원전 1차측 환경에서 표면산화 특성이 니켈기 합금의 균열개시 저항성에 미치는 영향

(Influence of surface oxidation on the resistance to crack initiation of Ni-base alloys in PWR primary water)

2019. 10. 23

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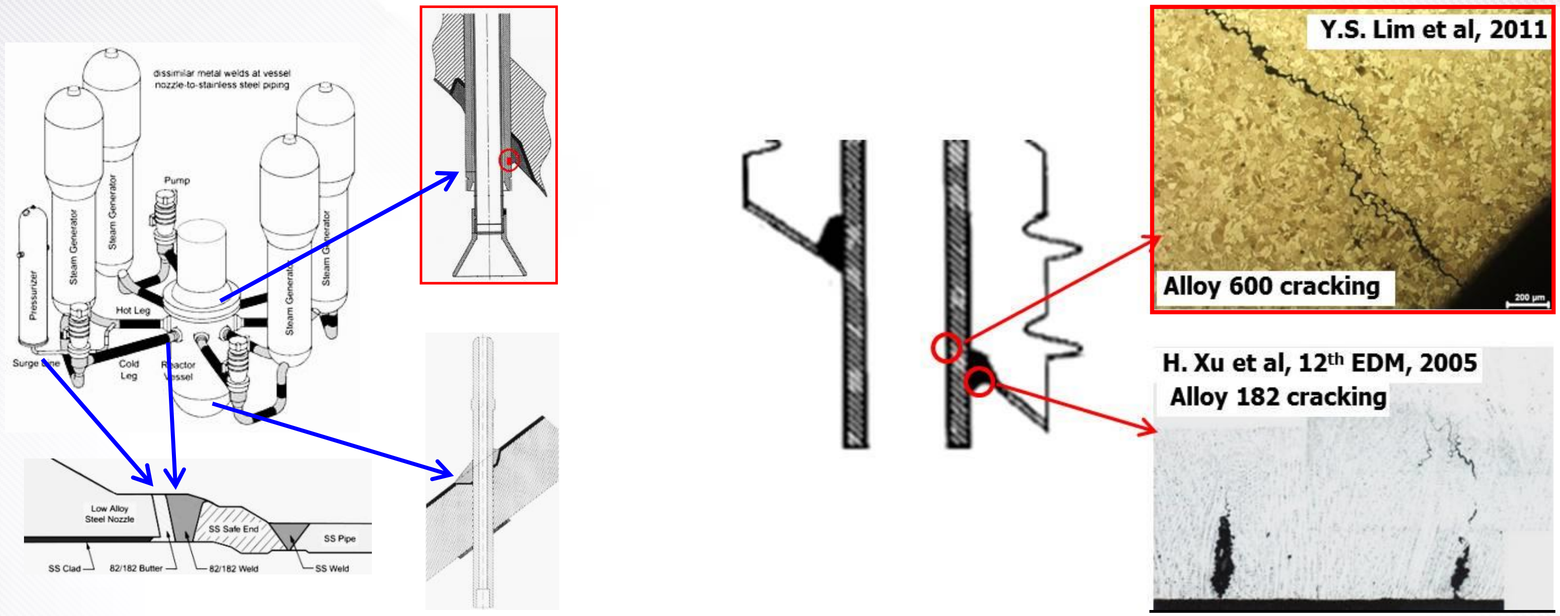
원전 1차측 환경에서 표면산화 특성이 니켈기 합금의 균열개시 저항성에 미치는 영향

CONTENTS

Results and Discussion: 1. CGR test, 2. Cracking behavior, 4. Micro-tensile test, 4. Surface oxidation test, 5. Influence of metallurgical factors on surface oxidation, 6. Influence of surface oxidation on cracking behavior

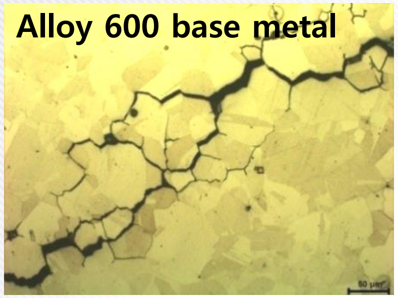
01 Cracking Issues in PWR Primary Water

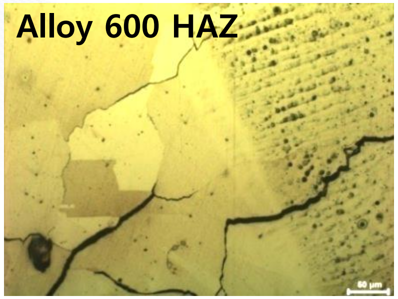


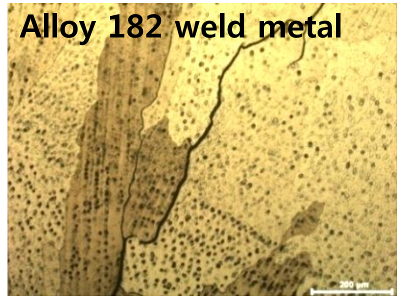
Cracking issues in PWR primary water

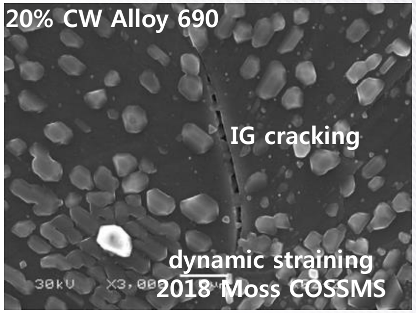
- Frequent cracking damage occurs in the RPVH penetration nozzles and SG tubes.
- PWSCC was found to be the main failure mechanism.
- Alloys 600 and Alloy 182 are very susceptible to PWSCC.
- Alloy 600: Ni-16Cr-7Fe (wt%), Alloy 690: Ni-30Cr-9Fe (wt%)
- Alloys 690 and 152 are much higher resistant to PWSCC than Alloys 600 and 182.
- The surface oxidation behavior of Alloy 690 can be quite different from that of Alloy 600 because of the different Cr concentration.

