Cr and Co release reduction from stainless steels in PWR and BWR

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Background

Influence of metallic ion release from stainless steels on the dose rate

- Co release
  - Co content in stainless steels from contamination in raw material
  - Co release to coolant
  - Co raise the dose rate in coolant
  - ^{60}Co has long half-life, 5.7 years

EPRI; Restricted less than 0.05%

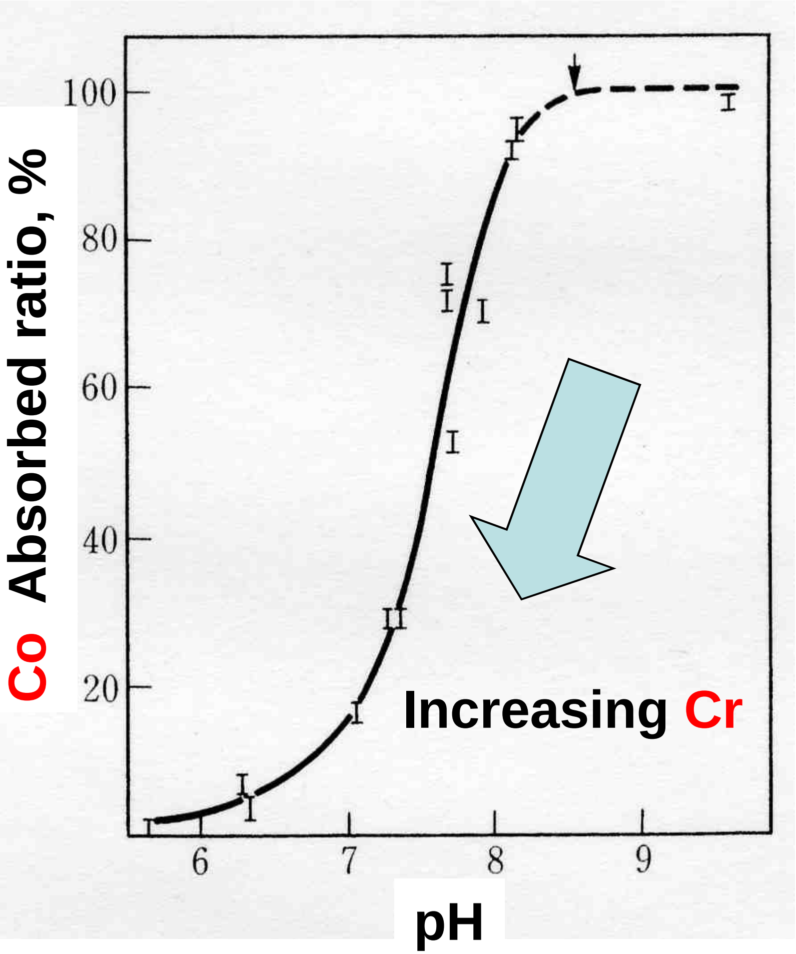
Background

・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



Conventional Technologies

1. Reduction of Co release

- Pure raw material selection; Scraps

↓

- Min. 0.05 – 0.20%
- High cost

2. Reduction of Cr release

- No commercial productions for stainless steels

New Method of Co Release Reduction

1. Reduction of Co release

Pure raw material selection;

- Hot metal; Pure Fe
- A little selected scraps

↓

- Less than 0.02%
- Low cost

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New Method of Cr Release Reduction

