The Effect of Surface Treatment on Reducing Metal Release from Alloy 690 SG Tubing in PWR Primary Water

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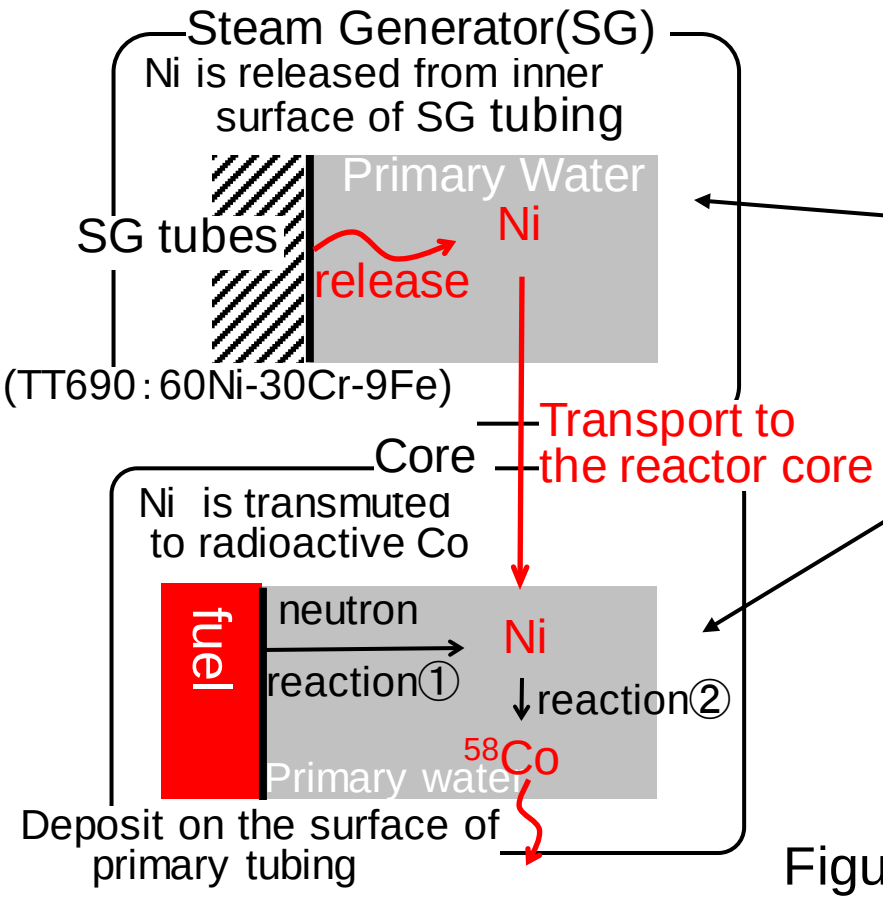
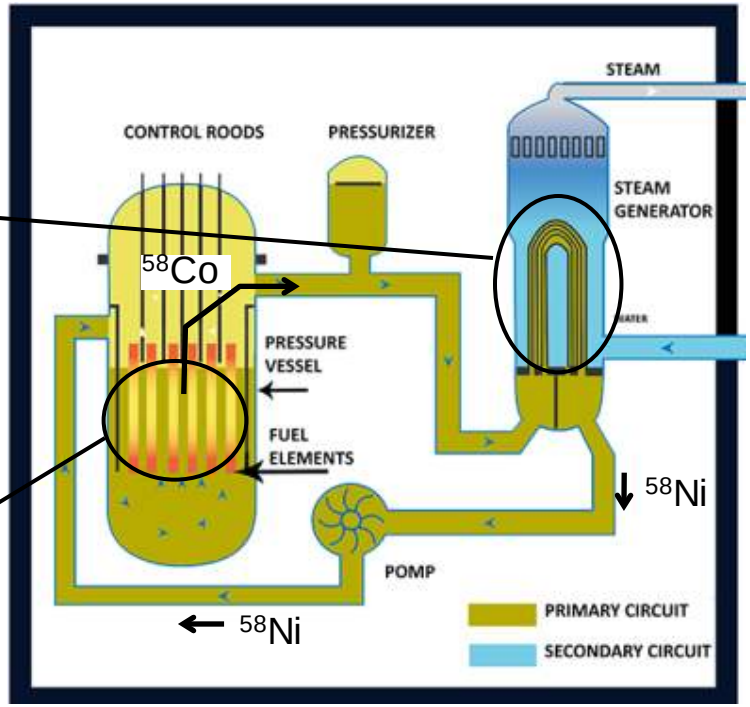
Background

- Alloy 690 is SG tubing material, which contains 60% Ni.
- Ni converts into ^{58}Co by neutron irradiation.





reaction①：$^{235}U+n \rightarrow$ fission product+n
reaction②：$^{58}Ni+n \rightarrow {}^{58}Co$（β decay, half life 71days）

Figure1　Ni release from SG tubing in PWR.

