Reduction methods of Cr and Co release from stainless steels in PWR and BWR

Hiroyuki ANADA (1), Kiyoko Takeda (2) and Tetsuo Yokoyama(1)

Sumitomo Metal Industries, Ltd.

(1)   Specialty tube works, 1 Nishino-cho, Higashi Mukohjima, Amagasaki, Japan

(2)   Cooperated Research Center, Fuso-cho 1-8, Amagasaki, Japan

The dose rate reduction in the aspect of structural materials is one of the key issues. This paper describes the pre-filming technology to reduce Cr and Co release from feed water heart tube and the reduction method of Co content in stainless steels which influence directly Co release to coolant. Co content in stainless steels generally increases with the contamination in raw material. Reduction of Co content was achieved to less than 0.02% by controlling raw material mixture. These methods can be applied to the every stainless steel, which expect to contribute reduction of radioactivity in the coolant of PWR and BWR. Pre-filming to the inner surface of TP304 tube, 19.0mm in diameter for the feed water heater tubes was conducted under several conditions. As a results, Cr release rate from the pre-filmed tube decreased approximately to be one third compared with that from the bare tube. The oxide film on the inner surface after pre-filming was consisted mainly of CrMn mixed oxide and slight Fe_2O_3. These oxide films were considered to be a moving barrier during corrosion.

1.   Introduction

Reduction of dose rates in light water reactors has been very important issue; therefore, a lot of methods has been proposed and applied. Reducing content of elements which have long half-time from nuclear materials is very important for reduction of radioactivity. Especially, ^{60}Co has long half-life, 5.7 years therefore, content of Co should be decreased as low as possible. Stainless steels and Ni base alloys for structural materials contain slight amount of Co as contamination. Contamination level for Co was restricted less than 0.05% according to EPRI for the stainless steels that are used under severe Co release condition. Content of Co is allowed up to 0.2% in stainless steels those are used under not so severe conditions. Controlling contamination increase the manufacturing cost, therefore, the issue is to achieve extra-low content of Co without cost impact. Therefore it is important for us to develop the method for reduction of Co contamination without cost impact.

In addition to Co, Ni and Cr are important elements for reducing dose rate in the

coolant. Ni is released from stainless steels and Ni base alloys into the reactor coolant due to corrosion. Some of the corrosion products containing Ni ion are circulated with the coolant into the core where radiation field is high. When the corrosion products are irradiated, Ni is changed into long half-life Co.

Cr release generally decreases pH of the coolant, which increase solubility of the corrosion products such as Ni-Cr-Ferrite including Co[2]. As a result, dose rate increases with releasing corrosion products with radioactive elements. Pre-filming on surface of the materials is the effective method for prevention to release metallic ions from the material into the coolant. In Japanese BWR, the pre-filming was applied to the TP304L tubes in feed water heat exchanger, which has been successfully reducing the metallic ions into the coolant and decreasing radioactivity[1].

This paper describes that extra-low Co content stainless steel less than 0.02% without large cost impact and some fundamental data on the pre-filming methods for metal release to coolant.

2. Experimental procedure

2.1. Material

TP304L seamless tube for feed water heater with extra-low content of Co was prepared commercially with an electric furnace for a test sample tube. It was noteworthy that extremely low content of Co was achieved to be 0.019% by avoiding the contamination of Co from the raw material.

2.2. Pre-filming and characterization for oxide film

Pre-filming on inner surface of TP304L seamless tube was aim to be selective oxidation of Cr and Si, whose oxide films expected to act as an barrier for metallic ion release from the tube to environments. The Pre-filming tests in the laboratory were performed by a heat treatment under various dew points in flowing H_2 gas.

The sample tube was cut and opened longitudinally 50mm in length followed by placing in the reaction tube. The dew point controlling gas flowed into the reaction tube and heated at 1060C for 5 minutes and cooled in the furnace. The controlled gas was H_2 with various dew points from –50 to –10 degree C in order to vary the oxidation potential for selective oxidation. This expected to change chemistry, thickness and morphology of the oxide film. One of the tubes was oxidized in the air for comparison.

In addition to the laboratory test, the pre-filming was performed in the

commercially used production line. The dimension of the sample tube was 15.9 mm in diameter, 1.0 mm in thickness and approximately 20 m in lengths, which is the same size as the feed water heat exchanger tube. The pre-filming condition was the same as that of the solution heat treatment at 1060 degree C for 5 minutes. The oxygen potential was controlled by the dew point in the atmosphere of the hydrogen furnace.

2.3. Characterization on the pre-filming

The pre-filming was characterized by XPS of which condition is summarized in Table 1. The depth profiles of Fe, C r, Ni Si and Mn were obtained by sputtering of Ar ion.

