Hydrogen Content Analysis System in Post-irradiation Examination Samples

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Abstract

To analysis the hydrogen content of fuel rods cladding we found a hydrogen content analysis system. The gas, which releases from sample melting by pulse heating furnace, get into the infrared detector and the results can be calculated by the calibration curve. Due to the high radioactivity of post-irradiate sample, the system have been optimal improved and experimental procedure designed reasonable to satisfy the standard of radioactive concentration and exhausting. Four samples have been analysis, two are normal position and the others are failure position. The results show that the hydrogen contents of normal position samples are 133ppm and 168ppm, whereas the hydrogen contents of failure position samples are 1720ppm and 519ppm. The hydrogen contents of failure position samples are higher than that of normal position samples as expected. Meanwhile it reveals that the system has a good prospect in the post-irradiation examination.

Key words: Post-irradiation examination; Hydrogen content; system development

1. Introduction

The damage mechanism of fuel rods in pressurized water reactor is one of the important subjects of safe operation of nuclear power plant. The fuel rod cladding is the first layer of the fuel rod containment system, the strength and integrity of the fuel rod cladding is very important. Damage to the fuel rods will increase the radioactive background in the reactor, affecting the radiation from structural materials in the reactor, posing a threat to the safety of the staff and increasing the risk of radionuclide leakage in the surrounding environment of the nuclear power plant. Therefore, the performance of the fuel rod cladding should meet the requirement of environmental radioactive emission limit requirements and the principle of radiation protection optimization as much as possible . There are many reasons for the damage of the fuel rods cladding in the nuclear power plant, such as the abrasion in primary loop, the manufacturing defects (welding defects, etc.), the delayed hydride cracking (DHC) etc.[1-3]. In this work, we found a radioactive hydrogen content analysis system and measured the hydrogen content of damage fuel rods cladding as well as integrity fuel rods cladding. Before the measurement of hydrogen content, the samples tested by OM, SEM, EDS first, combined with hydrogen content measurement it can provide a theoretical basis to the reason of fuel rods cladding damage.

There are many reasons for the occurrence of a failure, as mentioned above, after a failure, the Zr alloy in the position of failure reacts with the cooling water in first loop as the reaction:

$$2H_2O \rightarrow 4H^+ + 2O^{2-} \qquad Zr^{4+} + 2O^{2-} \rightarrow ZrO_2$$

A large amount of ZrO2 is generated at the failure. In the process of oxide film growth, residual H2O, H+ or H2 get into the cladding tube, it is easier to hydrogenation reaction take place due to the low H/Zr reaction chemical activate energy in the position of stress concentration or defective area of cladding tube inner wall, so it is easier for H+ or H2 depositing in these position and form the ZrHx [4-5]. With the passage of time, the H solubility

in Zr alloy gradually saturated, ZrHx precipitation phase size increases lead to stress field strength increase and will cause more H to be deposited there resulting in more ZrHx, which eventually reaches the critical conditions of hydrogen induced delayed cracking [6], and where the hydrogen content is usually much higher than the normal position, so by measuring the hydrogen content at the failure position can be further analyze the causation of failure.

2. Experiment

Radioactive hydrogen content analysis system can make quantitative measurement of hydrogen content in steel, refractory metal, inorganic materials. Radioactive samples gasified under high temperature and released hydrogen through the helium carrier will enter the oxidant into H2O. Because of the specific infrared absorption spectra of H2O molecules, the infrared absorption spectra will change through the H2O and the computer software for data processing to get the original data. Then by calibration curve get in advance the hydrogen content can be calculated.