Scope

Pre-filming on the inner surface of SG tubing is expected to reduce Ni release in the early operation period.

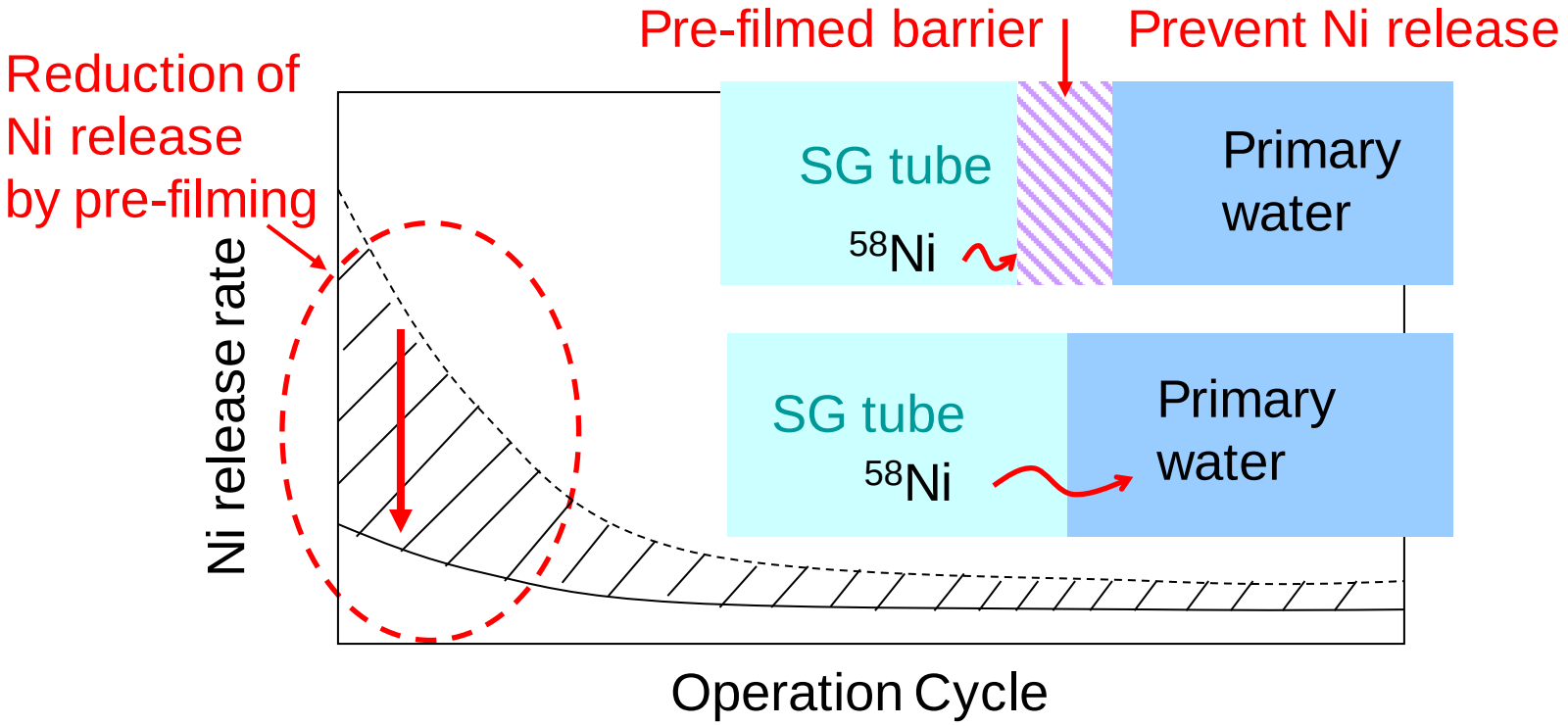


Figure 2 Image of reduction of Ni release by pre-filming.

Objective

To clarify the effect of Pre-film on Ni release and the Ni release behavior on pre-film.

To simulate an actual PWR primary water environment, the recirculation type metal release test system, which mainly focused on high flow velocity, was introduced.

