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

Sumitomo Metal Industries, Ltd.

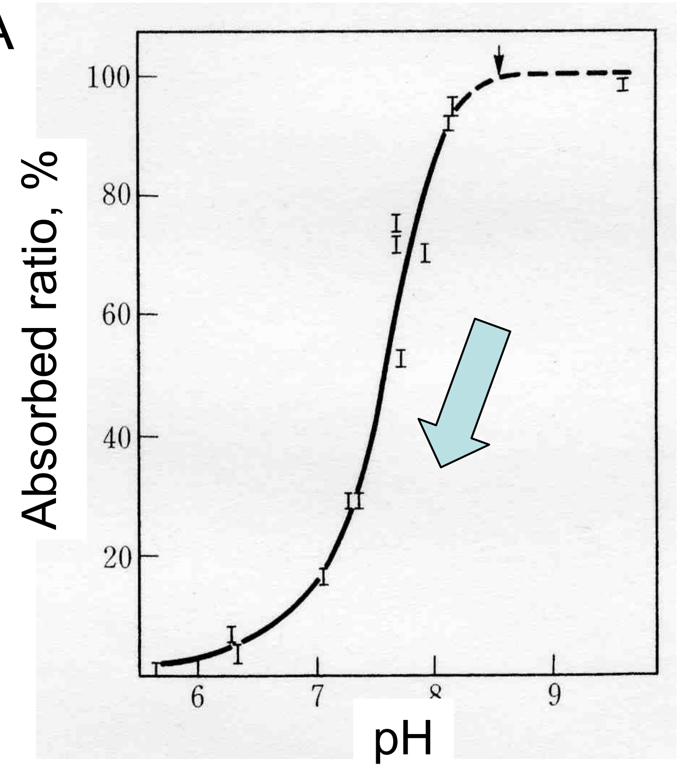
Hiroyuki ANADA

Kiyoko TAKEDA

Tetsuo Yokoyama

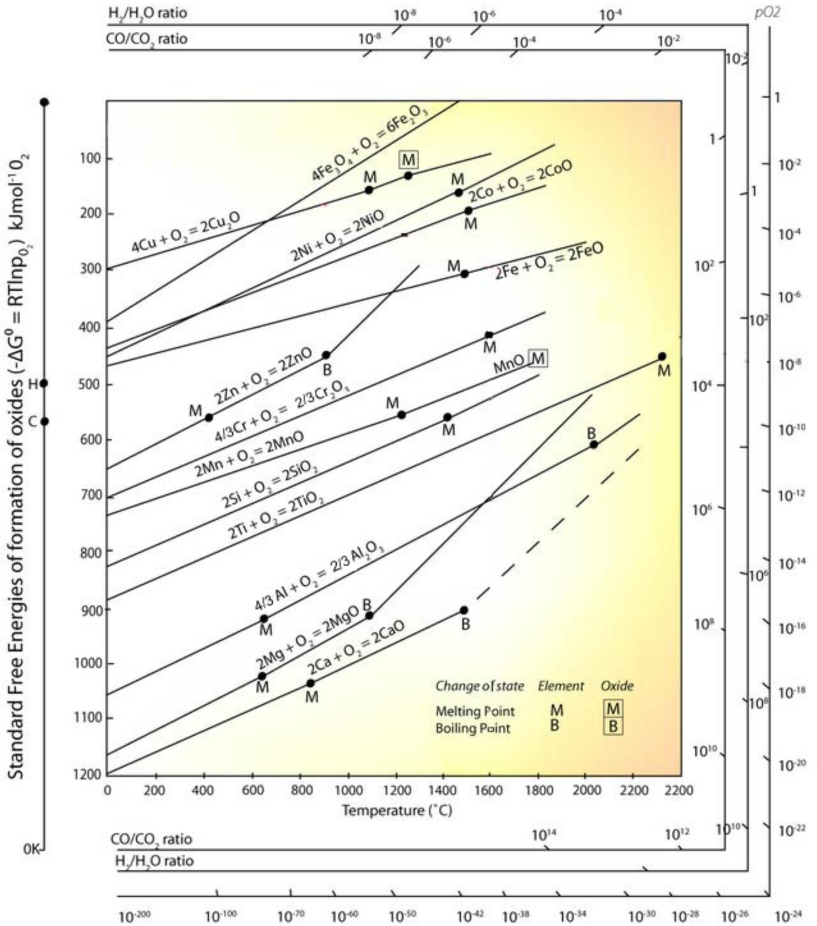
Background

- 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 H_2 with slight amount of O_2 content controlled by dew point
    - Dew point; -10 to -50 deg.C in H_2
  - Application to feed water heater tube for BWR
    - Pre-filming applied to the actual manufacturing process

Melting

Cold draw
15.9 mm dia

Pre-filming; Solution treatment >1000degC
H_2 environment adding H_2O