2. Reduction of Cr release

Pre-filming technique

Cr oxide film by control oxygen content during a heat treatment

Protective Cr oxide film for Cr release into coolant

New Method of Cr Release Reduction

2. Reduction of Cr release

- Control of oxygen content during heat treatment in manufacturing process

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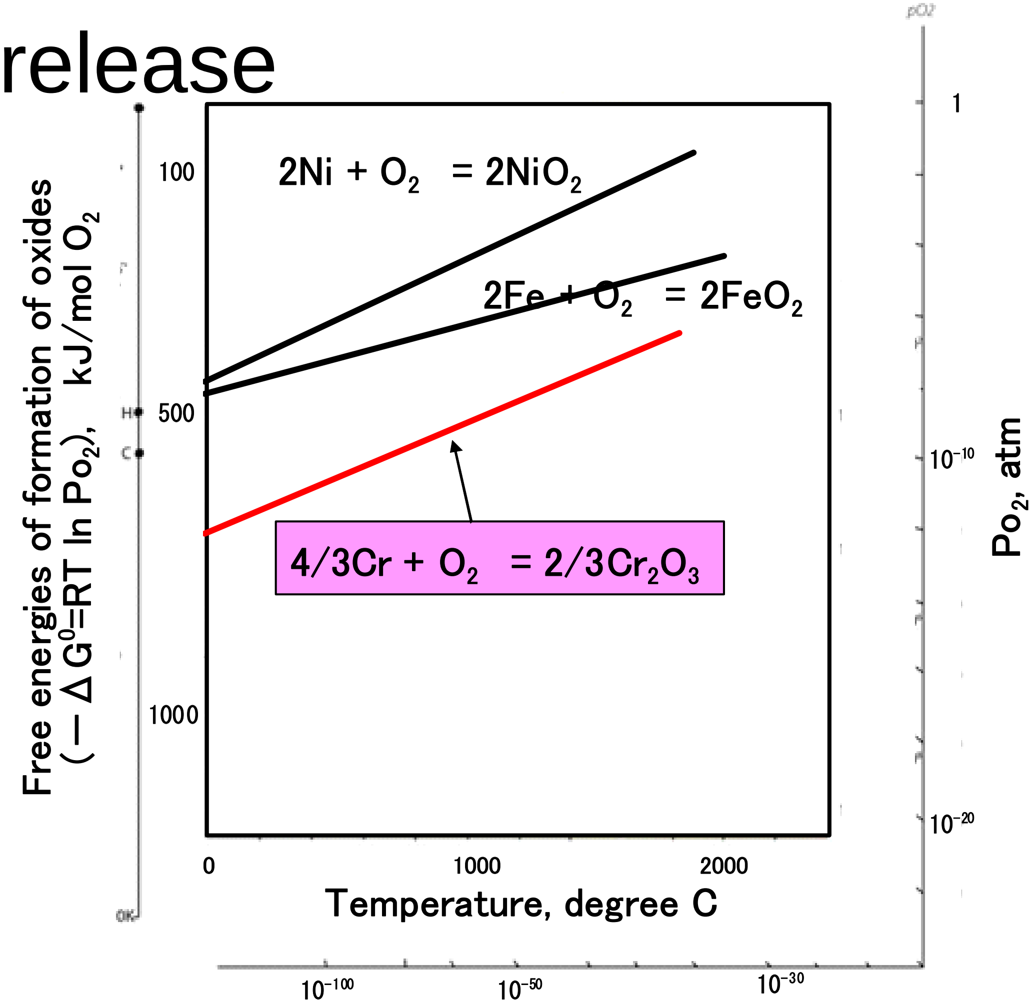
- Selective oxidation of Cr in stainless steel



Experimental Procedure -Material-

- Material

  TP304L; Raw material selection, hot metal in addition to scraps

- Pre-filming on inner surface of the tube, 15.9 mm dia.

  1. Laboratory test
     - Heat treatment in H_2 with slight amount of O_2 content controlled by dew point; -10 to -50 deg. C in H_2

  2. Application to feed water heater tube for BWR

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

1. Color and Oxide morphology
   - Naked eyes and SEM

2. Oxide structure identified by XPS
   - Depth profile of the chemistries by Ar sputtering
   - Chemical state analysis

Experimental Procedure

- 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 hr.

– Cr and Co content in the test water was analyzed.