2.1 Experimental system

Sketch of the experiment system shown in Figure 1. Hydrogen analyzer (LECO Co. Ltd. Model H836) as a primary inclusion system equipped with multiple filters. The whole experimental device is contained in the glove box as the secondary inclusion system. The pressure in glove box is kept 200Pa below the standard atmospheric pressure. The residual gas discharged from the experimental system by filtered through the COUGAR filter. The exhausted gas is discharged into the hot cell ventilation system. Throughout the experiment, the ambient radioactivity level in the glove box was monitored by less than 3μSv/h.
The size of the glove box is 1200mm (length) × 1200mm (width) × 1150mm (high) as shown in Figure 2, to meet the requirements of sample injection and cooling water the glove box sampling window size is 300mm × 400mm. The hydrogen measurement range is 0.1ppm-2500ppm of 1g sample, hydrogen measurement accuracy is 0.05ppm or 2% RSD. For the stability of the helium gas pressure at 22psi, as the system may stop if gas pressure fluctuations exceed 10%, the pipes connection between the helium carrier gas outlet and inlet as short as possible to keep the gas flow stable.

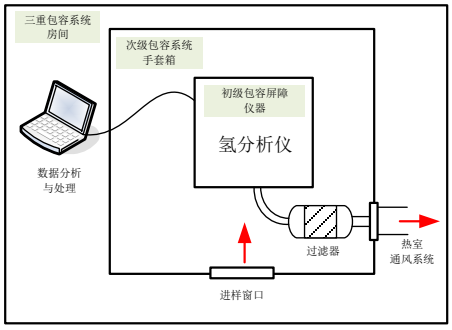

Fig.1 Sketch of the experiment system

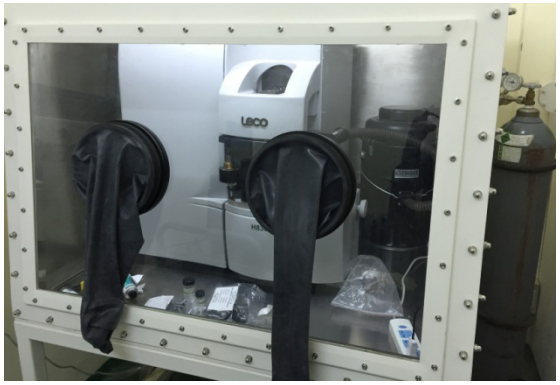

Fig.2 Physical diagram of experiment system

2.2 Sample preparation

As the high radioactivity of fuel rods cladding the entire sample preparation process must be completed in the metallographic cutting glove box, as shown in Figure 3. The sample is cleaned in advance before cutting. First 40% concentration of nitric acid solution for 20min ultrasonic cleaning, and then dehydration of ethanol dehydration 10min and cleaning with cotton wool wipe. In the process of cutting the sample, the upper limit of the detection of the

hydrogen analyzer is 2,500ppm for 1g sample, and the mass of the cut sample is determined to be about 0.1g in consideration of the lower limit of the weighing and the precise range of the electronic balance. When the weighing is completed, the sample is placed in a self-made portable small lead tank and the sample is transferred from the metallographic cutting glove box to the hydrogen analysis system glove box. The radioactive activity of the surface of the lead tank must be measured before the transport to ensure that there is no radioactivity leak or levels of exemption. Only one sample is transported per test to ensure that the environmental radioactivity background of the hydrogen analysis glove box remains as low as possible.

Fig.3 Metallographic cutting glove box

3. Results and discussion

3.1. Calibration

The calibration material was LECO 502-881 standard hydrogen contained titanium, the nominal hydrogen content is 45 ± 6ppm, three independent tests have been done (Figure 4):

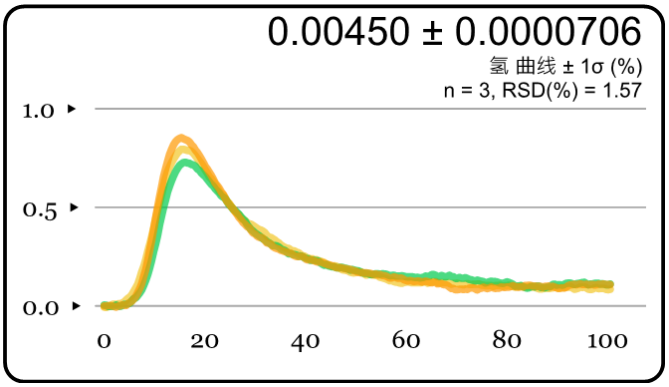

Fig.4 Calibration sample results

The calibration curves of the hydrogen content were obtained by linear fitting of the three points which were obtained by the integral spectra. Due to the large hydrogen content at the hydrogenation failure[7], the hydrogen content of calibration sample is only 45ppm, and this study only needs to verify the difference between hydrogen content in the normal and failure parts, i.e., it can be estimate the causation of failure from the order of the amount of hydrogen