Experimental procedure

- The specimens are Alloy 690 tubing having an outer diameter of 19 mm and an inner diameter of 17 mm.
- Pre-filming:

  Annealed at 1100°C in hydrogen with 2000 ppm water vapor in order to form Cr-oxide film on the surface.
- Non pre-filming (as a reference):

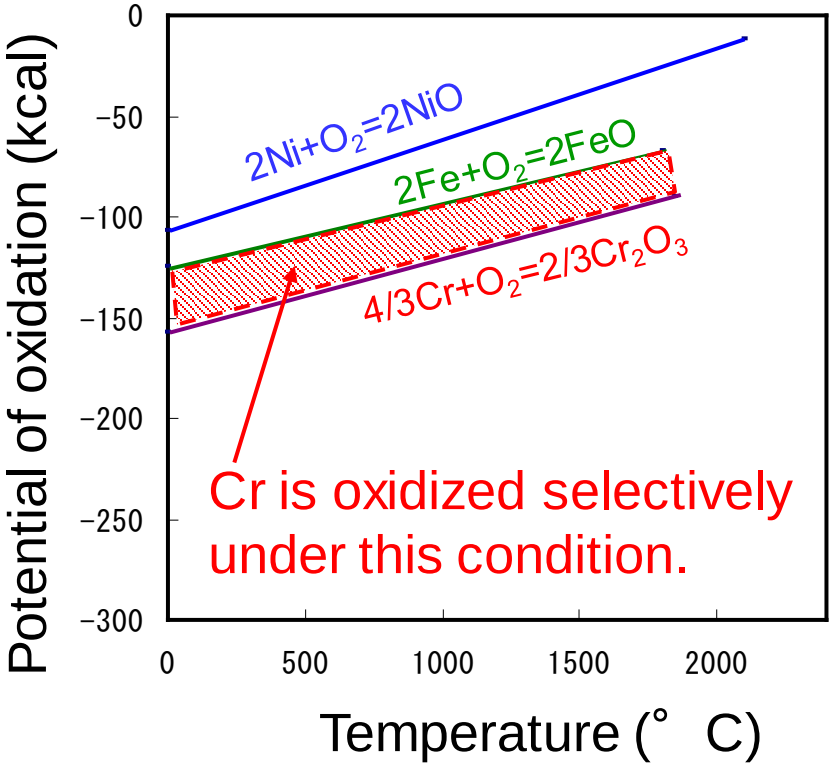
  Annealed at 1100°C in dry hydrogen.
- Both test tubing were thermally treated at 725°C in vacuum for 10 h.

Table 1 Chemical composition (mass%)

C	Si	Mn	S	Ni	Cr	Fe	Cu
0.02	0.3	0.3	<0.001	59.3	29.5	10.0	<0.1

Experimental procedure

Forming Cr-oxide film on Alloy 690



Alloy 690 contains 30% Cr.

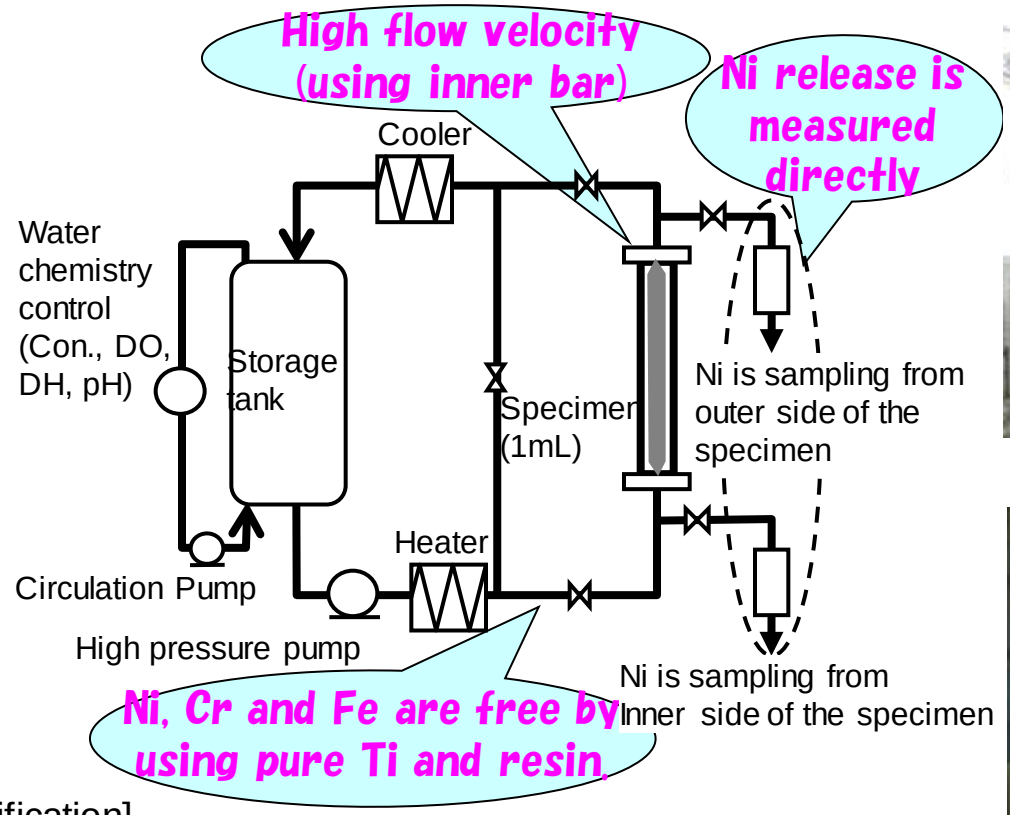
⇩

Cr-oxide can be formed on the surface of Alloy 690 by control of temperature and potential of oxidation.