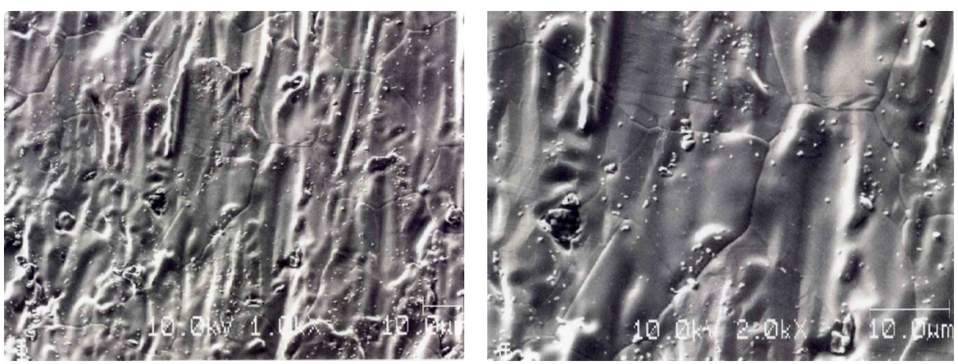
Result -Co content-

	New method	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%

Result - Pre-filming oxide in the lab. test

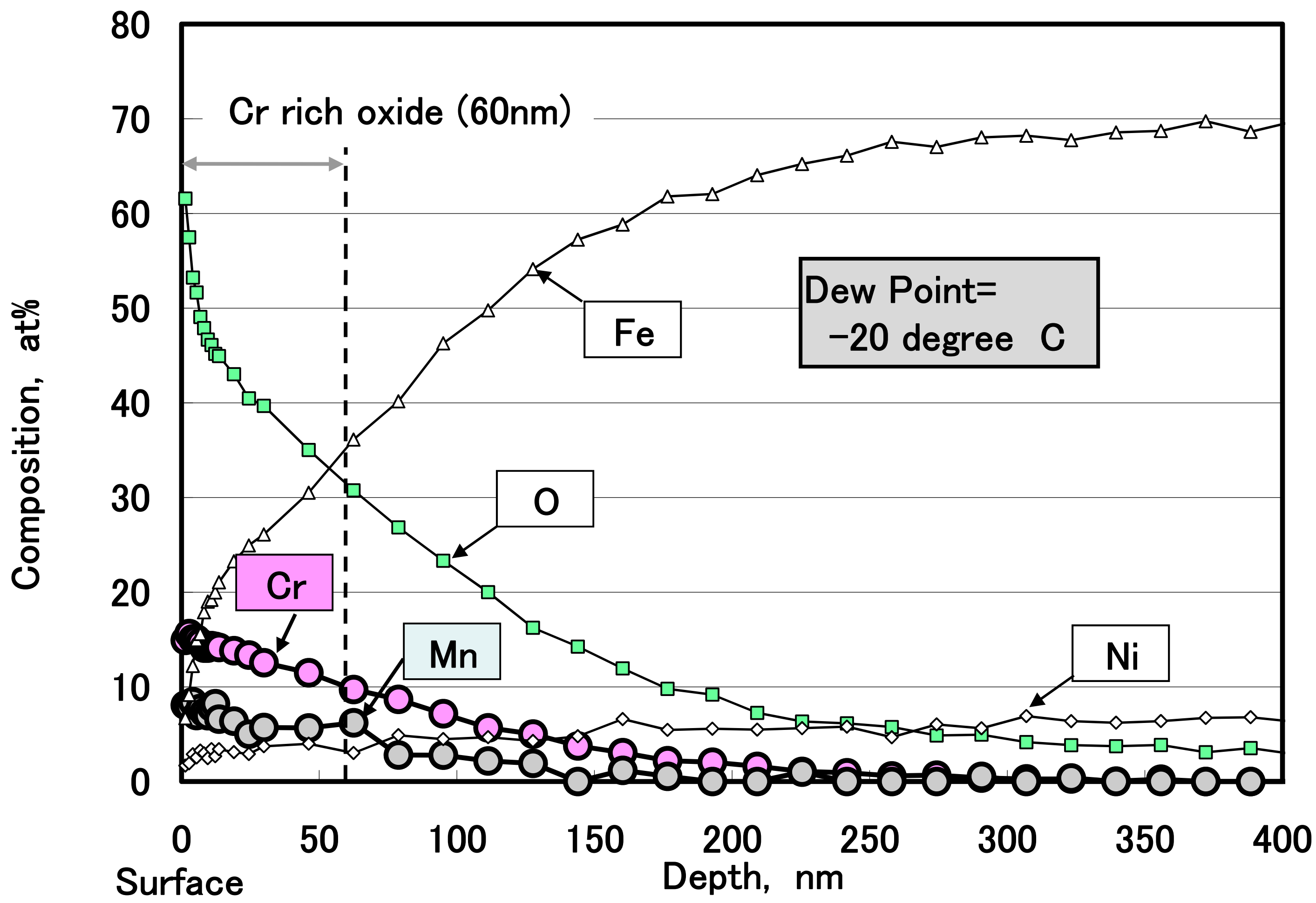
- Thin oxide formed by heat treatment under controlled dew point in H_2

