Development of the electrochemical testing techniques in hot-cell

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Abstract

In order to evaluate intergranular corrosion properties of irradiated austenitic stainless steels, the electrochemical measurement technique including sample preparation, which is able to perform in hot-cell using manipulator, was developed. Consistency of electrochemical test results obtained with the developed measurement technique inside and outside hot-cell was confirmed using non-irradiated austenitic stainless steel samples.

1. Introduction

Austenitic stainless steels are extensively used as the reactor structural components because of their excellent corrosion resistance in those environments, in addition to high ductility and fracture toughness. But under high-temperature high-pressure water environment, austenitic stainless steels have susceptibility to intergranular corrosion, which causes the reduction of ductility, reduction of fracture toughness, and irradiation-assisted stress corrosion cracking (IASCC). IASCC is degradation process that affects LWR structural components exposed to neutron radiation [1].

It is known that SCC of materials in high-temperature, high-pressure water depends on three factors: a susceptible material, relatively high stress, aggressive environment, moreover IASCC susceptibility depends on the effects of irradiation against three factors multiply [2,3]. The radiation induced segregation (RIS) of austenitic stainless steel is the phenomenon that quantity of Cr of the grain boundary lacks by neutron irradiation. Herewith, the corrosion resistance of the grain boundary degrades, and IASCC susceptibility increases.

As one of the techniques to detect chromium depletion in the grain boundary, there is the method of electrochemical potentiokinetic reactivation ratio measurement (EPR) which is electrochemical testing to evaluate grain boundary corrosion sensitivity.

Because the handling of a sample preparation and the test jigs for radioactive samples are difficult in the electrochemical measurement using manipulator, there are extremely few proper examples for irradiated austenite stainless steels.

In this study, development of the electrochemical testing techniques with the Japanese Industrial Standards (JIS), which is able to perform in hot-cell using manipulator, is introduced.

2. Experimental procedures

Figure 1 illustrates the schematic view of conventional electrochemical measurement equipment. The conventional electrochemical measurement system is constructed with potentio/galvanostat, electrolytic cell, thermostatic water bath, and deaeration instrument. Conventional measurement is generally performed by three-electrode system, where specimen is used as working electrode, a silver-silver chloride electrode (SSE) is used as reference electrode, and a platinum sheet is as a counter electrode, respectively.

Some problems arise, when the electrochemical measurement is performed with conventional systems using manipulator for high-dose irradiated samples. Because the most of the apparatus are glass product, so it is very sensitive work to handle them with a manipulator in hot-cell, and those apparatus must be handled with care to avoid the fracture of glass instruments.

In this study, the improved preparation method of working electrode and salt bridge, countermeasure against noise from facilities and a power supply are introduced.

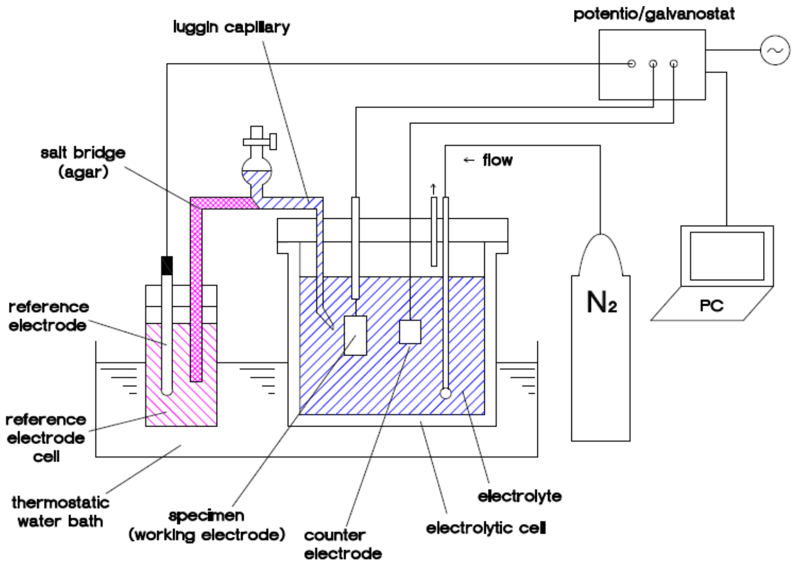

Fig. 1. Schematic view of conventional electrochemical measurement system.

2.1 Sample preparation

In electrochemical measurement, it is important that a fringe of electrode surface must be covered completely to avoid the formation of crevice under the resin. Fig. 2 shows the schematic view of coating-type electrode that is one of the general working electrodes. The coating-type electrode is prepared by connecting lead cable to the edge of specimen using spot welding, and prepared by painting the surface of the specimen with insulation paint. However, welding and painting are difficult to perform in hot-cell using manipulator.