Figure 3　Relationship between temperature and potential of oxidation.

Experimental procedure

Recirculation type metal release test



[Specification]
Test solutions are contacted to pure Ti or resin.
Max. temp. is 330 ° C.
Max. pressure is 17.5 MPa
Flow rate 5 L/min (calculated to 1.7m/s(Re=22000))

Figure 4 Recirculation type metal release test equipment.

Experimental procedure

Test condition of recirculation type metal release test

Table 2 Test condition of recirculation type metal release test

Test solution	1000 ppm B + 2 ppm Li
Temperature	325° C
Pressure	15.5 MPa
Dissolved oxygen	<10 ppb
Dissolved hydrogen	2.6 ppm
Flow rate	5 L/min
Flow velocity	1.7 m/s (calculated)
Test time	Pre-filmed: 620 h, Non Pre-filmed: 1129 h

The flow velocity in the actual plant is estimated* at approximately 5.5 m/s.

* “Handbook of Water Chemistry of Nuclear Reactor System”, Atomic Energy Society of Japan, (2000), p.122

Results and discussion

XRD analysis of pre-film before metal release test

- Cr_2O_3 and $MnCr_2O_4$ were detected from the pre-film.
- According to Ellingham phase diagrams, it was considered that Cr was mainly oxidized in the main elements (i.e., Ni, Cr, and Fe) of Alloy 690.

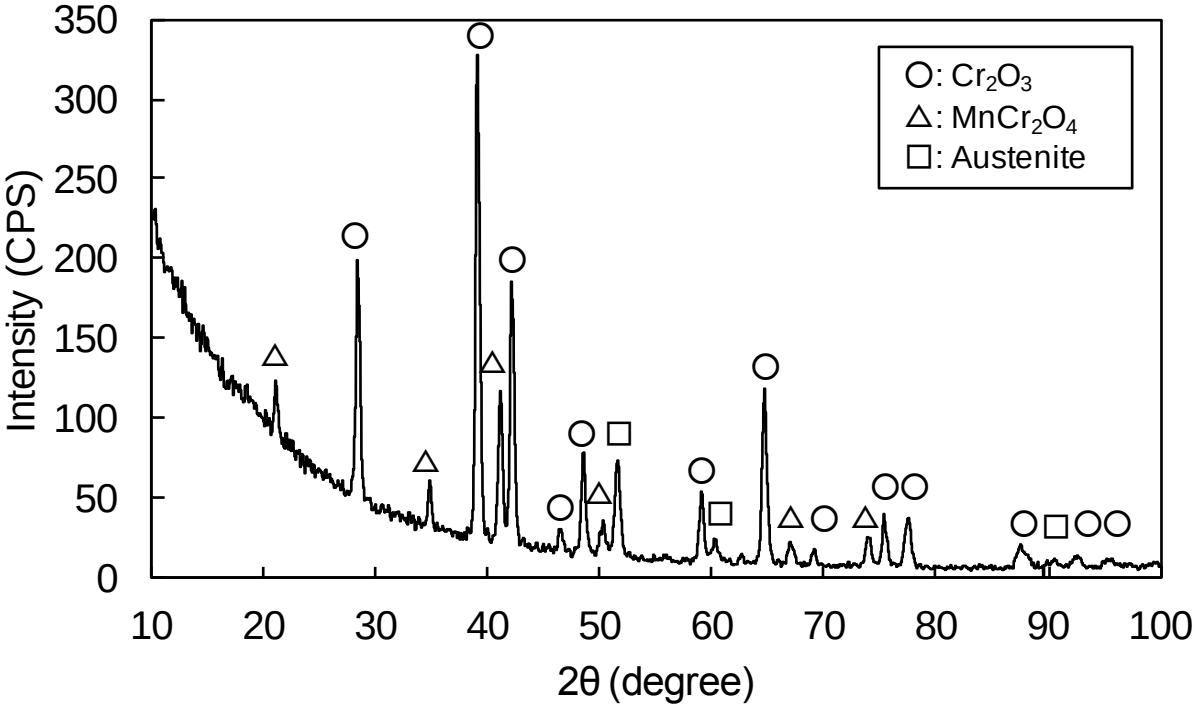


Figure 7 XRD analysis of pre-filmed Alloy 690 tubing before the metal release test.

Results and discussion

SEM observation and EDAX analysis of Pre-film

- Pre-film had uniform thickness with minute structure.
- Cr was distributed over the whole of the Pre-film.