DP, O_2 ; Low ⇒ High



SEM images
Surface pre-filmed at -25deg. C

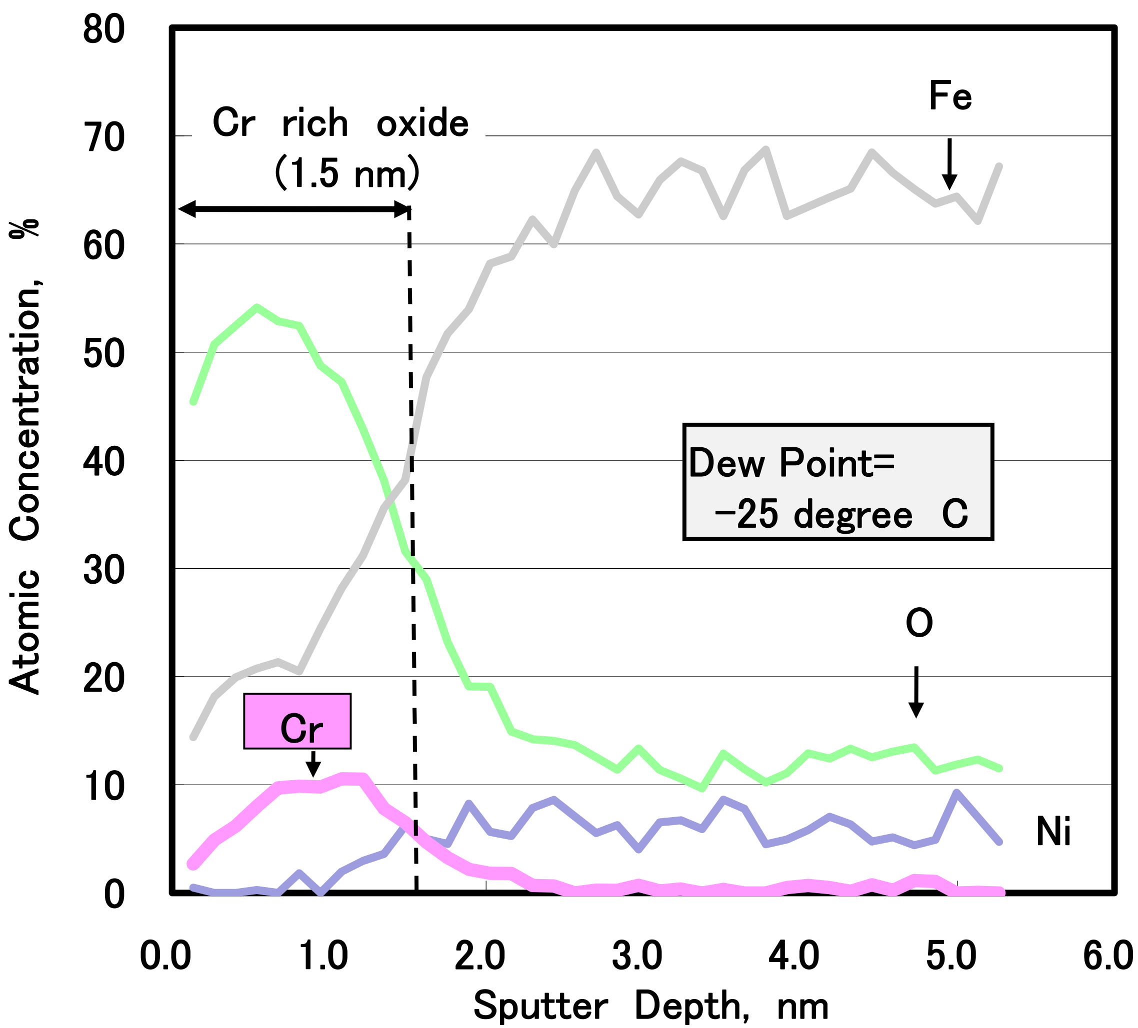
Result -Depth profile of the pre-filming oxide