Table 1 Characterization of pre-filming oxide by XPS

Item	Condition
X ray	Al K-alpha line, 1.49eV
Analyzed area	200 micron in diameter
Sputtering ion	Ar+, accelerated at 2 kV
Sputtering area	1mm x 1mm

2.4. Corrosion test

Contents of Cr and Co in the circulated test water were measured during the corrosion test at 215 degree C in the refreshed autoclave. The test temperature was selected as the same as temperature for the feed water heater tube.

3. Results and discussion

3.1. Reduction of Co content in stainless steels

One of the effective method to reduce dose rate in the coolant, is to lessen Co content in the stainless steels that are used for

Table 2 Chemical composition of TP304L

C	Si	Mn	Cr	Ni	Co	Fe
0.018	0.39	1.2	18.3	8.4	0.019	Bal.

structural materials. In typical stainless steel making, scrap metals and alloying elements are used as raw materials. Generally, these materials include Co as a contamination element.

In order to reduce Co content in stainless steels, contamination of Co should be removed. To be concrete, it is important to select the scraps metals and alloying elements that are not contaminated by Co. Hot metal was used for reduction of contamination.

3.2. Pre-filming

The oxide film was formed according to the oxidation potential during the heat treatment. Figure 1 shows the inner surface of the tubes on which thin oxide film was formed in the laboratory test. The color of the oxide was changing gradually from shiny metallic to grey with increasing dew point. This suggests that high dew point provided enough oxygen for oxide film growth.

Figure 1 The inner surface pre-filmed under the laboratory conditions showing the effectiveness of dew point during heat treatment

Figure 2 shows the morphology of the pre-filming inner surface that was heat treated with the commercially used hydrogen furnace. The tube was sandblasted by SiO_2 prior to the pre-filming heat treatment in order to remove any oxide or contaminations. The uniform oxide film and very fine oxide granules less than a few nm were observed on the surface with some stuck SiO_2 grits.
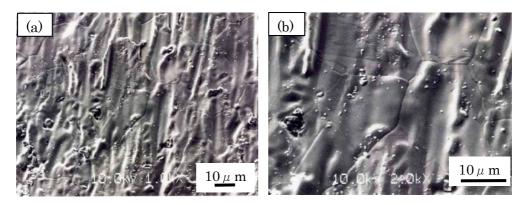

Figure 2 Morphology of the inner surface of the pre-filmed tube

Figure 3 indicates the result of chemical analysis on pre-filming oxide by XPS. The pre-filming heat treatment was conducted at 1060 degree C for 5 minutes under -20

degree C in dew point. The depth profiles of the main elements in TP304L were depicted from the surface to the matrix as a function of the depth from the surface. The depth was converted from the sputtering rate of Cr oxide. Content of Cr oxide and Mn oxide increased, and content of Fe reduced from the matrix to the surface gradually. The oxide film was more than 60nm in thickness.
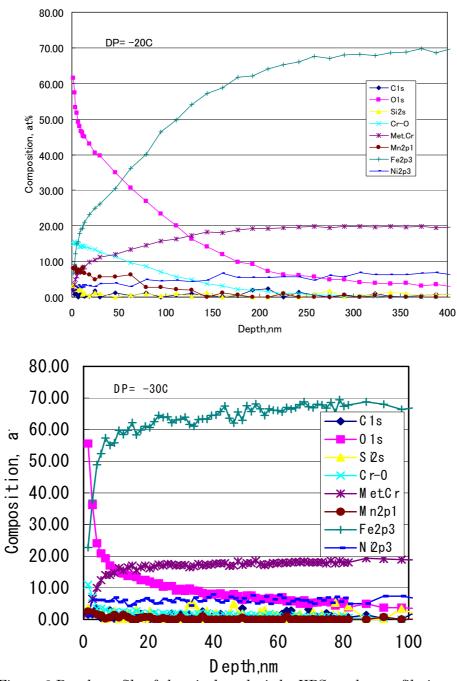

Figure 3 Depth profile of chemical analysis by XPS on the pre-filming surface

The depths profile in DP –30 degree C specimen are depicted also in Figure 3. Thickness of oxide was extremely thinner than that in DP-20 degree C specimen. The contents of Cr and Mn increased near the surface, which suggests that Cr-Mn mixed oxide formed near the surface.