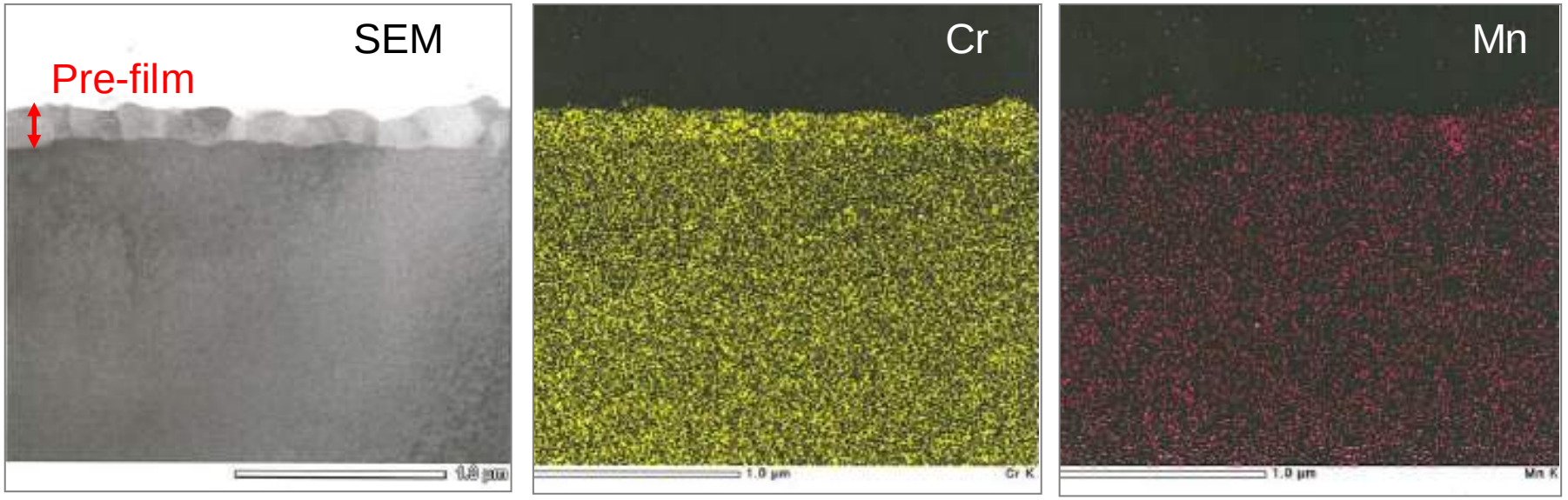


Figure SEM observation and EDAX analysis of pre-filmed Alloy 690 tubing.

Results and discussion

Ni release rates in simulated PWR primary water

- The Ni release rate of non pre-filmed Alloy 690 tubing decreased with test time like conventional studies.
- The Ni release rate of pre-filmed Alloy 690 tubing also decreased with test time promptly.
- The Ni release rate of pre-filmed Alloy 690 tubing is much lower than that of non pre-filmed Alloy 690 tubing.