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.

Result -Co content-

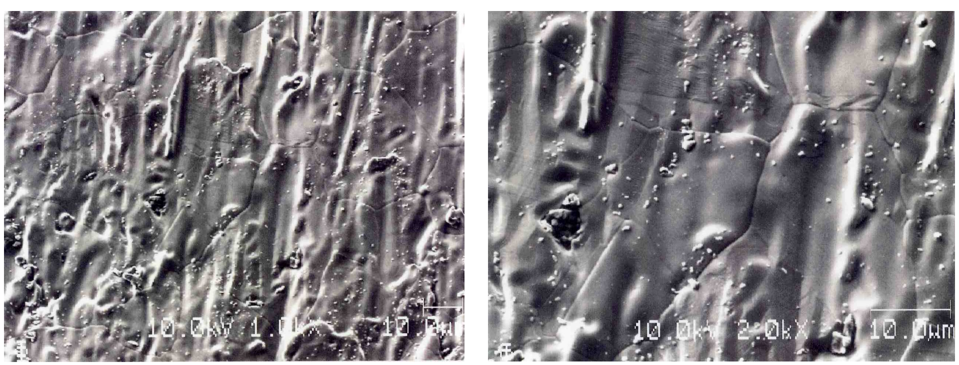
- Extra-low Co content was achieved by controlling raw material without large cost impact
- Japanese experience of application in LWR
  - Feed water heater tube for Some Japanese BWRs

	This study	Conventional method
Melting	-Small amount of selected scraps -Hot metal, pure Fe from blast furnace	Selected pure scraps Large cost impact
Facility	-Combination of blast furnace and electric furnace -Suitable mixing, small cost impact	Electric furnace
Co, %	Less than 0.02%	0.05%