content without getting the accuracy quantitative data. So the 45ppm standard sample results with the original least squares method can be used as a calibration curve. The calibration expression of measurement results is shown below:

$$C = 1.32233729A$$

Table.1 Calibration sample results

No.	Nominal hydrogen content /ppm	Mass/g	Hydrogen content/ppm	STD/%
Sample-1	45±6	0.1158	45	
Sample-2	45±6	0.1146	44.3	1.57
Sample-3	45±6	0.1140	45.7	

3.2. Results

4 typical normal and failure position were selected from the two failure fuel rods as analytical samples, labeled as 1-4 #, respectively. The selected samples were subjected to OM metallographic observations before the hydrogen content measurements were taken shown in Figure 5-8. It can be seen from the figure, 1# and 3# samples for the normal parts of the sample which the hydrogen content is less and uniformity, whereas the hydrogen content of 2# and 4#, which was cutting from failure position, is more than that of 1# and 3#. The failure position of 2# sample shows a "sunburst" shape and cladding tube external hydrogen of 4# sample distribution is also very dense.

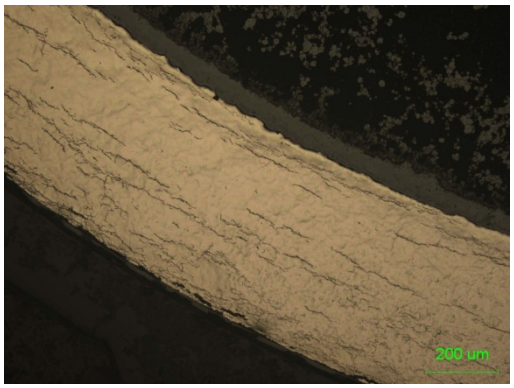

Fig.5 1# sample normal position metallograph

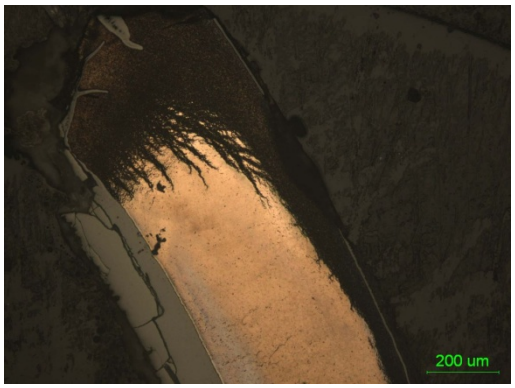

Fig.6 2# sample failure position metallograph

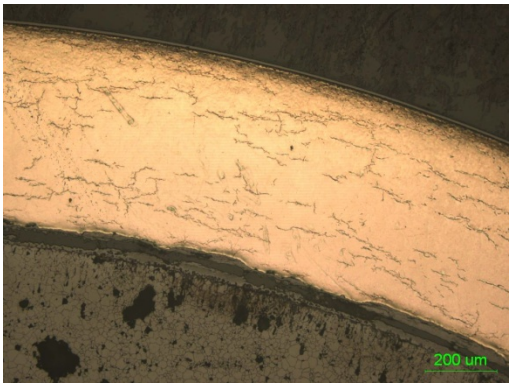

Fig.7 3# sample normal position metallograph

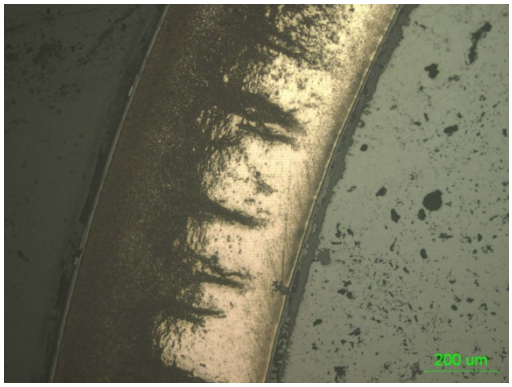

Fig.8 4# sample failure position metallograph

Due to the difficult in cutting sample in the glove box and the quantitative of sample is limited, the normal position of the cladding tube 1#, 3# samples were cut in two samples, failure position of 2#, 4# samples were cut in one sample respectively. The measurement time of each sample is about 1min, the hydrogen content measurement results shown in Figure 9-12.