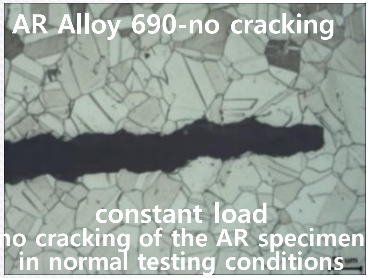
01 Cracking Properties of Ni-base alloys in PWR primary water

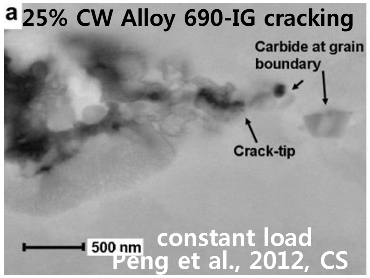


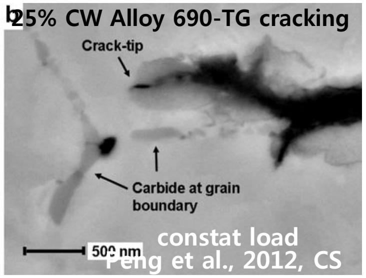


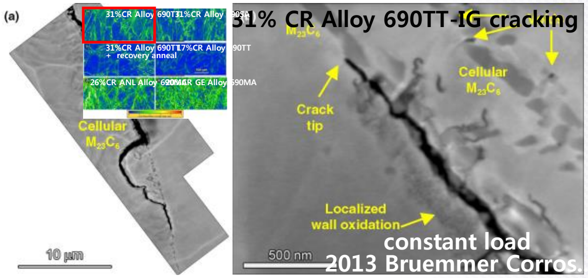


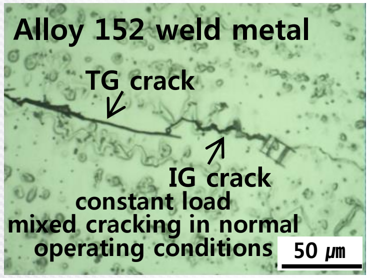


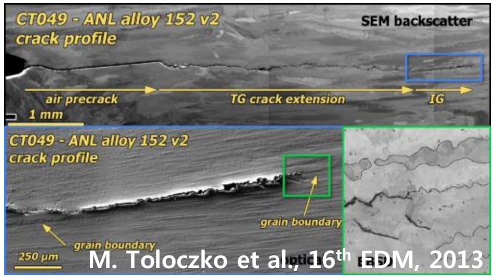








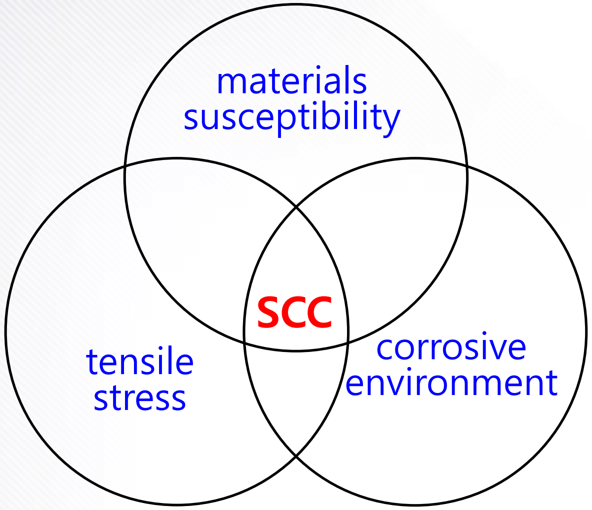




- Alloys 600, 182: mostly IG cracking,
- Alloys 690, 152: mixed (IG and TG) cracking in many cases

- The cracks in Alloys 600 and 182 propagate along the grain boundaries. However, cracks in Alloys 690 and 152 do not necessarily propagate along grain boundaries. It depends mainly on the materials used and the experimental conditions applied.

01 Proposed PWSCC Mechanisms



slip dissolution/film rupture
hydrogen enhanced localized plasticity
corrosion-enhanced plasticity
hydrogen embrittlement
internal and IO oxidation
percolation
creep rupture
bubble formation
ordering
:

susceptibility to SCC (metallurgical effects)
degree of cold work, yield strength (dislocation density, grain size), chemical composition, inter-/intra-granular Cr carbides, sensitization, surface state, etc

tensile stress
operating stress, residual stresses due to expanding or straightening, welding, etc

corrosive environment
water chemistry, pH, DO and DH concentrations, operating temperature, etc

Experimental evidence seems to suggest that one single and simple mechanism cannot explain the occurrence of SCC in its entire spectrum.

02 Objectives of This Study

❖ It is well known that,

- Alloys 690 and 152 are much higher resistant to PWSCC than Alloys 600 and 182.
- Cracking of Alloys 600 and 182 is always intergranular, however cracks in Alloys 690 and 152 show an mixed mode of intergranular and transgranular cracking.

↓

❖ Cracking is known to be closely correlated with the surface oxidation phenomena.

↓

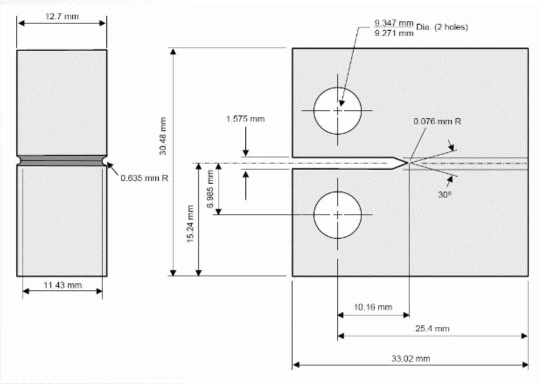
❖ The aim of this study is (1) to investigate the cracking resistance and cracking behavior by CGR test, and then (2) to understand how the surface oxidation and metallurgical factors affect the cracking properties of Ni-base alloys in PWR primary water.

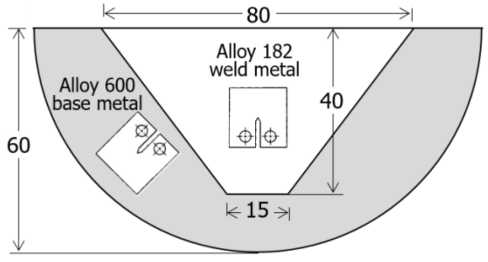
03 Preparation of CT Specimens for CGR Test

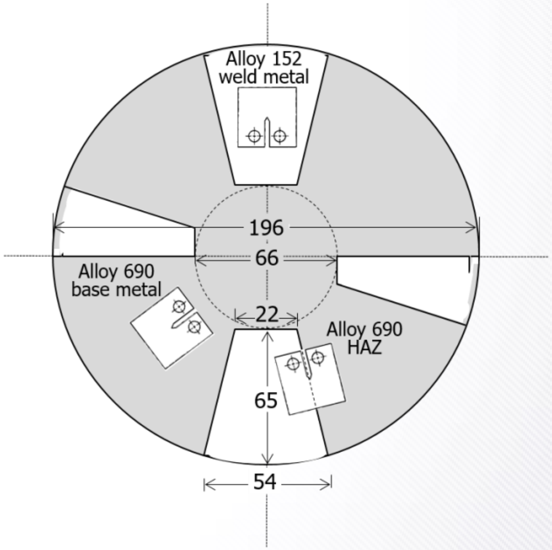
Chemical compositions of test alloys (wt%).