Figure 3 shows the resin-molding type electrode that enabled to prepare samples using manipulator. Specimen was connected to the lead cable by using conductive paste, and molded into epoxy resin. After the solidification of the epoxy resin, gap was created between specimen and epoxy resin due to contract of resin. The gap will exert an adverse effect on the measurement, therefore, the gap was filled with adhesive.

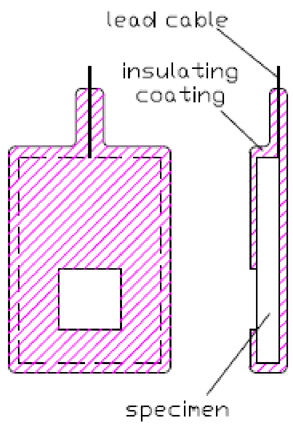

Fig. 2. Schematic view of coating-type electrode (conventional way).

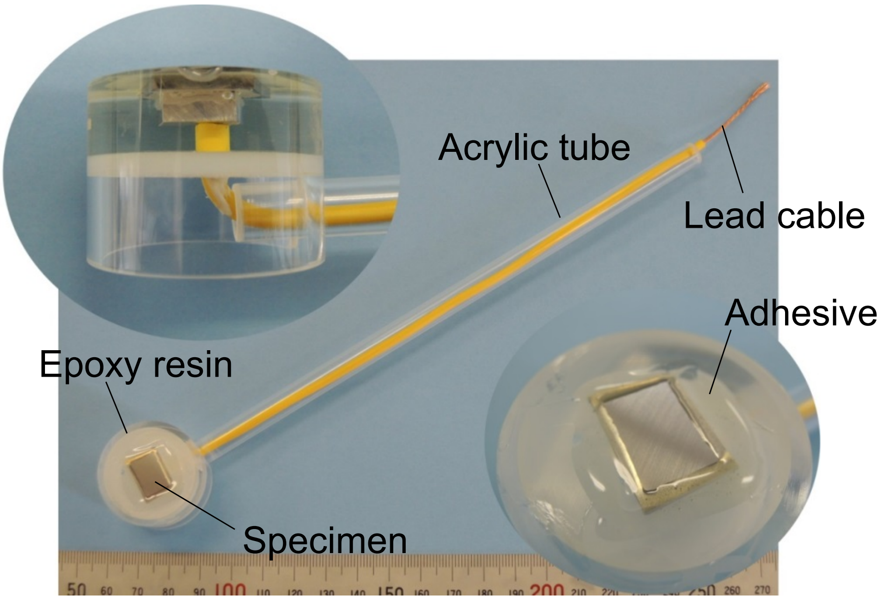

Fig. 3. Resin molding-type electrode.

2.2 Replacement of the salt bridge

As shown in Fig. 1 a salt bridge has been used to establish conduction between reference electrode cells and electrolytic cells with preventing mixture of each electrolytic solution, in the electrochemical measurement. A salt bridge is generally prepared by injecting the agar melted with electrolyte in the glass tube for each measurement. Since it is difficult to prepare a salt bridge in the hot cell using manipulator, platinum bridge produced by SYRINX Co., Ltd. was adopted. Figure 4 shows the view of platinum bridge. On the tip of the platinum bridge, platinum wire is penetrated. It is possible to get electrical conduction by the micro gap existing between the platinum wire and glass tube. In addition, as platinum bridge does not use agar, it has the merit that it can be reused only by washing.

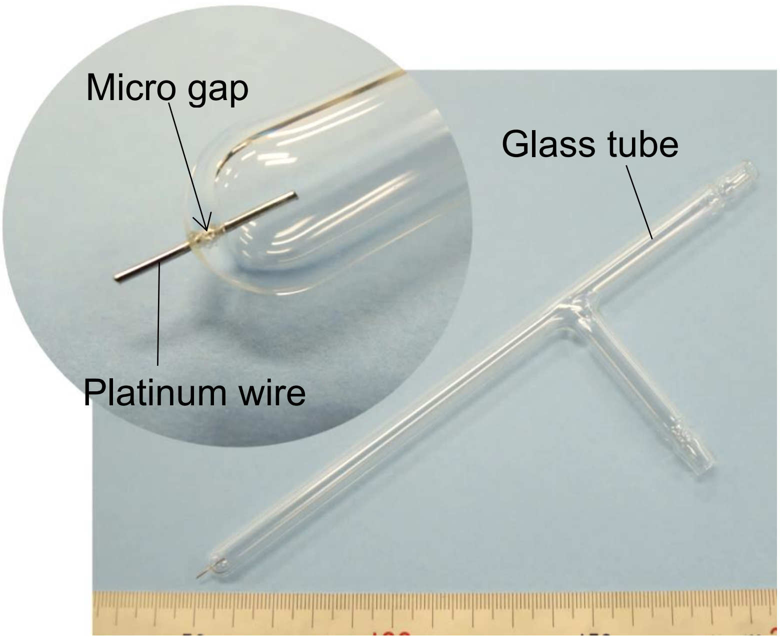

Fig. 4. Platinum bridge.