Pre-filming oxide in the lab. test

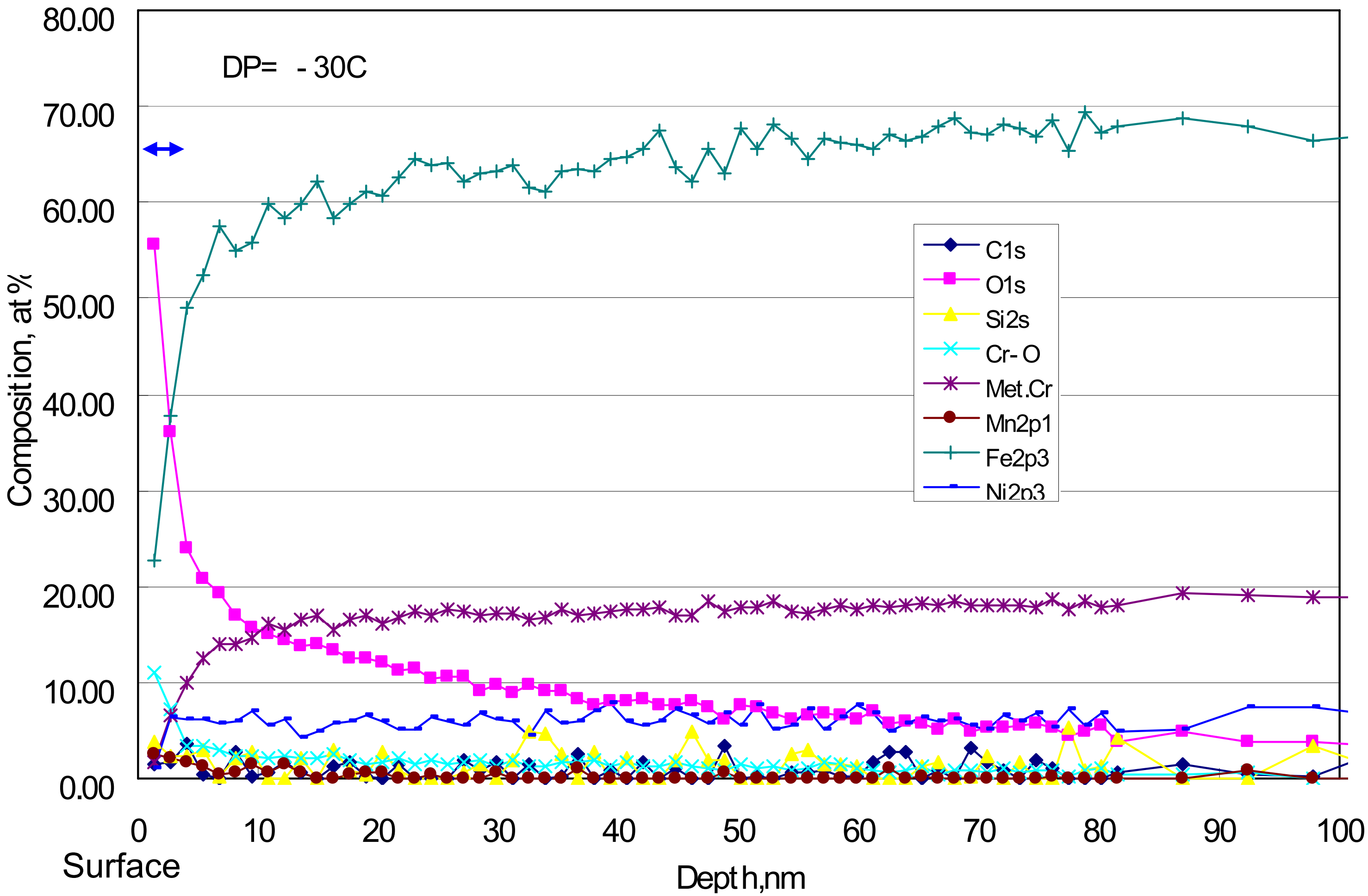
- Thin oxide formed by heat treatment under controlled dew point in H_2

DP -10 -20 -25 -30 -40 -50



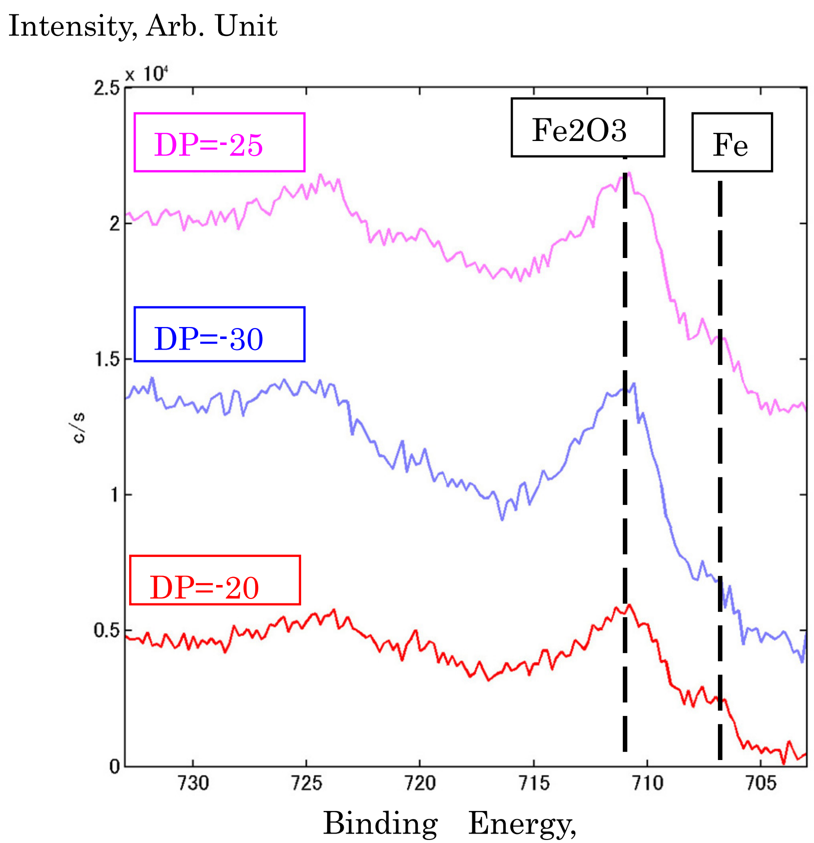
SEM images
Surface pre-filmed at -25degC