Application of pre-filming for feed water heater tube

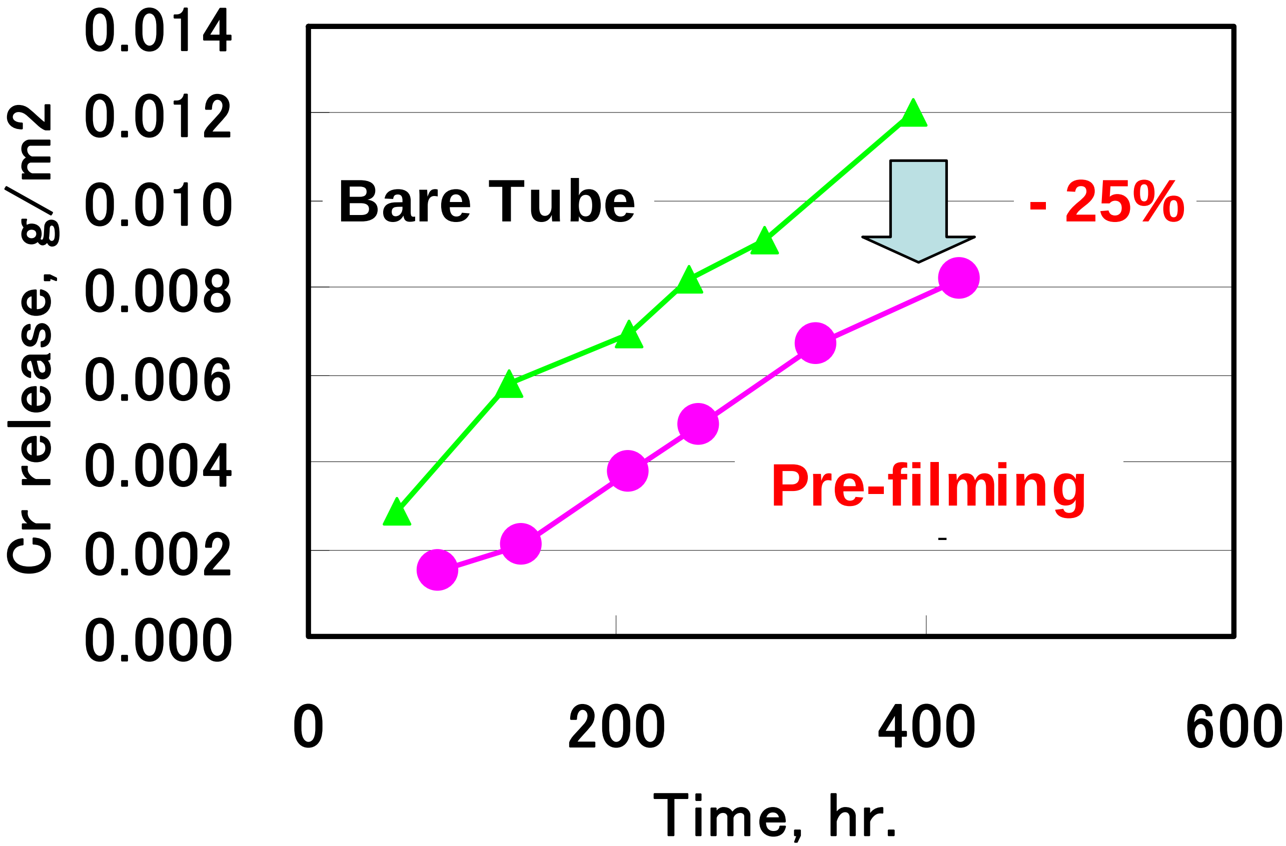
- Specification; TP304L
- 15.9mm dia.
- Pre-filming condition
  - Atmosphere ; In H_2, DP= - 25deg.C
  - Temperature; 1060deg.C