	Cr	C	Fe	Ni	Mn	Si	Ti	Al	S	P
Alloy 600	16.06	0.055	6.66	75.44	0.68	0.03	0.21	0.19	0.001	0.014
Alloy 690	28.66	0.014	9.39	60.60	0.29	0.44	0.21	0.20	0.0001	0.004
Alloy 182	16.22	0.05	2.91	70.65	7.42	0.05	0.04	0.45	0.001	0.010
Alloy 152	30.10	0.03	14.70	48.30	4.03	0.57	0.10	0.05	0.007	0.029

Locations and directions of CT specimen pick-up

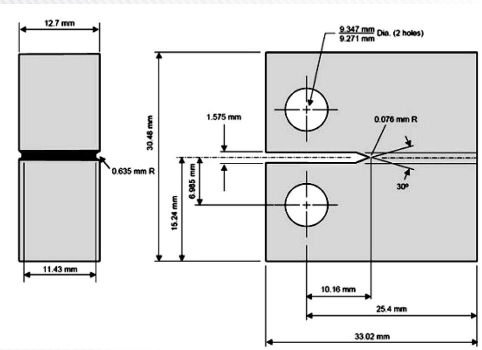






- The CT specimens were taken such that the cracking planes were parallel to the growth direction of the primary dendrites for weld metals, parallel to the radial direction of the round bar for base metals.

03 CGR and Surface Oxidation Tests



½T CT specimen pre-cracked about 2 mm long by fatigue before PWSCC test.

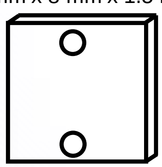
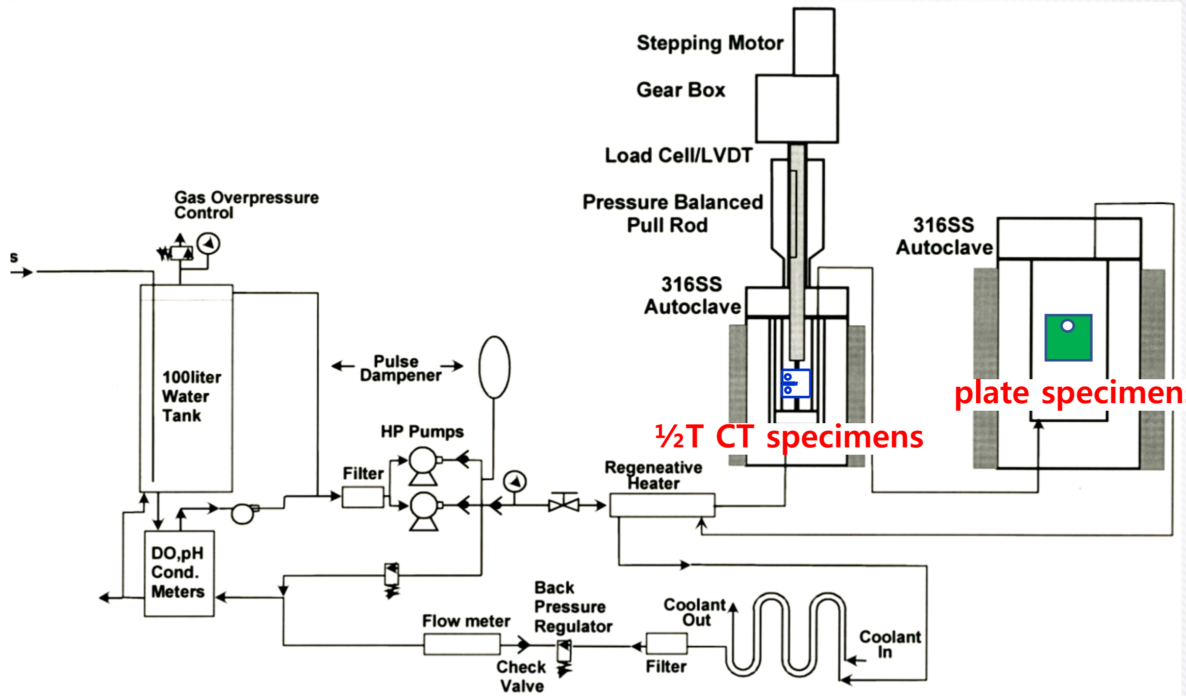
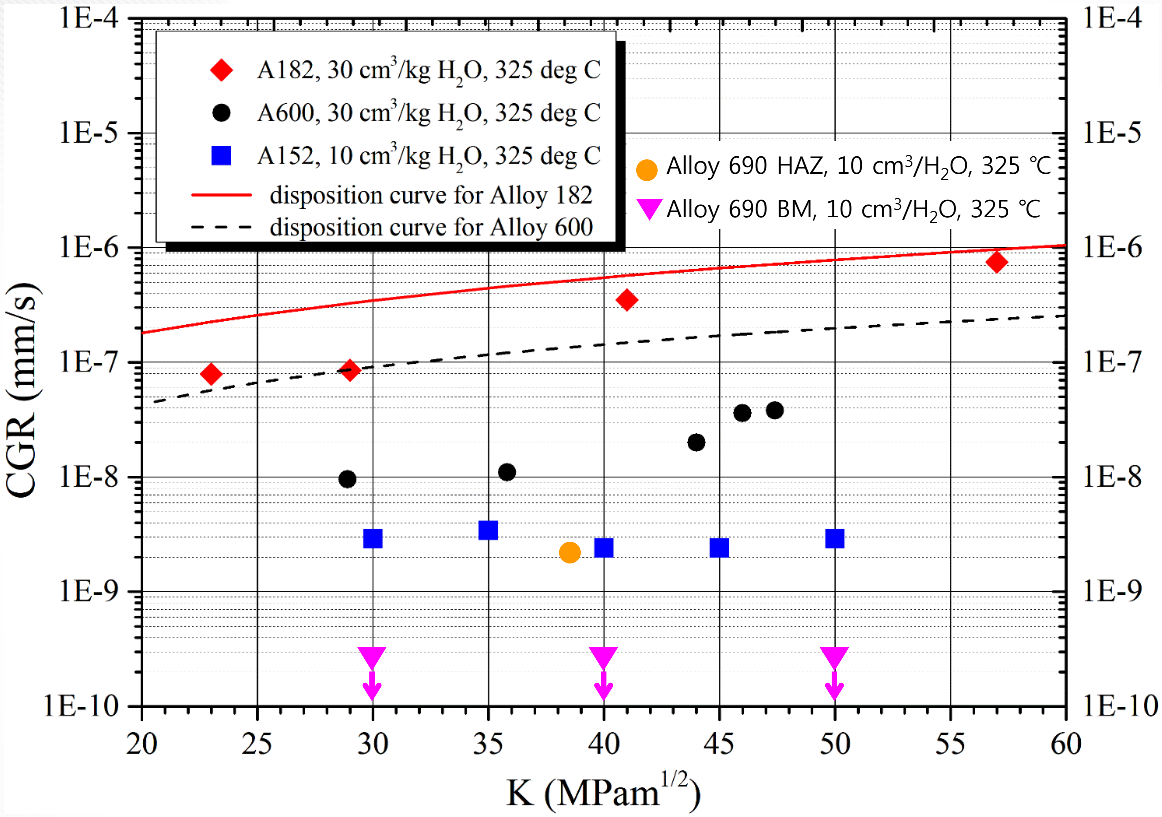