Depth profile of the pre-filming oxide



Structure of the pre-filming oxide

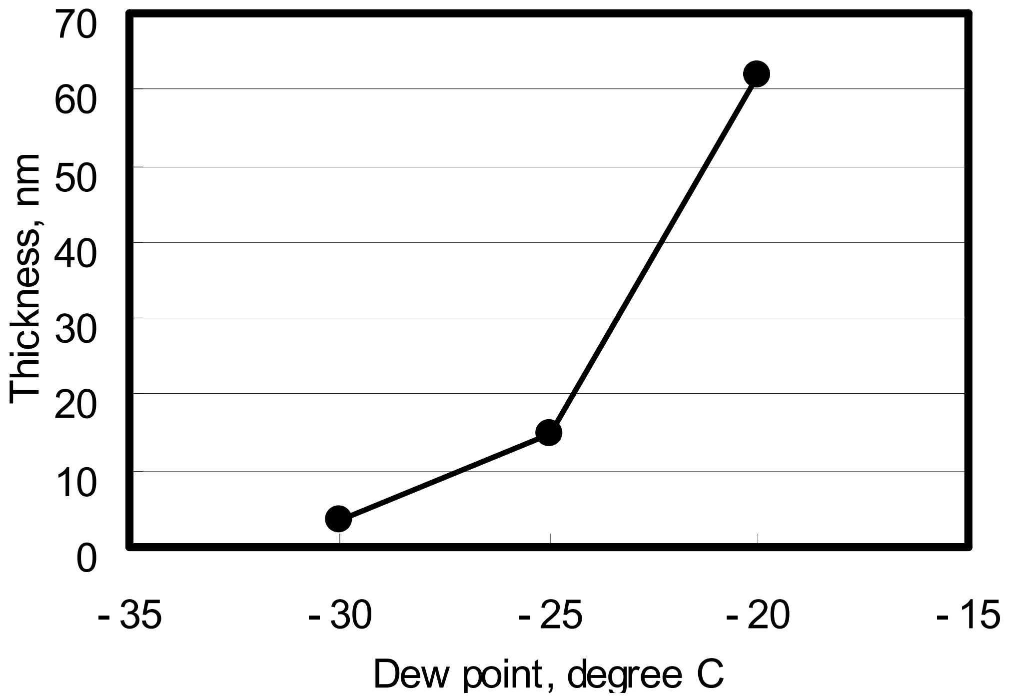
- Cr-Mn mixed oxide layer formed adjacent to the matrix.
- Fe_2O_3 or Fe_3O_4 layer formed at the surface of the oxide



