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Corrosion inhibition of steam generator tubesheet by Alloy 690 cladding in secondary side environments

Do Haeng Hur *, Myung Sik Choi, Deok Hyun Lee, Jung Ho Han, Hee Sang Shim

Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong-gu, Daejeon 305-353, Republic of Korea

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ABSTRACT

Denting is a phenomenon that a steam generator tube is distorted by a volume expansion of corrosion products of the tube support and tubesheet materials adjacent to the tube. Although denting has been mitigated by a modification of the design and material of the tube support structures, it has been an inevitable concern in the crevice region of the top of tubesheet. This paper provides a new technology to prevent denting by cladding the secondary surface of the tubesheet with a corrosion resistant material. In this study, Alloy 690 material was cladded onto the surface of an SA508 tubesheet to a thickness of about 9 mm. The corrosion rates of the original SA508 tubesheet and the Alloy 690 clad material were measured in acidic and alkaline simulated environments. Using Alloy 690 cladding, the corrosion rate of the tubesheet within a magnetite sludge pile decreased by a factor of 680 in 0.1 M $NiCl_2$ solution at 300 °C, and by a factor of 58 in 2 M NaOH solution at 315 °C. This means that denting can drastically be prevented by cladding the secondary tubesheet surface with corrosion resistant materials.

1. Introduction

Denting is a phenomenon by which a steam generator tube is distorted from the outer surface to the direction of the inner surface by a volume expansion of corrosion products of tube support and tubesheet materials adjacent to the tube. The corrosion and oxide growth of the materials are accelerated in both acidic and alkaline environments resulting from the impurity concentration process associated with boiling within the tube/tube support crevices and tube/tubesheet crevices in which sludge is accumulated [1]. Since denting imposes a slow straining on the tube, it accelerates stress corrosion cracking on both the primary and secondary sides of the tube [2,3]. Therefore, denting has been a precursor of stress corrosion cracking.

Three major strategies were implemented to mitigate the denting [4,5]. The tube support materials were changed from carbon steel to stainless steel, and its geometries were modified from a drilled hole type to a trefoil, quatrefoil, or egg crate type, depending on manufacture. Because denting is a result of a corrosion process, the water chemistry was also improved by strictly controlling the amount of impurities and oxygen in the secondary water. Nevertheless, denting has been an inevitable problem in the crevice region of the top of tubesheet (TTS).

Denting at the TTS has been a significant concern regardless of the tube material, i.e., Alloy 600, Alloy 690, and Alloy 800 [6,7]. This is because it is a mechanical process resulting from a volume expansion of the corrosion products of the tubesheet materials. It should also be noted that the corrosion rate of low alloy tubesheet materials is accelerated due to the presence of corrosion products accumulated at the top of the tubesheet. Therefore, a reduction of the corrosion rate of the tubesheet material should be a key strategy to prevent tube denting at the TTS, as well as an improvement of the secondary water chemistry.

This paper provides a new technology to prevent denting by cladding the secondary side surface of the tubesheet with a corrosion resistant material. In this study, Alloy 690 material on the surface of a SA508 tubesheet was cladded to a thickness of about 9 mm. The corrosion rates of the original SA508 tubesheet and Alloy 690 clad material were measured in acidic (0.1 M $NiCl_2$) and alkaline (2 M NaOH) simulated environments.

2. Experimental methods

Forged low alloy steel, SA508 was used as a tubesheet material, which is currently one of the major materials used in pressurized water reactor steam generators. Alloy 690 material on the secondary surface of the SA508 tubesheet was cladded to a thickness of about 9 mm using a submerged arc welding technique.

Corrosion coupons were made by cutting the Alloy 690 clad layer and SA508 tubesheet, respectively, to a dimension of about 25 mm × 45 mm × 1 mm thick. The specimens were ground using silicon carbide paper down to grit 600, ultrasonically degreased in acetone, and finally weighed.

Corrosion rate measurements were made in two different environments: 0.1 M $NiCl_2$ solution at 300 °C for 150 h in a Ti

* Corresponding author. Tel.: +82 42 868 8388.
E-mail address: dhhur@kaeri.re.kr (D.H. Hur).

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autoclave, and 2 M NaOH solution at 315 °C for 500 h in a Ni autoclave. The measured pH of 0.1 M $NiCl_2$ and 2 M NaOH solution at room temperature was 5.8 and 13.1, respectively. These solutions were chosen to simulate corrosive environments which may be formed in the crevices between tube and tubesheet of the TTS. The secondary side surface of the tubesheet during the operation period is always covered with sludge. To simulate this condition, some coupon specimens were also located within the magnetite sludge pile. The particle size and purity of the magnetite was about 1 μm and 99%, respectively. No attempt was made to control the content of dissolved oxygen in the test solutions before and during the tests. The test apparatus is illustrated in Fig. 1. Two coupons per each material were exposed to the solution at the same elevation from the bottom of the autoclave. Two coupons per each material were also located at the same elevation inside the magnetite pile. The surface area of each coupon was about 20 cm^2, and the volume of the test solution was 700 ml.

Electrochemical corrosion tests were conducted in aerated 0.1 M $NiCl_2$ solution at room temperature. The specimens were mechanically polished using 600 grit silicon carbide paper and then ultrasonically cleaned in acetone. A saturated Calomel electrode and a platinum wire electrode were used as a reference and counter electrode, respectively. Polarization curves were obtained from the corrosion potential at a scan rate of 20 mV/min toward the cathodic and anodic directions, respectively.