Result - Application of pre-filming



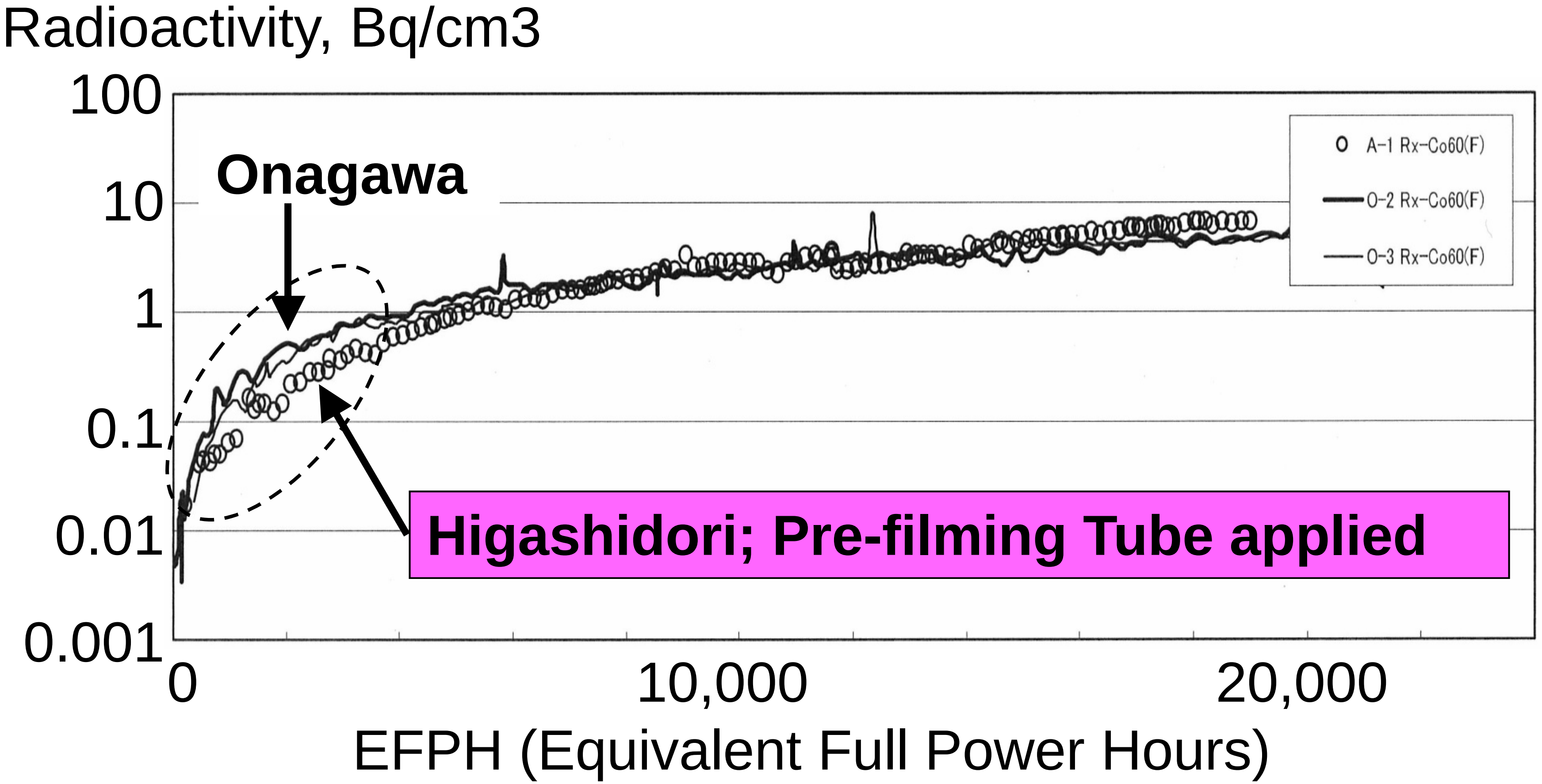
Result - Cr release from the tube

- Pre-filming reduced 25% of Cr release



Autoclave test;
215deg.C

Result - Experience of Japanese BWR



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

Conclusion

- New Method of Co & Cr release reduction from stainless steel tubes to coolant :

(1) reduces Co content in stainless steels less than 0.02% without large cost impact.

(2) reduces 25% of Cr release from stainless steels tubes

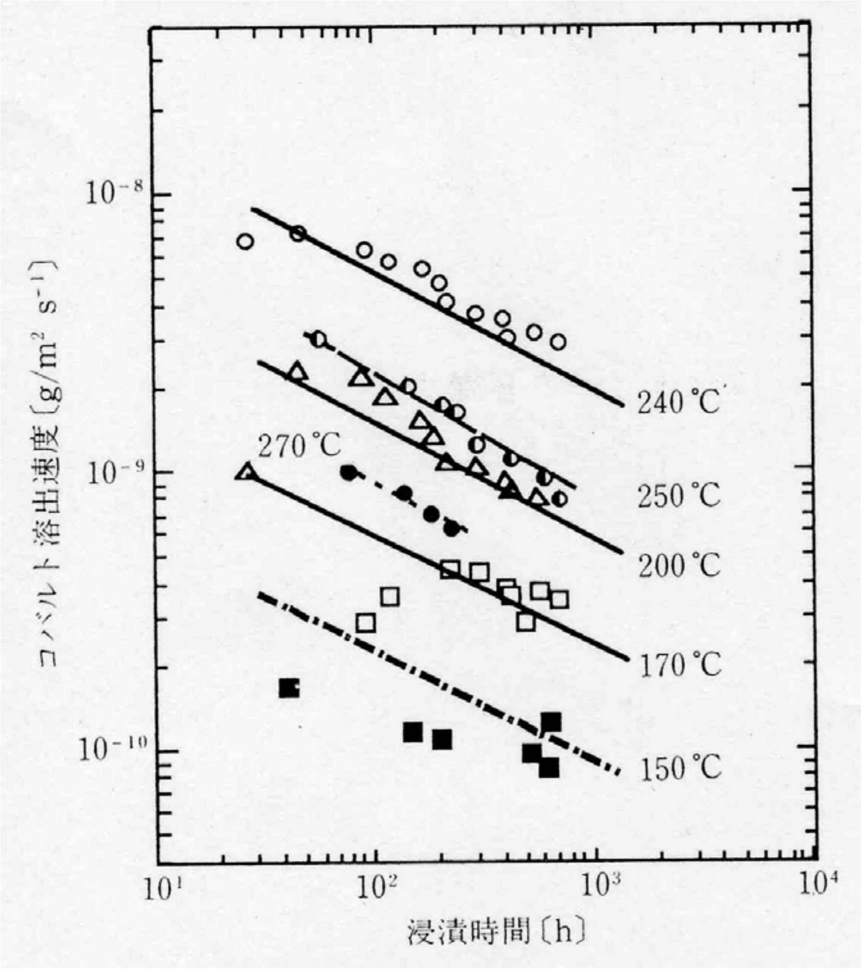
(3) is applied for Higashi-dori BWR plant, and contributed to reduce the dose rate and to be No.1 plant in whole BWR