Plate specimen for surface oxidation test



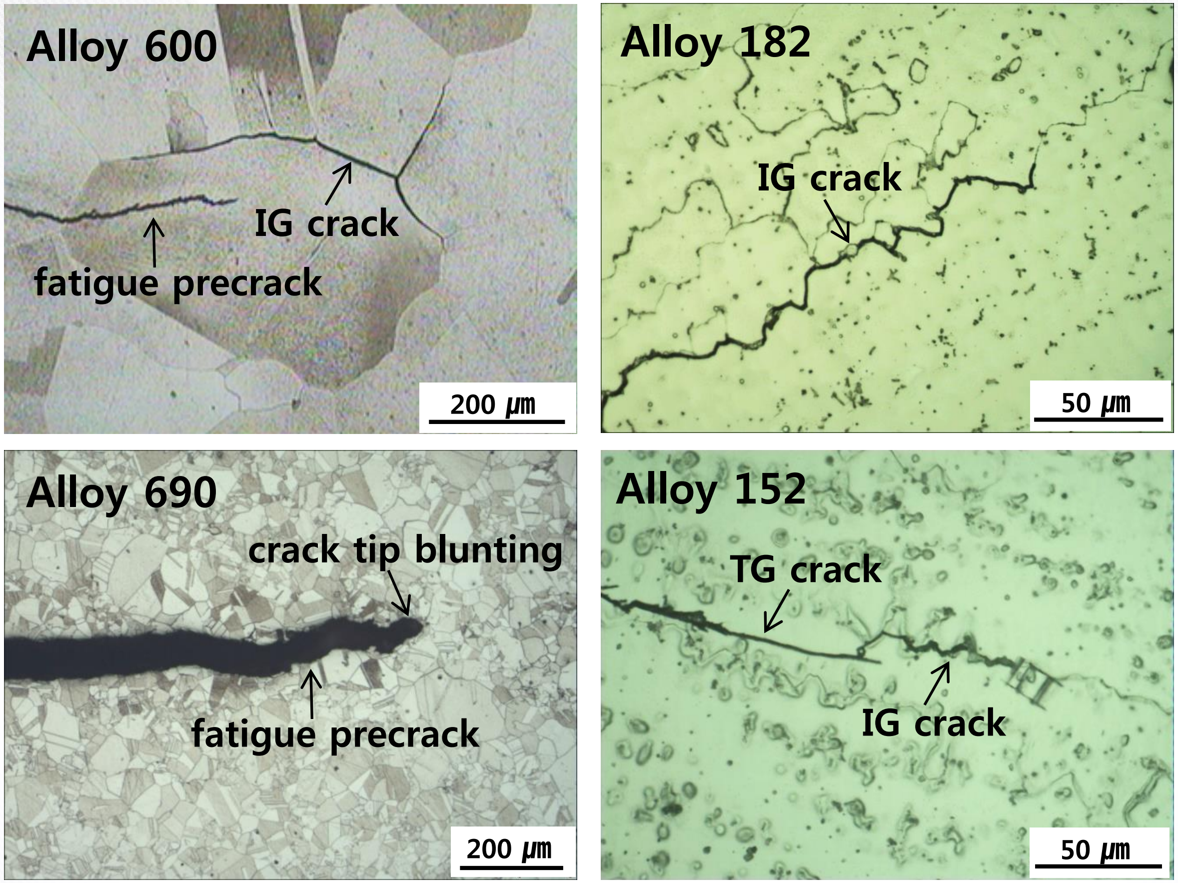
- PWSCC test was conducted in a simulated primary water condition
  pure water with 1200 ppm B + 2 ppm Li, 325 ℃, 30 cm^3/kg H_2
  test duration for surface oxidation: ~ 5 months
- The plate specimens for surface oxidation test were finally polished using 0.3 ㎛ alumina powders before PWSCC test.