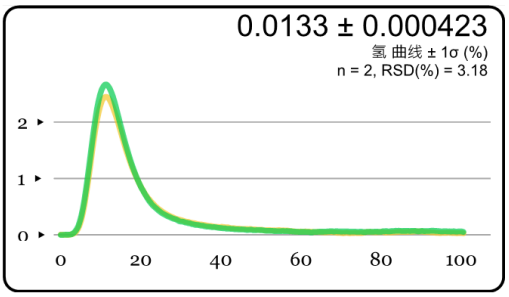

Fig.9 1# sample normal position hydrogen content

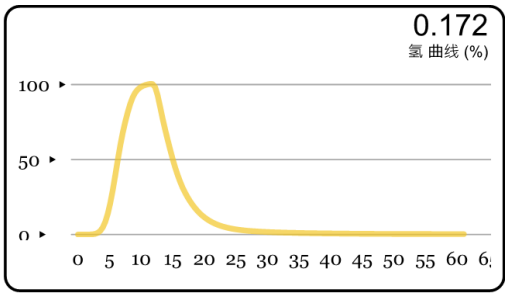

Fig.10 2# sample failure position hydrogen content

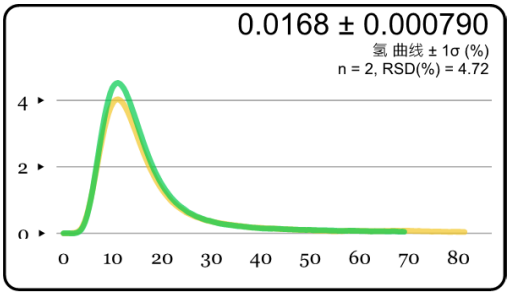

Fig.11 3# sample normal position hydrogen content

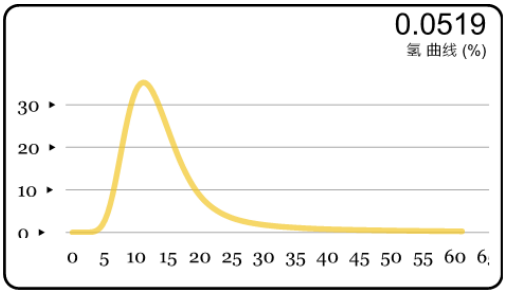

Fig.12 4# sample failure position hydrogen content

The results are shown in Table 2:

Table 2. Failure rods cladding hydrogen content results

No.	Average mass/g	Average hydrogen content/ppm	STD/%
1#	0.0578	133	3.18
2#	0.1242	1720	/
3#	0.0726	168	4.72
4#	0.1624	519	/

The measurement results consistent with the OM metallographic observation results as expected, the hydrogen content at the failure position is much higher than that of normal position. It shows that the system and the analytical method are feasible and can provide theoretical support for the further study of the damage mechanism of fuel rod cladding.

4. Conclusion

The hydrogen concentration analysis system of the irradiated sample was successfully developed. The system meets the environmental radioactive monitoring limit requirement and the thermal discharge limit of the hot cell during the whole experiment. At the same time, the system successfully completed the verification test and the measurement result was the same as expected, i.e., the fuel rod cladding parts of the hydrogen content much higher than that of normal position. The next step will be on the failure fuel rod cladding system of hydrogen content analysis experiments, including the contrast between failure rods and complete rods, the study of hydrogen content comparison between different burn-up level of the failure rods, combined with other analytical methods on the fuel rods failure to provide experimental and theoretical basis.

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