Future work

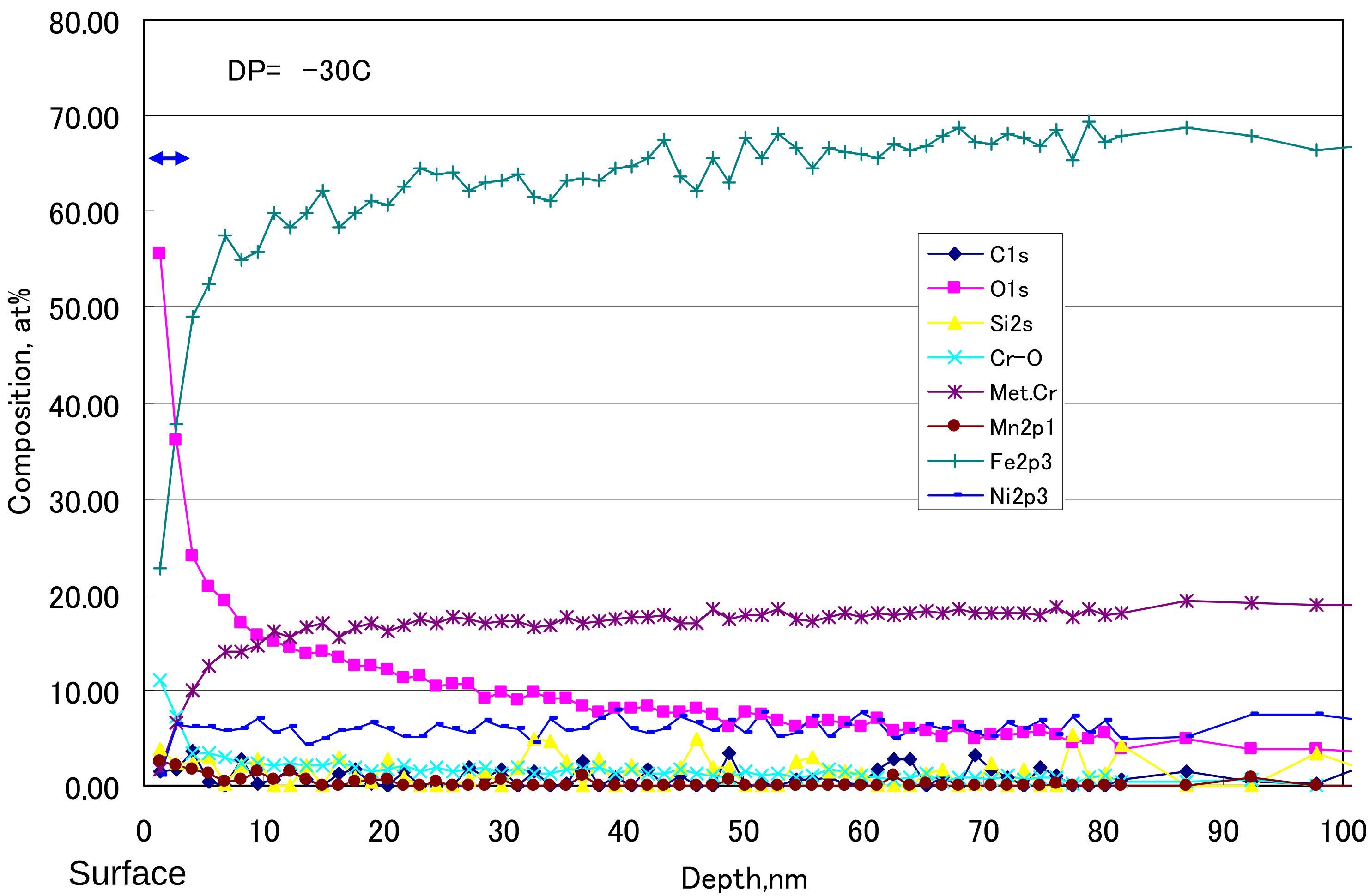
- Challenge to reduction of Ni release from steam generator tube for PWR.
  - Pre-filming technique using by oxygen potential control

Thank you for your attention!