Fe_2O_3 Cr-Mn oxide(mainly) (FeO and Fe, Ni)
TP304 matrix

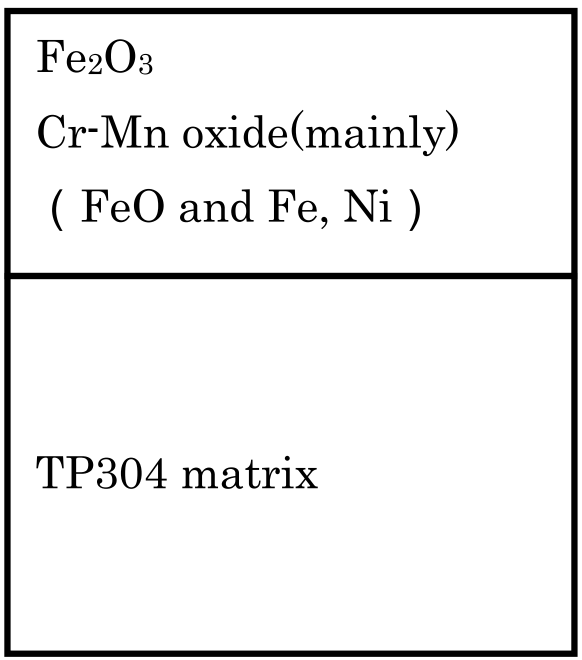
Thickness of pre-filming

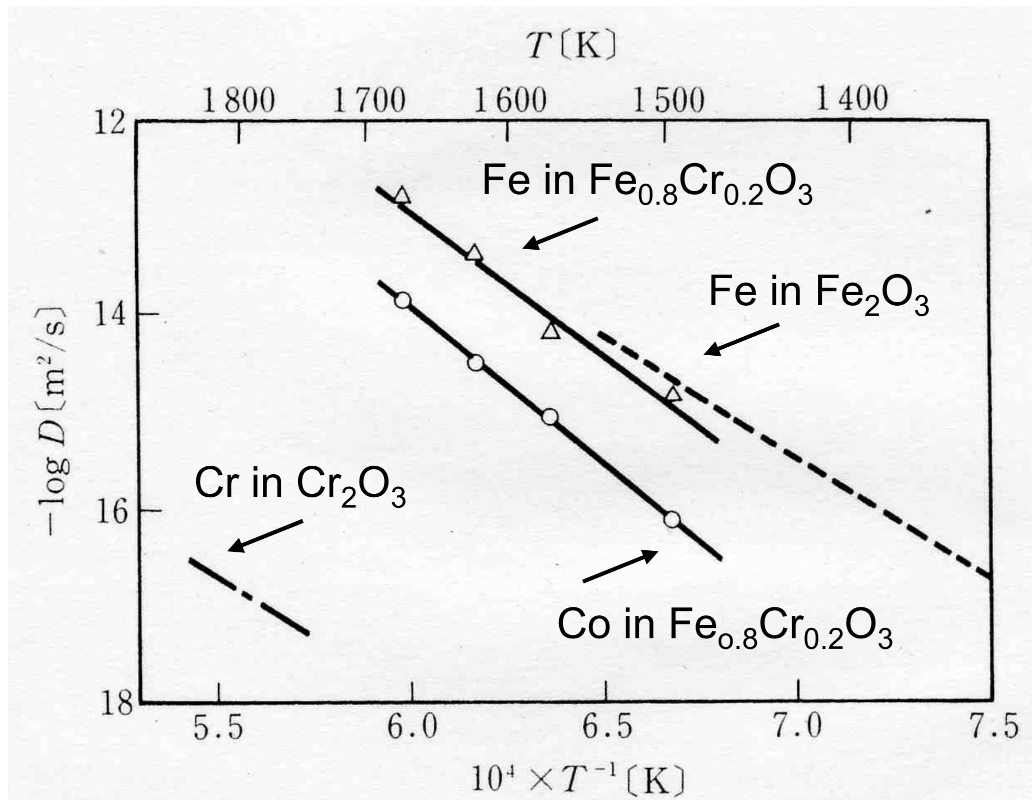
- Thickness of the pre-filming increase with increasing DP.
- Suitable pre-film thickness for will be selected easily.
- This might contribute to the effectiveness of the barrier layer