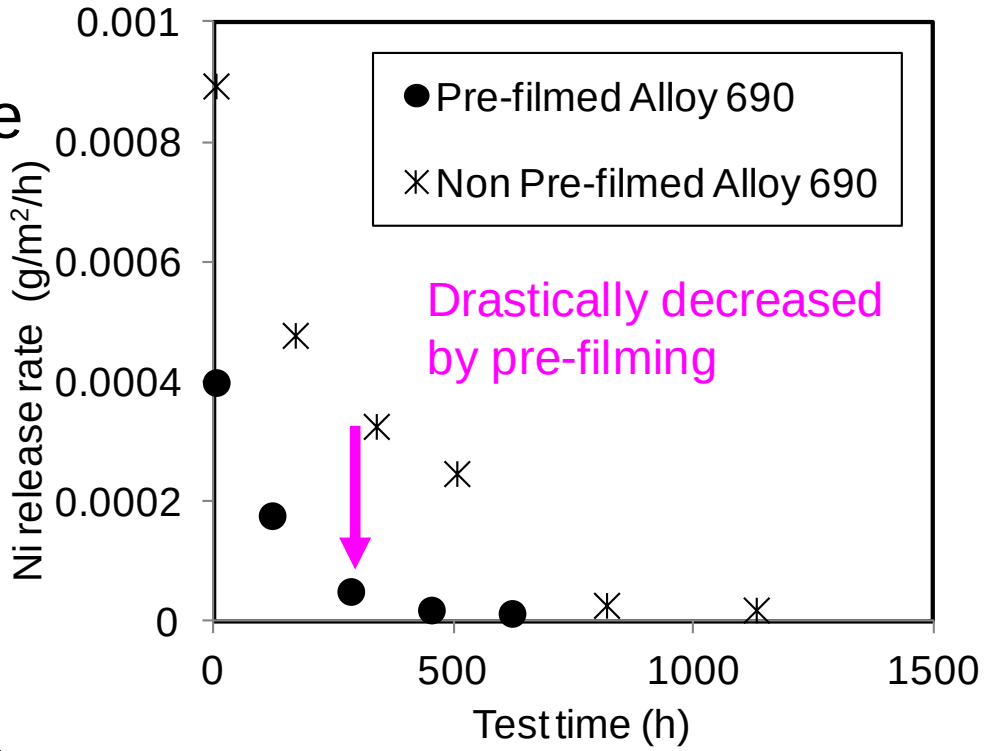
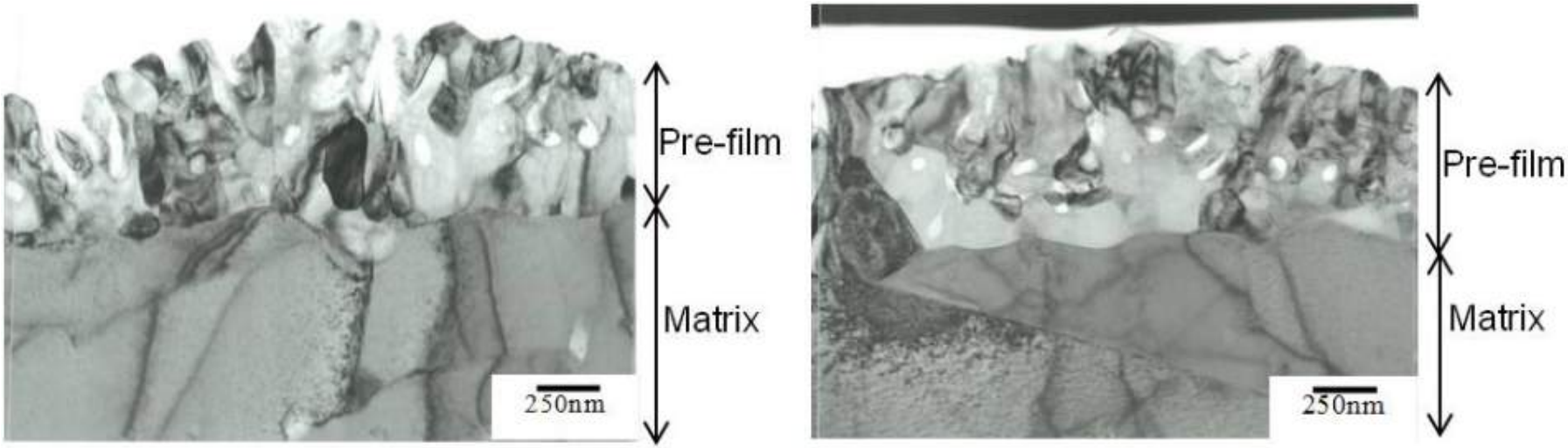


Figure 6 Ni release rates in simulated PWR primary water at 1.7 m/s.

Results and discussion

TEM observation of Pre-film before/after the test

- The pre-film on Alloy 690 was stable even at a high flow velocity of 1.7 m/s.



Before metal release test

After metal release test

Figure 9 Cross sectional TEM observation of pre-filmed Alloy 690 tubing.