04 CGRs of Ni-base Welds in PWR Primary Water



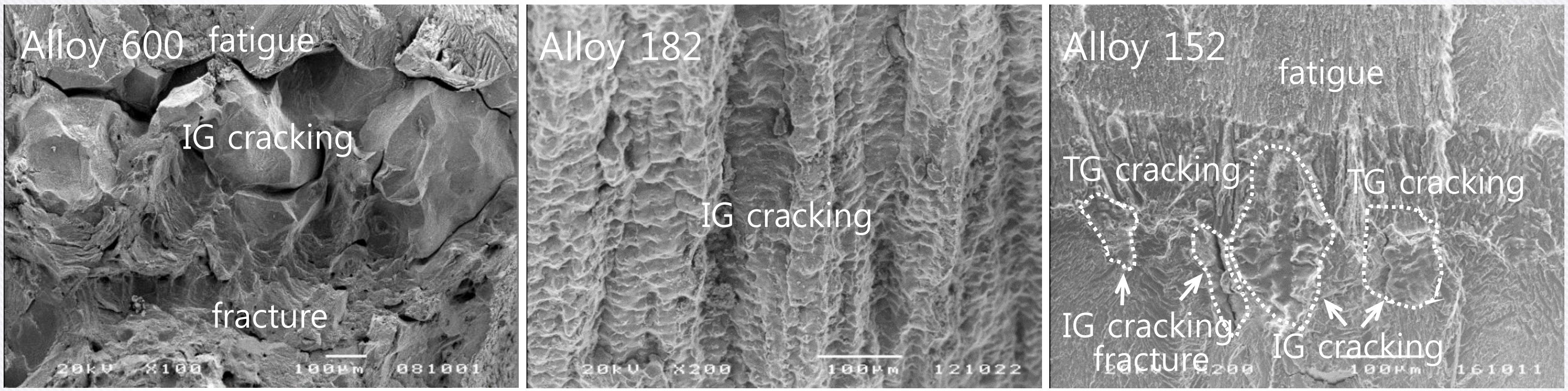
- CGRs of Alloy 182 were roughly 2 orders higher than those of Alloy 152.
- CGRs of Alloy 152 were very low in the normal operating conditions of plants. However, they appear not to be immune to PWSCC.
- Cracking of Alloy 690 did not occur in the simulated normal operating conditions of a PWR.

04 Cracking Morphologies of Ni-base Welds



- The cracks in Alloys 600 and 182 propagated along the grain boundaries, indicating that the grain boundaries are the preferential paths for cracking in these alloys.
- Alloy 690 did not crack in the simulated normal operating conditions.
- The cracks of Alloy 152 advanced in a mixed (TG + IG cracking) mode. A secondary crack was branched off from the propagating TG crack, becoming an active IG crack.

04 Fracture Morphologies of Ni-base Welds

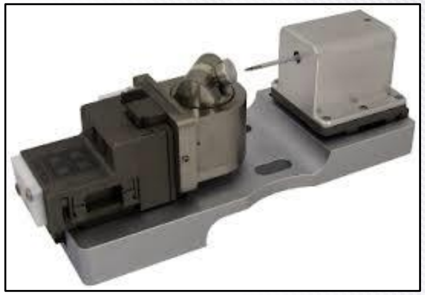


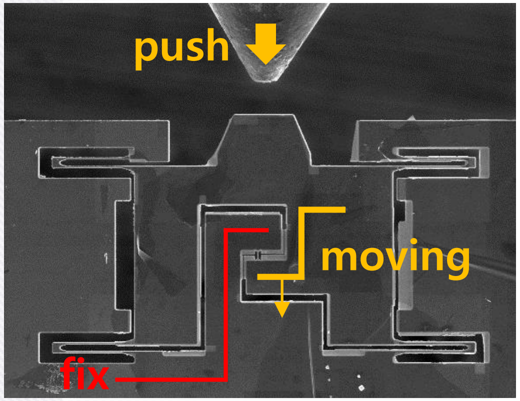
- The cracking mode of Alloy 600 is clearly IG cracking.
- The grain shapes of the Alloy 182 weld metal are clearly visible, providing evidence of IGSCC.
- Most of the PWSCC region of Alloy 152 showed TG cracking; however, some areas were fractured by IG cracking. These results clearly demonstrate that the cracks in the Alloy 152 weld metal propagate in a mixed mode.

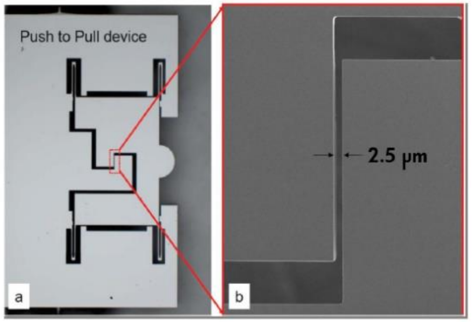
04 in-situ nano-indentation testing of Alloy 600 and 690 after oxidation test

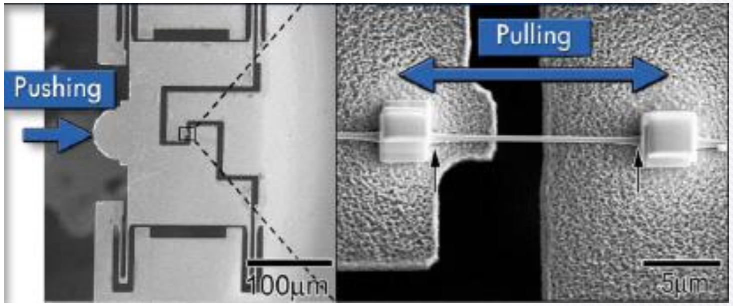
PI-87 PicoIndenter

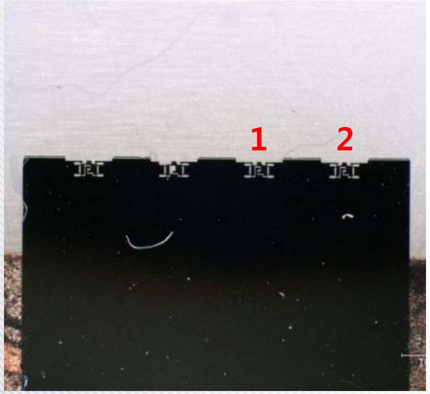
Maximum force : 10 mN
Maximum displacement : 5 μm

