℃, 650℃ and heated again by continuous heating.

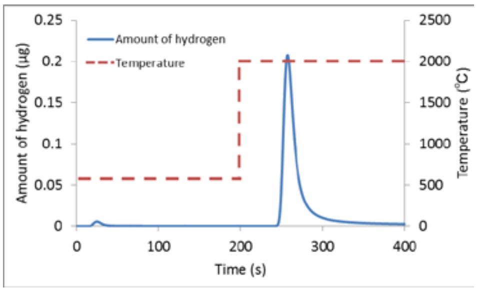


Fig.5 Result of two-step heating method with unirradiated cladding.

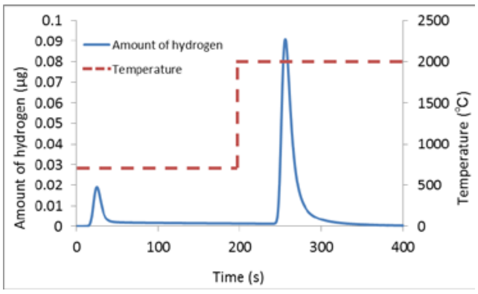


Fig.6 Result of two-step heating method with irradiated cladding.

5. Conclusion

Determination procedure of the optimal temperature for the hydrogen release only in the oxide layer was developed to the two-step heating method. First step of this procedure, continuous heating is performed to determine the temperature for the hydrogen release from the oxide layer using the sample which is provided from the nearest position of the two-step heating sample. Next, in the two-step heating method, the hydrogen was released from oxide layer at the temperature of first step, and the hydrogen in the metal phase was released at the temperature of second step. As the results of confirmation test, this method is valid for irradiated cladding to estimate the embrittlement of the high burnup fuel claddings.

Reference

[1] A. Hermann, et al., "Hydrogen distribution between fuel cladding metal and overlying corrosion layers," Proc. Int. Topical Meeting on LWR fuel performance, Park City, USA,372–384 (2000).