The chemical state of the pre-filming surface was identified using by the chemical shifts of the Fe-2p orbital as shown in
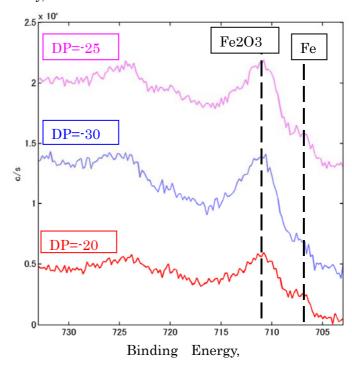
Intensity, Arb. Unit

Figure 4 Fe_2O_3 formed on the surface, showing effectiveness of dew point

Figure 4. The peak of 2P3/2 was observed at 710.7eV in binding energy that corresponds to the Fe_2O_3 peak and FeO peak, which shifted from metallic Fe peak 707 eV.

The pre-filming oxide consisted of mainly Cr-Mn mixed oxide containing slightly Fe_2O_3 as illustrated in Figure 5. FeO, metallic Fe and metallic Ni might be included in the oxide film. It was well-known that diffusion rate of Co ion in Cr rich oxide was smaller than that in Fe rich oxide [2] The Cr rich oxide film, therefore, might act as a barrier to corrosion, especially metal ion release to the high temperature water.
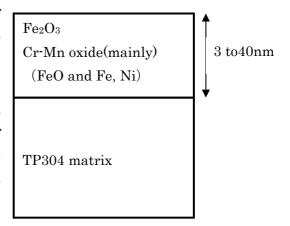

Figure 5 Multi-oxide layers in the pre-filming on TP304

The thickness of oxide apparently depends on the dew point, i.e., oxygen content in the environment of heat treatment. Thickness of the oxide apparently became

thinner with decreasing dew point during. The growth of the Cr rich layer might also contribute to reduce Co diffusion from the matrix to high temperature water. This method was applied for to typical feed water heater tubes and pre-filming was performed by the actual hydrogen furnace. The depth profile obtained by XPS indicated that the multi-layered oxide was formed as depicted in Figure 6. Cr rich layer was adjacent to the matrix and Fe rich layer was formed at the outer of the Cr rich layer. Thickness of the pre-filming oxide was approximately less than 10nm, which was thinner than that of the laboratory test.
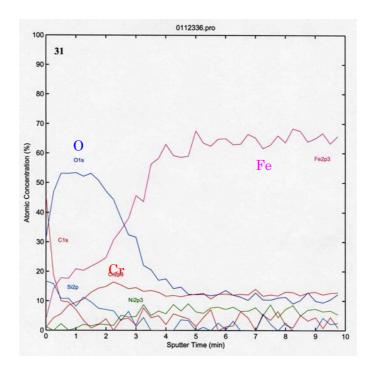

Figure 6 Depth profiles of the chemistries in pre-filming oxide

3.3. Metal ion release

The autoclave test was performed to measure the metal ion release into the refreshed water at 215 degree C. The test water was extracted from the loop and the content of Cr and Co in the test water was chemically analyzed. Co was less than analytical limit. Cr release added up and the results were depicted as a function of the test time in Figure 7. The Cr release adding up from the pre-filing tube was two third that from the bare tube (without pre-filming). It was considered that the pre-filming was effective for the Cr release from the heat exchanger tube to the reactor coolant. As mentioned before, Cr rich oxide layer formed on the inner surface of the tube, which contributed to decrease the Cr release from the tube.
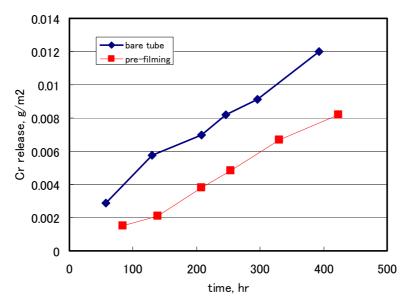
Figure 7 Relationship between test time and Cr release adding up in the refreshed type autoclave

4. Conclusion

Metallic ion release from the stainless tubes was evaluated. Extra-low Co content TP304 tube was prepared and was pre-filmed to study the metallic ion release. As a result, the following conclusions were extracted.

(1) The extra-low Co content less than 0.02% was prepared by selection for the raw material. This was effective for reducing Co release from the stainless steels.

(2) Pre-filming on TP304 was effective for Cr and Co ion release from the heat exchanger tubes to high temperature water.

(3) Chemical composition and thickness of the pre-filming oxide was able to select by controlling oxygen potential during the solution heat treatment. Cr-Mn mixed oxide film might act as a barrier layer for Cr and Co release.

Reference

[1] Jun-ichi Satoh, Proceedings of Thermal and nuclear power engineering society, p72-p73 October 23 2008, Sendai Japan

[2] M.A. Blesa, R.M. Larotonda, A.T.G. Maroto, A.E.Regazonni; Colloids Surf., **5**, p.197(1982)

[3] T.Tsuji, K. Tsumura, K. Naito; J. Nucl. Mat. **138**, p215, (1986)