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

2009 ISOE North America ALARA Symposium
EPRI Radiation Protection Conference
January 13, 2009
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Background

- Co content of stainless steels and Ni base alloys
  - Co as impurity is one of major resources
  - EPRI; Restricted less than 0.05%
  - Issue; Reduce Co content ALARA

- Cr release
  - Corrosion of the stainless steels release Cr into coolant.
  - Decrease pH in the coolant with increasing Cr content in coolant
  - Absorbed Co ion on the surface resolved into the coolant
Objectives

- How to reduce Co content from stainless steels
  - Less than 0.02% without cost impact
  - Suitable raw material selection;
    - Scraps
    - hot metal from BF

- Pre-filming to feed water heater tubes
  - Protective oxide film, Cr-rich oxide layer, for Cr release into coolant
  - Selective oxidation of Cr in TP304L by control oxygen content during a heat treatment in a manufacturing process
Experimental Procedure -Material-

- **Material**
  - TP304L; Raw material selection, hot metal in addition to scraps
  - Extra-low Co content less than 0.02%

- **Pre-filming on inner surface of the tube, 15.9 mm dia.**
  - Laboratory test
    - Pre-filming by heat treatment in H₂ with slight amount of O₂ content controlled by dew point
    - Dew point: -10 to -50 deg.C in H₂
  - Application to feed water heater tube for BWR
    - Pre-filming applied to the actual manufacturing process

- **Diagram:**
  - Melting
  - Cold draw 15.9 mm dia
  - Pre-filming; Solution treatment >1000degC
    - H₂ environment adding H₂O
    - Selective oxidation of Cr
Experimental Procedure

- Characterization of pre-filming oxide
  - Color and Oxide morphology
    - Naked eyes and SEM
  - Oxide structure identified by XPS
    - Depth profile of the chemistries by Ar sputtering
    - Chemical state analysis

- Cr and Co release from the pre-filmed tube to coolant
  - Corrosion test in pure water
  - Refreshed type autoclave at 215 deg.C for 450 h
  - Cr and Co content in the test water was analyzed.
Extra-low Co content was achieved by controlling raw material without large cost impact

Japanese experience of application in LWR
- Feed water heater tube for Some Japanese BWRs

<table>
<thead>
<tr>
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<th>This study</th>
<th>Conventional method</th>
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<tbody>
<tr>
<td>Melting</td>
<td>-Small amount of selected scraps</td>
<td>Selected pure scraps</td>
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<tr>
<td></td>
<td>-Hot metal, pure Fe from blast furnace</td>
<td>Large cost impact</td>
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<tr>
<td>Facility</td>
<td>-Combination of blast furnace and electric furnace</td>
<td>Electric furnace</td>
</tr>
<tr>
<td></td>
<td>-Suitable mixing, small cost impact</td>
<td></td>
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<tr>
<td>Co, %</td>
<td>Less than 0.02%</td>
<td>0.05%</td>
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Pre-filming oxide in the lab. test

- Thin oxide formed by heat treatment under controlled dew point in H₂

SEM images
Surface pre-filmed at -25degC
Depth profile of the pre-filming oxide

![Graph showing depth profile and composition analysis]

Composition, at %

- C1s
- O1s
- Si2s
- Cr-O
- Met.Cr
- Mn2p1
- Fe2p3
- Ni2p3

Surface vs Depth, nm
Structure of the pre-filming oxide

- Cr-Mn mixed oxide layer formed adjacent to the matrix.
- Fe$_2$O$_3$ or Fe$_3$O$_4$ layer formed at the surface of the oxide.

![Graph showing intensity and binding energy with peaks at different DP values and labeled regions for Fe$_2$O$_3$, Cr-Mn oxide, and TP304 matrix.]
Thickness of pre-filming

- Thickness of the pre-filming increase with increasing DP.
- Suitable pre-film thickness for will be selected easily.
- This might contribute to the effectiveness of the barrier layer
Diffusion of Co in oxide

- Diffusion coefficient of Co decrease with increasing Cr content in oxide.
- This suggests that Cr rich layer adjacent to the matrix acts as a protective film.

<table>
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<tr>
<th>FeO</th>
<th>Cr-Mn oxide (mainly)</th>
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<tr>
<td></td>
<td>(FeO and Fe, Ni)</td>
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<td></td>
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<tr>
<td>TP304 matrix</td>
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Application of pre-filming for feed water heater tube

- **TP304L**
- **Pre-filming**
  - In $\text{H}_2$, DP=25deg.C
  - 1060 degC
- **Cr rich oxide layer**
  - 5 nm in thickness
- **Same condition as that for Higashi-dori plant**
Cr release from the tube

- Pre-filming
  - actual feed water heater tube.

- Cr release
  - Pre-filming reduced 25% of Cr release

- Applied to Higashidori BWR

Autoclave test; 215 deg.C
Experience of Japanese BWR

- Feed water heater tube in Higashi-dori BWR,
  - Jun-ichi Satoh, Proceedings of Thermal and nuclear power engineering society, p72-p73 October 23 2008, Sendai Japan
- Pre-filming technique contributes reduction of dose rate in the early stage of operation

Radioactivity, Bq/cm3

[Graph showing radioactivity levels over time with markers for Onagawa and Higashidori]
Conclusion

• Extra-low Co content TP304 tube was prepared and was pre-filmed to study the metallic ion release.

(1) The extra-low Co content less than 0.02% was achieved using by pure hot metal without large cost impact. This was effective for reducing Co release from the stainless steels both in BWR and PWR.

(2) Pre-filming on TP304 was effective for Cr and Co ion release from the feed water heater tubes to high temperature water. This was successfully applied for Higashi-dori BWR plant, and contributed to reduce the dose rate and to be No.1 plant in whole BWR
Future work

• Challenge to reduction of Ni release from steam generator tube for PWR.
  – Pre-filming technique using by oxygen potential control

Thank you for your attention!
Co release into coolant
Outline

• Background
• Objectives of this study
• Experimental procedure
• Result - fundamental study in laboratory test
• Result – application