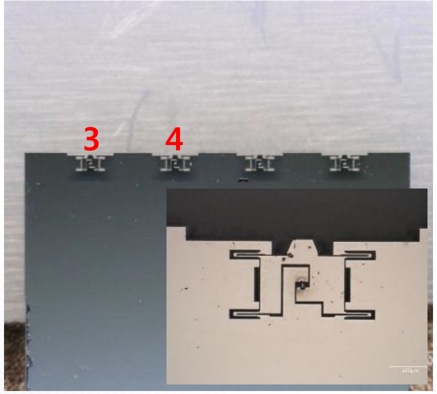


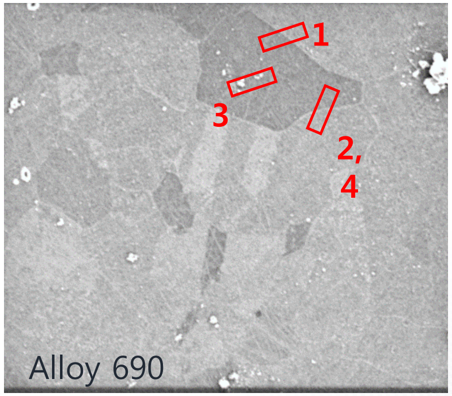


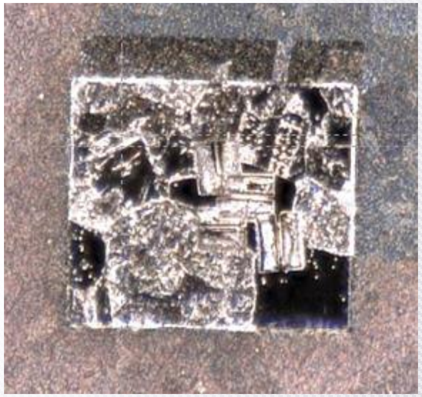












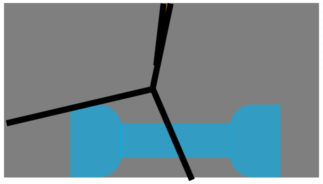
04 in-situ nano-indentation testing of Alloy 600 and 690 after oxidation test

Fracture test of the grain boundaries below the internal oxidation layers of Alloys 600 and 690

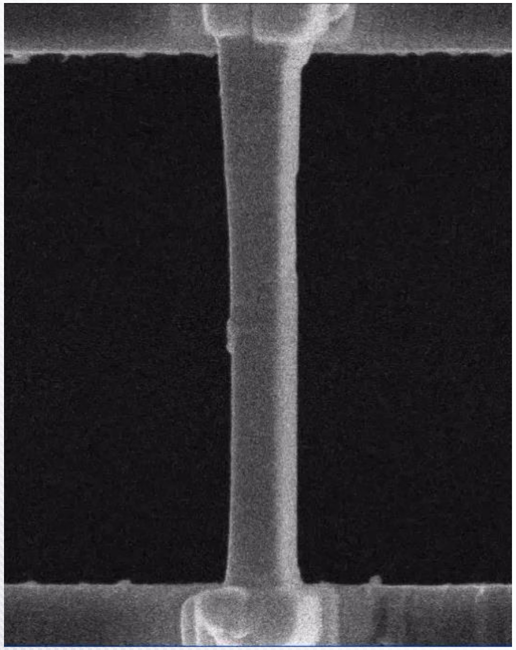
device gap : 15 um, Thickness : 2 um, Sample width : 2 um, Loading rate : 5 nm/s