Diffusion of Co in oxide

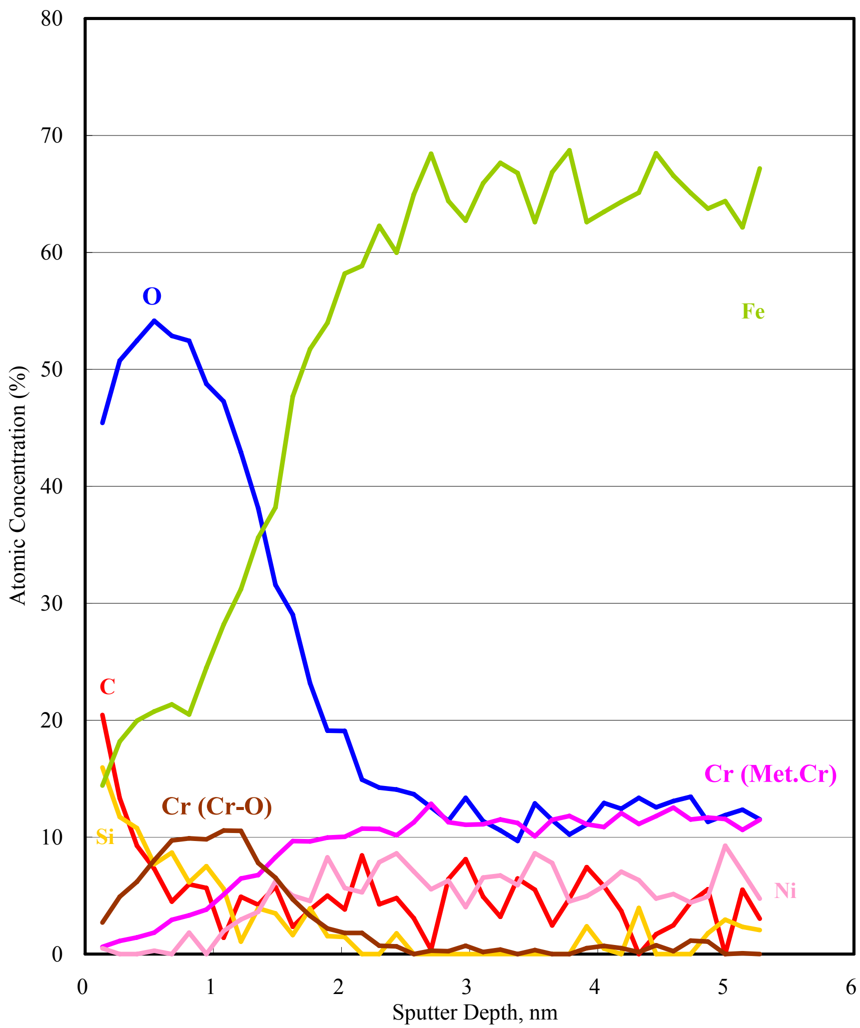
- Diffusion coefficient of Co decrease with increasing Cr content in oxide.
- This suggests that Cr rich layer adjacent to the matrix acts as a protective film.