2.3 Countermeasure against noise

There are electrical noises occurred from various instruments in hot laboratory facilities. The weak current in the order of pA - μA needs to be detected in the electrochemical measurement, so electrical noise affecting the measurement result must be thoroughly removed. Thus, countermeasure against noise must be performed.

The schematic view of the countermeasure against noise adopted is illustrated in Fig.5. Two countermeasures for noise were performed. One is employing the noise-cut transformer to reduce noises form power supply. The other is the covering measurement cable with shielding material from outside hot-cell to inside, to avoid the noise from the facilities.

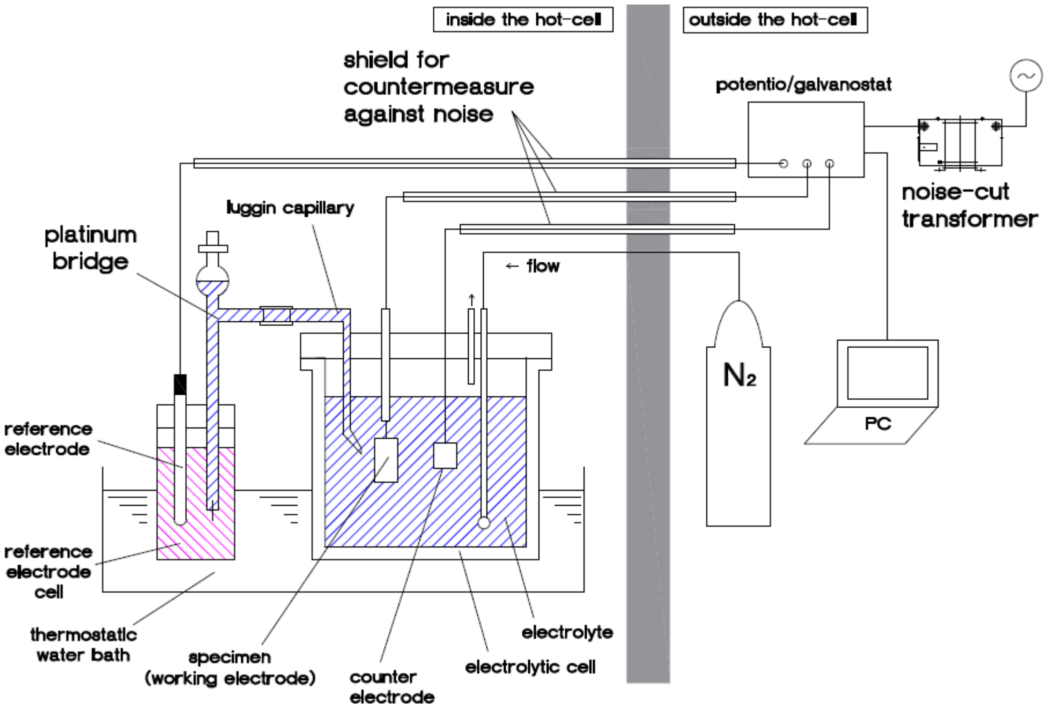

Fig. 5. Schematic of the countermeasure against noise

2.4 Noise measurement

The anodic polarization curves measurement compliant with JIS G 0579 for unirradiated SUS 304 was conducted to confirm the effect of countermeasure against noise employed.

2.5 Anodic polarization curves measurement

The anodic polarization curves measurement carried out inside and outside the hot-cell, for SUS 304, by adopted the improvement subjected 2.1-2.3. Table 1 summarizes the experimental conditions. The anodic polarization curves measurement was a method based on JIS G 0579, and the specimen used is unirradiated SUS 304. The electrode type used is coating type made outside the hot-cell and resin-molding type in hot-cell respectively. For method to link reference cell to electrolytic cell electrically, salt bridge outside the hot-cell and platinum bridge inside the hot-cell were applied.