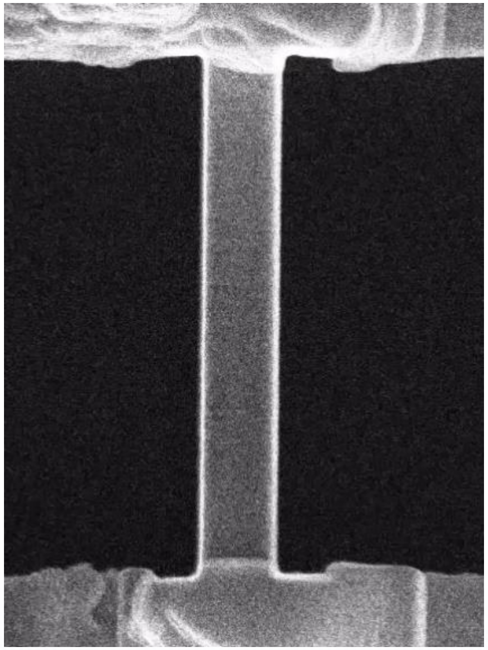
Alloy 600 / G.B. at surface

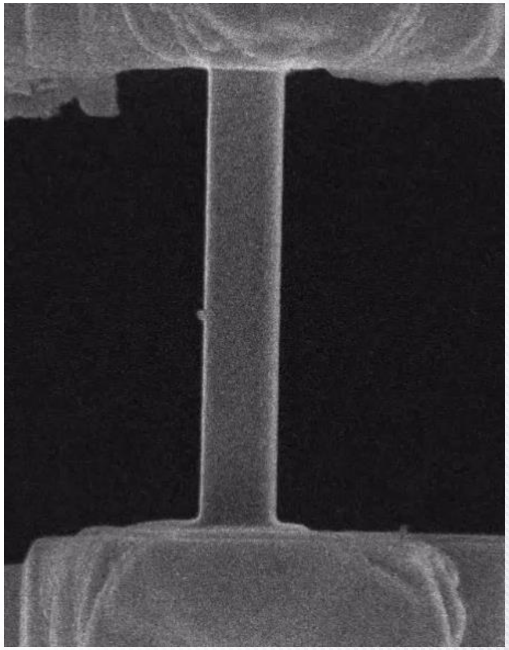
Alloy 690 / G.B. at surface



Alloy 690 / G.B. inside

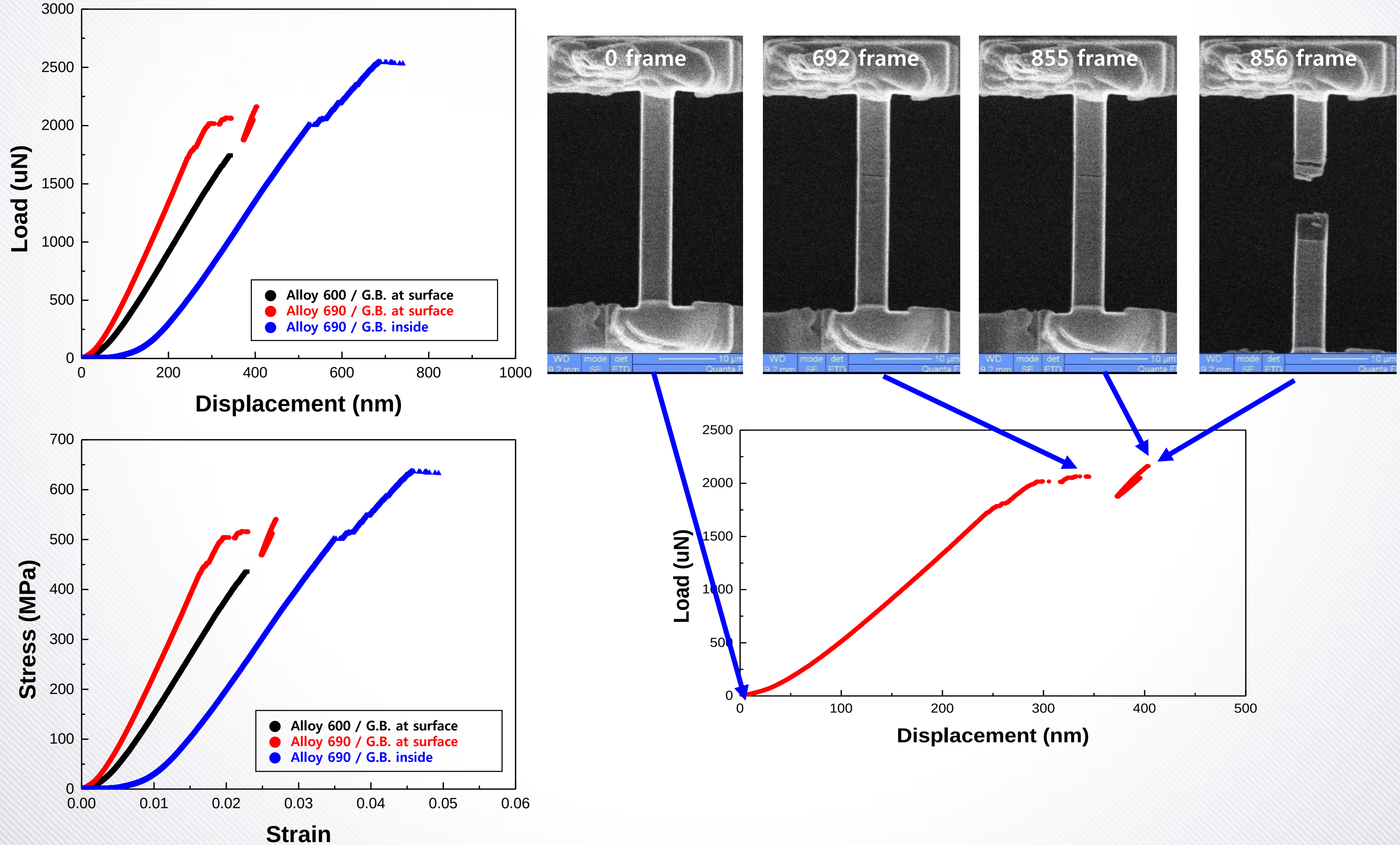




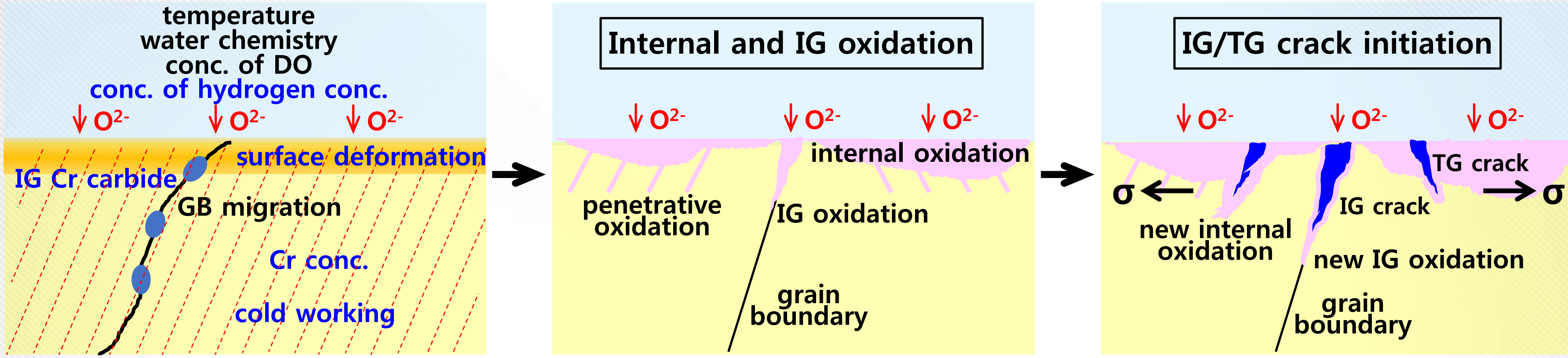


04 in-situ nano-indentation testing of Alloy 600 and 690 after oxidation test

» Test results – L-d curve



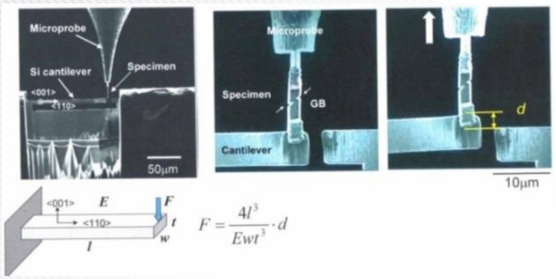
04 Influence of metallurgical factors on internal/IG oxidation and the resultant resistance to crack initiation of Ni-base alloys

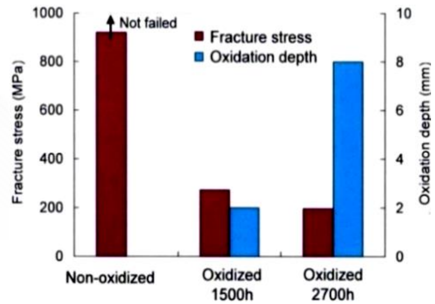


IG cracking can be triggered when the depth of IG oxidation exceeds a critical value that depends on the applied stress and the strength of the oxidized grain boundary.

#	factor	influence on SCC	remarks
1	Cr conc.	high Cr wt%: beneficial	Alloy 600 (16Cr-75Ni) prefers IG oxidation to internal oxidation, and vice versa for Alloy 690 (30Cr-60Ni) with no IG oxidation because of the innermost Cr_2O_3 layer.
2	hydrogen conc.	depends on hydrogen conc.	It is well known that Alloy 600 and 182 (16Cr) have the highest PWSCC susceptibility at the Ni/NiO equilibrium phase boundary (10 cc H_2 at 325 ℃)
3	IG Cr carbides	depends on the degree of cold working	IG Cr carbides act as another Cr source for the formation of the innermost Cr_2O_3 layer, and suppress internal and IG oxidation further. However, they can be a source of voids and micro-cracks in severely cold-worked Alloy 690.
4	cold working	detrimental	Severe cold working can lead Alloy 690 to an IG cracking by the introduction of high grain boundary strains.
5	surface deformation	depends on the degree of deformation	Mechamical poilshing increased the PWSCC resistance by promoting the formation of a protective oxide layer. Many SCC cracks also initiated along the recrystallized grain boundaries in the deformation layer.
6	GB migration	detrimental	GB migration in Alloys 600 and 690 is thought to be an important factor in the early stages of IGSCC incubation.