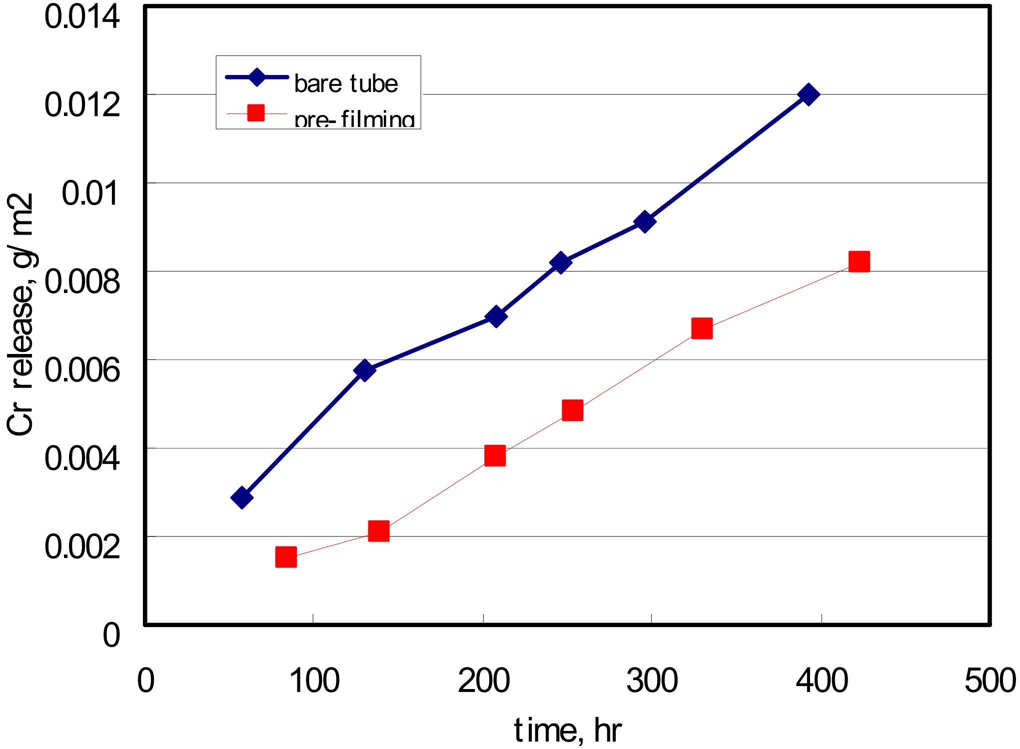
Application of pre-filming for feed water heater tube

- TP304L
- Pre-filming
  - In 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

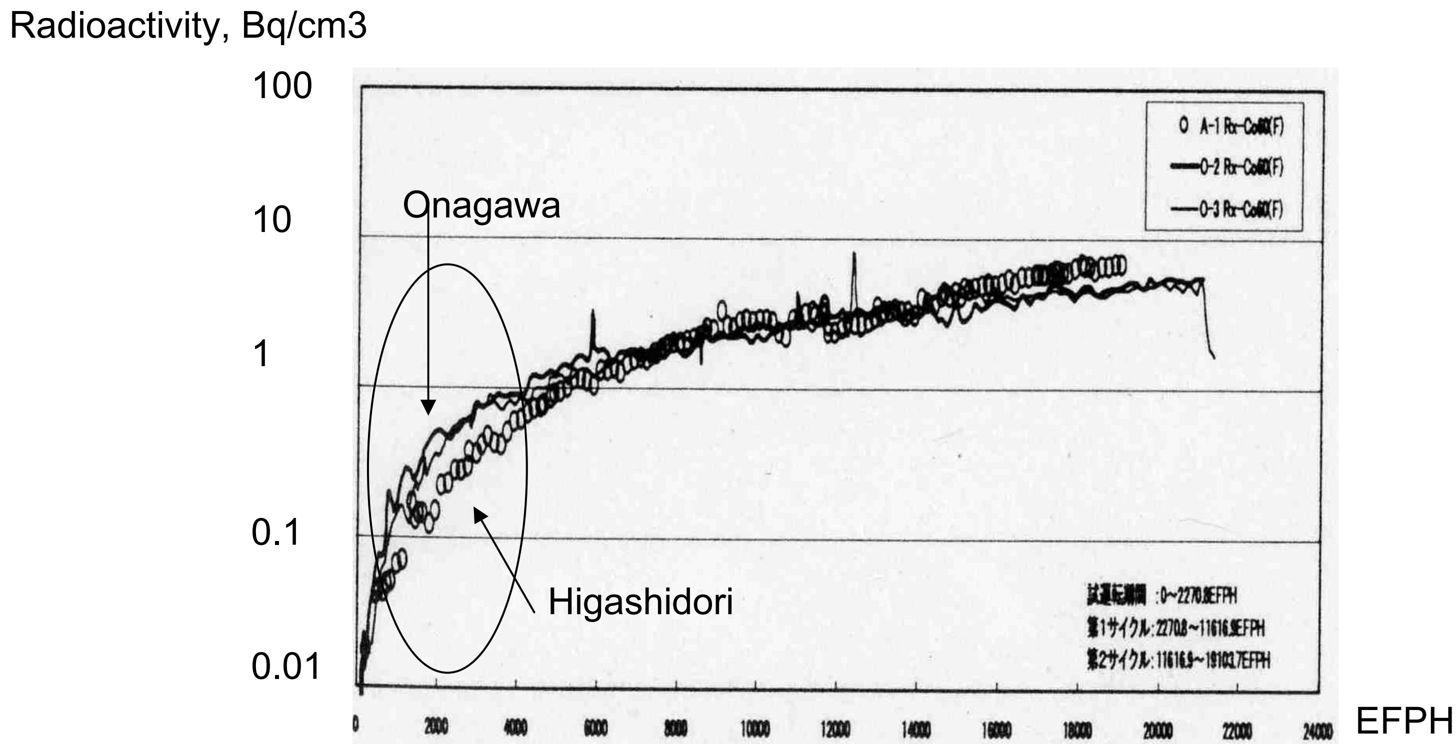
- Pre-filming
  - actual feed water heater tube.
- Cr release
  - Pre-filming reduced 25% of Cr release
- Applied to Higashi-dori BWR