Table 1 Experimental conditions

	Outside the hot-cell	Inside the hot-cell
Measurement method	Anodic polarization curves measurement (JIS G 0579)	
Specimen	SUS 304 (unirradiated)	
Test electrode type	Coating-type made by hand labor	Regin-molding-type made with a manipulator
Method to link reference cell to electrolytic cell electrically	By salt bridge	By platinum bridge
Countermeasure against noise	Existence	Existence

3 Results

3.1 Countermeasure against noise

Figure 6 shows an example of the results of electrochemical measurement before and after the countermeasure against noise. After countermeasure adoption the wave form is stable, though it is unstable before countermeasure adoption. The S/N ratio was improved to more than 10 times by adopting the countermeasure.

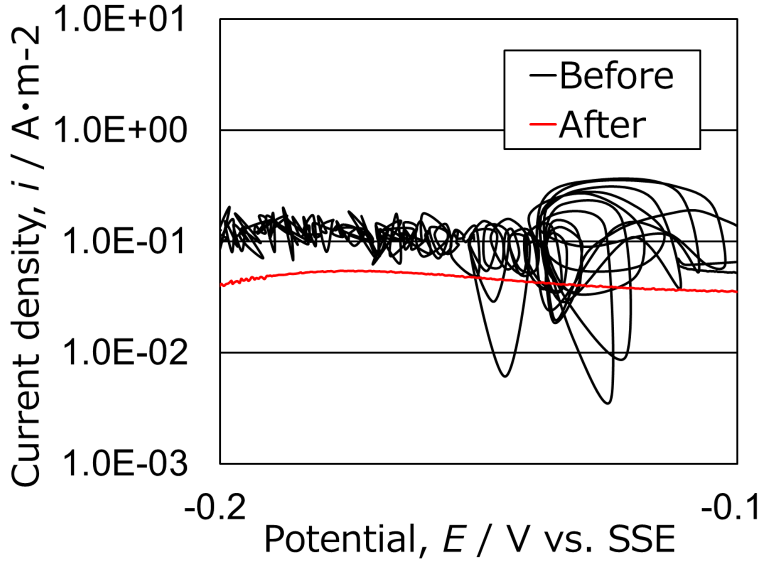

Fig. 6. Result of a measurement before and after countermeasure for noise.

3.2 Anodic polarization curves measurement

Figure 7 shows the results of anodic polarization curves measurement for SUS 304. By using the developed measurement technique, electrochemical test results obtained inside the hot-cell showed consistency with that obtained outside.

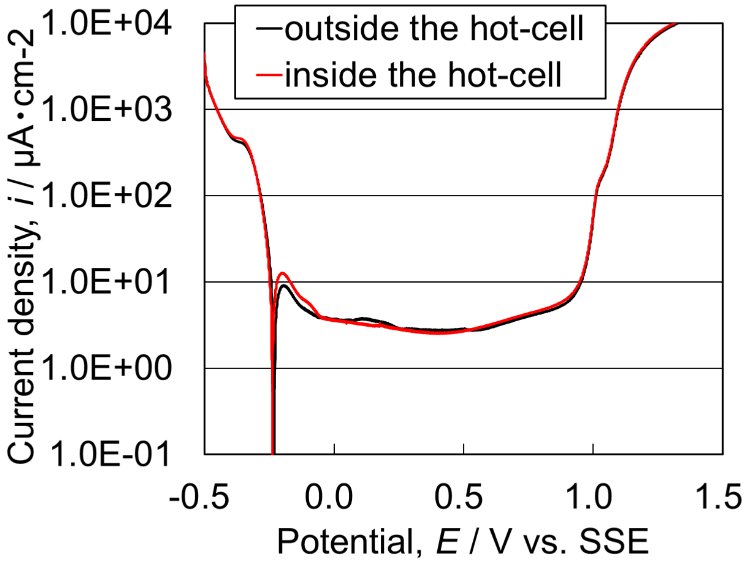

Fig. 7. Result of anodic polarization curves measurement for SUS 304

4. Conclusion

For the electrochemical measurement based on JIS G 0579 inside the hot-cell, methods of the sample preparation, getting electrical conduction without using a salt bridge and countermeasure against noise were developed. The experimental results reveal that the electrochemical measurement using irradiated materials in hot-cell can be performed by using above-mentioned technique. From these results, it is found that these techniques are thought to be applicable to other electrochemical measurements.

Currently, the challenge for development of EPR measurement with the JIS G 0580 in order to evaluate IASCC properties for irradiated austenitic stainless steels has been performed. In addition, for Fukushima Daiichi Nuclear Power Plant accident-related issues, in order to confirm effects of irradiation history in the reactor on crevice corrosion susceptibility of fuel assembly materials stored in a shared pool, the measurement of the crevice corrosion potential with the JIS G 0592 was performed [4].

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