3. Results

3.1. Corrosion in acidic environments

Fig. 2 shows the corrosion rates of the SA508 and Alloy 690 clad measured in 0.1 M $NiCl_2$ solution at 300 °C for 150 h. Both test materials indicated a weight loss. When exposed to the solution, the corrosion rate of SA508 was 0.873 mg/cm^2 h, while that of the Alloy 690 clad drastically decreased to 0.00163 mg/cm^2 h. Within the magnetite sludge pile, the corrosion rates of SA508 and Alloy 690 clad were 2.06 mg/cm^2 h and 0.00303 mg/cm^2 h, respectively. This means that the corrosion resistance of the tubesheet was improved by a factor of 540–680 by the Alloy 690 cladding. It was noted that the effect of Alloy 690 cladding on the corrosion prevention was more prominent in the corrosive environment of the magnetite pile.

On the other hand, the corrosion rates of the two materials inside the magnetite increased by about a factor of two, compared to those exposed to only the solution. Magnetite has a high electrical conductivity of $2.5 \times 10^4/\Omega$ cm at room temperature [8]. The released electrons during the corrosion process can rapidly be consumed for the cathodic reactions of hydrogen evolution and/or oxygen reduction [4] on the large surface of magnetite contacted with the specimens, resulting in an increase of the corrosion rates in the magnetite sludge pile. In operating steam generators, non-volatile impurities in the feed water concentrate within the sludge on the tubesheet [9,10]. Accordingly, the corrosion of the tubesheet is expected to increase not only owing to this magnetite effect but also to the impurity concentration in the sludge pile on the tubesheet.

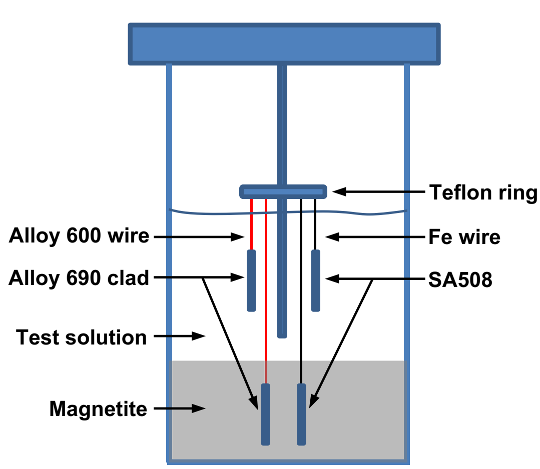

Fig. 1. Schematic of the test apparatus.

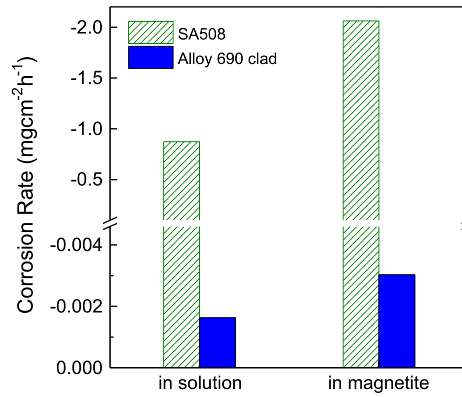

Fig. 2. Corrosion rates of SA508 and Alloy 690 clad in 0.1 M $NiCl_2$ solution at 300 °C.

The black and thick oxide was observed on SA508 specimens. The oxide layer of SA508 slightly ballooned and contained some visible cracks, indicating an apparent expansion of the oxide. Thus, a delamination split of the oxide parallel to the metal surface occurred by an external force. A cross sectional surface of the SA508 and Alloy 690 clad located inside the magnetite pile was observed using an optical microscope. As shown in Fig. 3(a), oxide was formed across the nearly total thickness of the SA508 coupons. An irregular black area of SA508 corresponded to the non-flatted surface due to a drop out of the brittle oxide during the specimen grinding and polishing steps for optical observation, which was confirmed by an observation using a scanning electron microscope. From the chemical analysis using an energy dispersive spectroscope, the oxide seems to be magnetite. However, no oxide layer was observed in the Alloy 690 clad, as shown in Fig. 3(b).

3.2. Corrosion in alkaline environments

Fig. 4 shows the corrosion rates measured in 2 M NaOH solution at 315 °C for 500 h. The SA508 indicated a weight loss, while the Alloy 690 clad showed a slight weight gain. When exposed to the solution, the corrosion rates of the SA508 and Alloy 690 clad were 0.0070 mg/cm^2 h and 0.00024 mg/cm^2 h, respectively. Within the magnetite sludge pile, the corrosion rate of the SA508 was 0.019 mg/cm^2 h, while that of the Alloy 690 clad drastically lowered to 0.00033 mg/cm^2 h. That is, the corrosion resistance of the tubesheet was improved by a factor of 29–58 by the Alloy 690 cladding. Similar to the result in the acidic environment, the corrosion prevention performance of the Alloy 690 cladding was more effective in the corrosive environment of the sludge pile.

3.3. Electrochemical behaviors

Fig. 5 shows the polarization curves of the SA508 and Alloy 690 clad materials measured in 0.1 M $NiCl_2$ solution at room temperature. The SA508 initially showed an active dissolution behavior and very high currents of about 0.1 A/cm^2 were maintained at more noble potentials. It was observed that a black thick scale was formed on the surface of the specimen after the tests. Therefore, it seems