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



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.

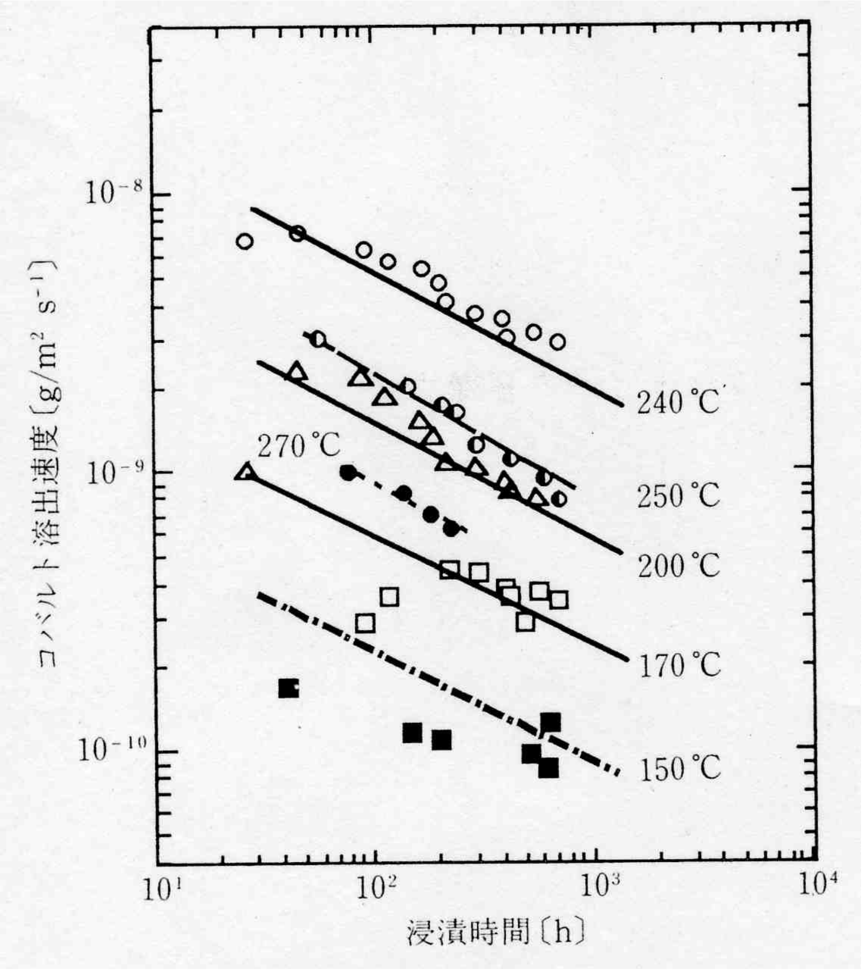
(2) Pre-filming on TP304 was effective for Cr and Co ion release from the feed water heater tubes to high temperature water. This was successfully applied for Higashi-dori BWR plant, and contributed to reduce the dose rate and to be No.1 plant in whole BWR

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