Results and discussion

Ni release rates in simulated PWR primary water

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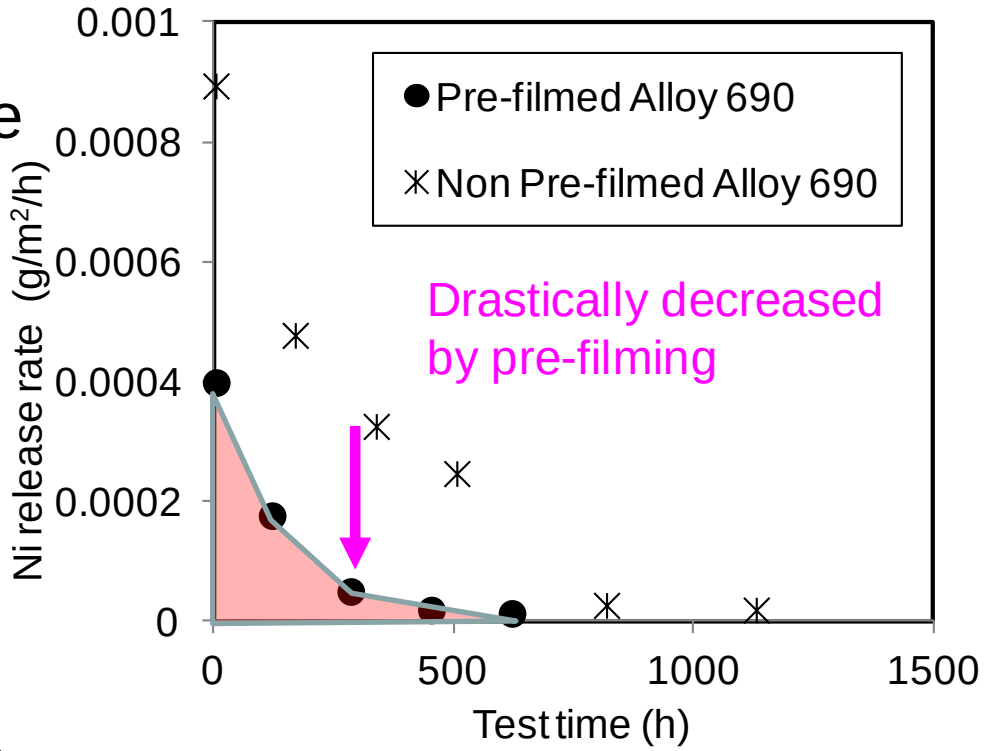
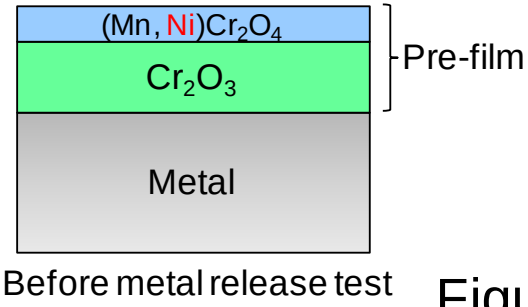


Figure 6 Ni release rates in simulated PWR primary water at 1.7 m/s.

Results and discussion

GDS analysis of Pre-film before/after the test

- The oxide film was highly Cr enriched before and after the metal release test.
- Concentrated Ni on the surface before the test considerably decreased with the decrease of Mn, in contrast to the increase of O in the pre-film.