Co release into coolant

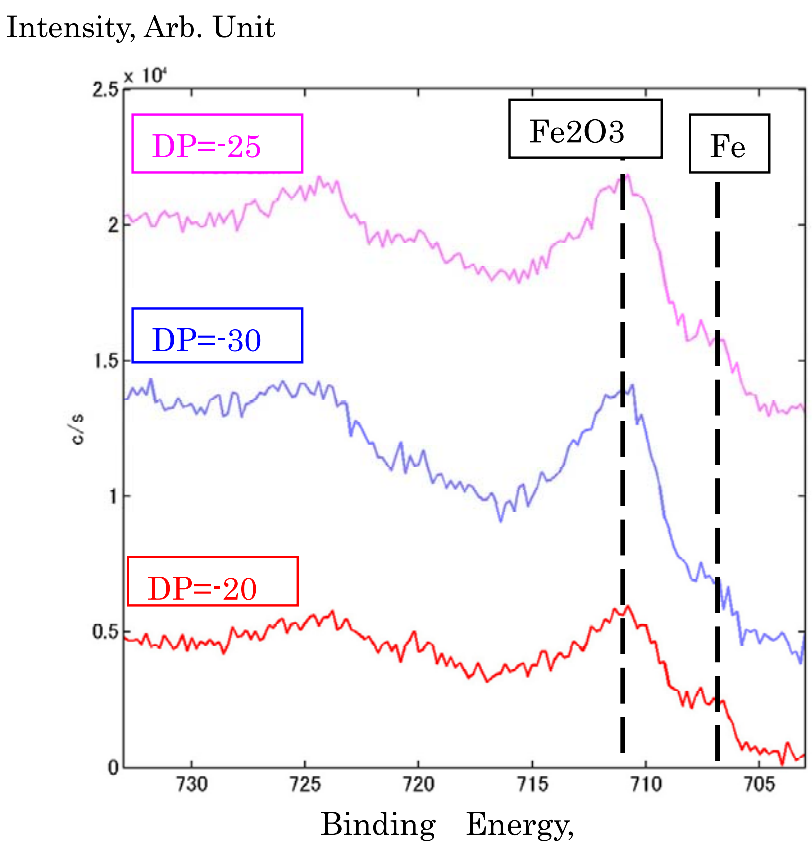


Depth profile of the pre-filming oxide



Structure of the pre-filming oxide

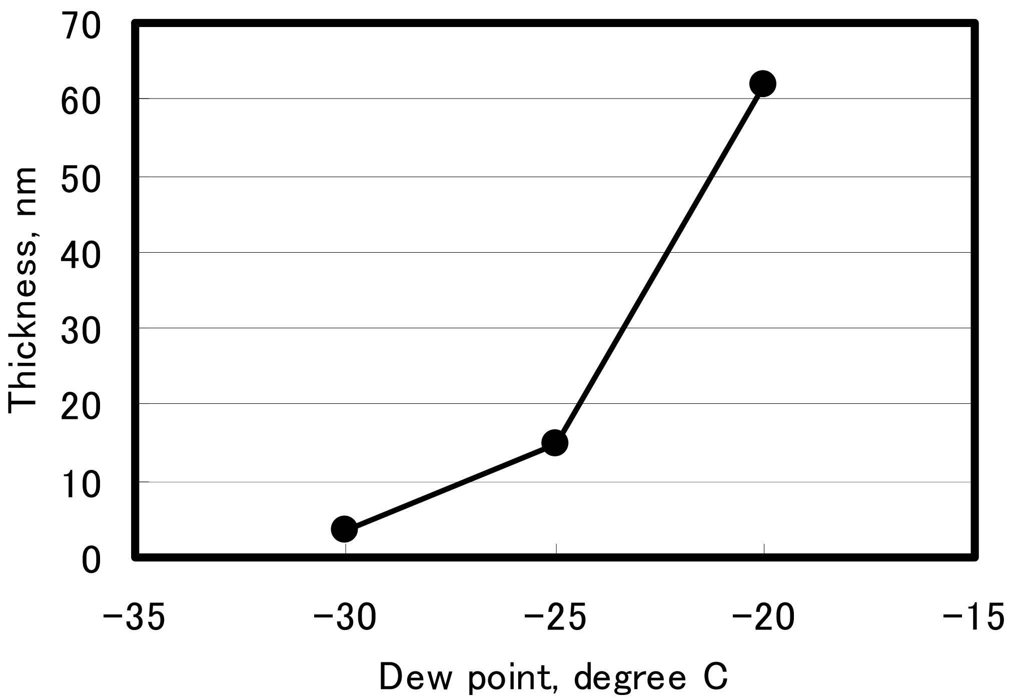
- Cr-Mn mixed oxide layer formed adjacent to the matrix.
- Fe_2O_3 or Fe_3O_4 layer formed at the surface of the oxide



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.