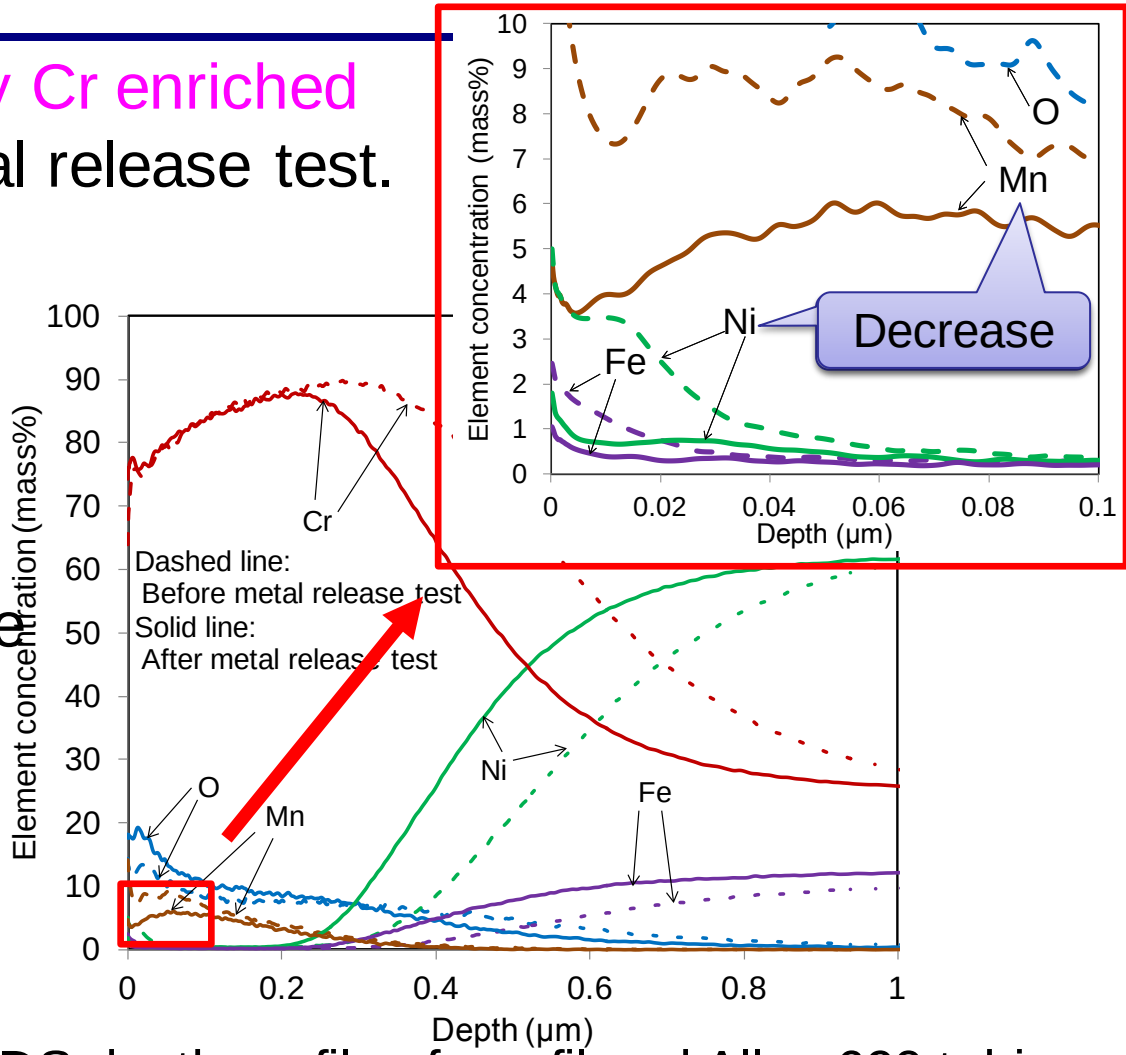


Figure 8 GDS depth profile of pre-filmed Alloy 690 tubing.

Results and discussion

Ni release behavior on pre-film

- A small amount of Ni was released from pre-filmed Alloy 690 at the beginning of the metal release test.
- The source of Ni released from pre-filmed Alloy 690 could be the surface layer of the pre-film.
- As shown in GDS depth profile, Ni and Mn decreased after the metal release test. It is assumed that Ni in $MnCr_2O_4$ is released.

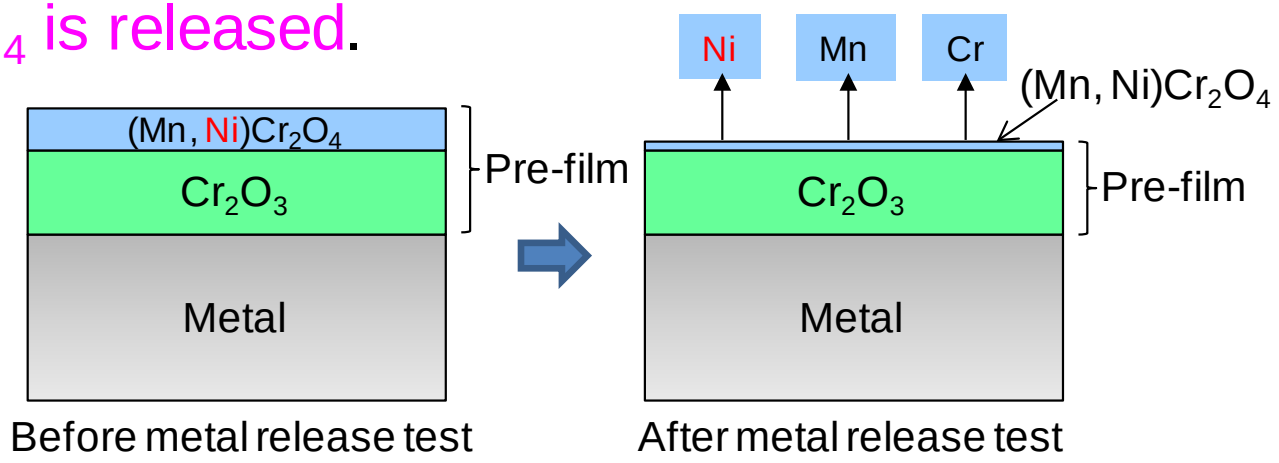


Figure 11 Schematic diagram of Ni release behavior on pre-film.

Conclusions

(1)Physical analysis showed that the Pre-film composed of mainly Cr_2O_3 layer, and the oxide layer had uniform thickness with dense structure .

(2)It was clarified that the Ni release rate of pre-filmed Alloy 690 at 1.7 m/s was much lower than that of non pre-filmed Alloy 690.

(3)However, a small amount of Ni was released from pre-filmed Alloy 690 at the beginning of the metal release test. The source of the small amount of Ni released from pre-filmed Alloy 690 could be the surface layer of the pre-film.

(4)It was also clarified that the pre-film on Alloy 690 was stable even at a high flow velocity of 1.7 m/s.

Thank you for your attention.

Physical analysis of pre-film

- X-ray diffraction (XRD; RIGAKU, RINT-2500H)
  - X-ray source: Co Kα (30 kV, 100 mA)
  - Angle of incidence: 0.3°
  - Scanning zone of 2θ: from 10° to 105°
- Glow discharge spectroscopy (GDS; HORIBA, GD-Profiler 2)
  - Analyzing area: 4 mm in diameter
  - Power capacity: 35 W
  - Pressure of Ar gas: 600 Pa
- Transmission electron microscope (TEM; RIGAKU, JEM-200CX)
  - Acceleration voltage: 200 kV