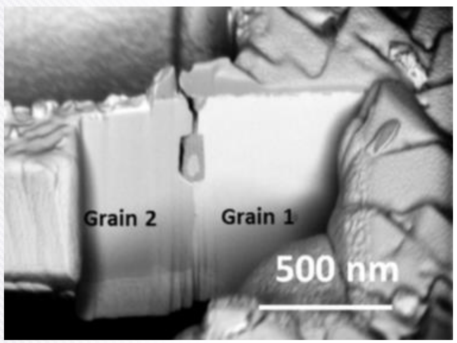
04 Influence of IG oxidation on IGSCC of Alloy 600





K. Fujii et al, INSS, 15th EDM 2011

The fracture strength of an oxidized GB decreased to 200 - 300 MPa with a brittle manner, from above 900 MPa for the alloy with a non-oxidized GB.

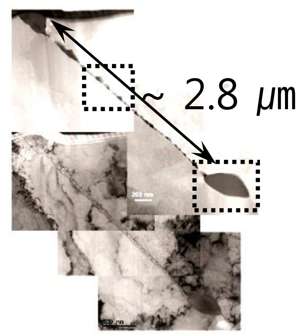


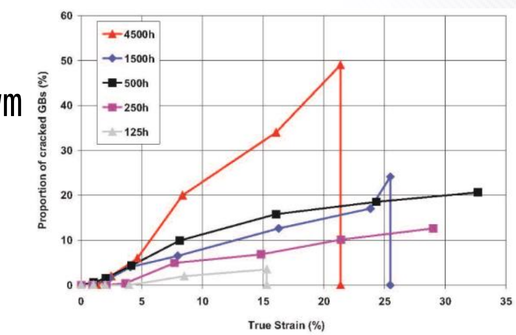
H. Dugdale et al, Acta Materialia, 61 (2013) 4707-4713

A crack propagated along a grain boundary, and then along the interface between the IG carbide and the matrix, when the specimen was oxidized.

L. Fournier et al, AREVA, 15th EDM, 2011

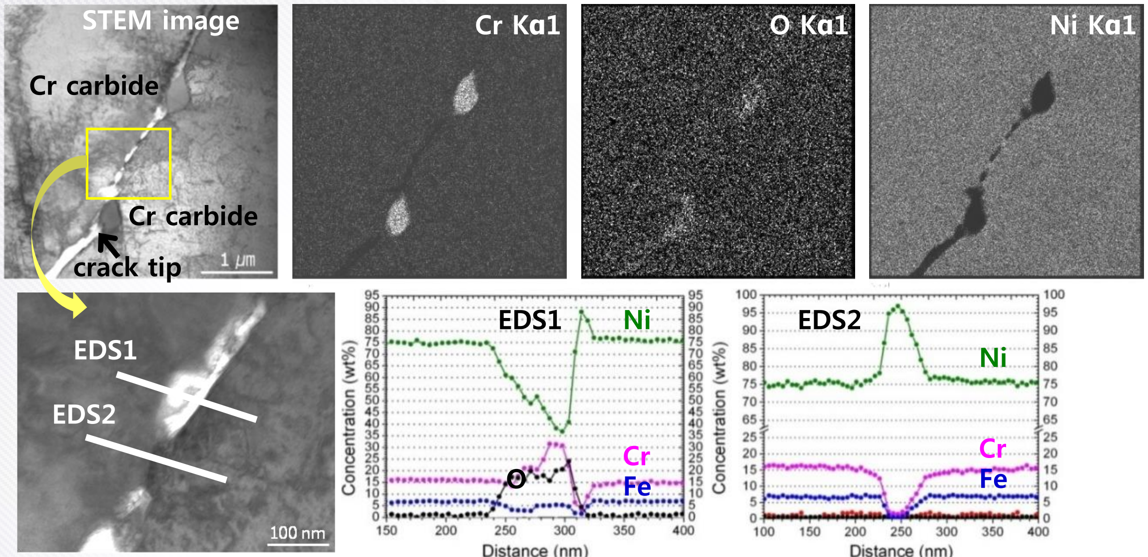
The proportion of intergranularly cracked grain boundaries were increased by IG oxidation before tensile tests.



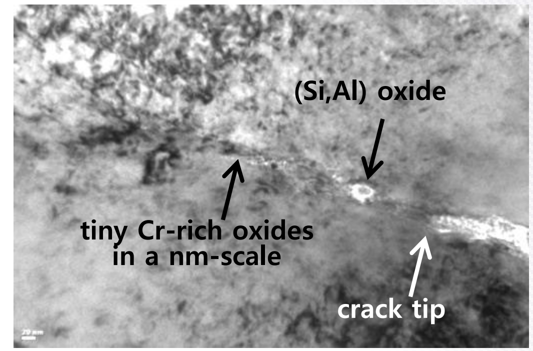


Oxygen diffusion into a grain boundary, and the resultant IG oxidation significantly weakens the grain boundary strength. As a result, the cracks in Alloy 600 can propagate easily along the grain boundaries by IG oxidation.

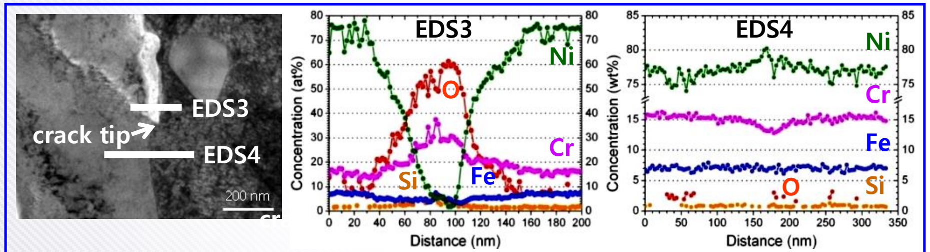
04 Internal and IG oxidation phenomena around a crack tip of Alloy 600 exposed to simulated PWR primary water

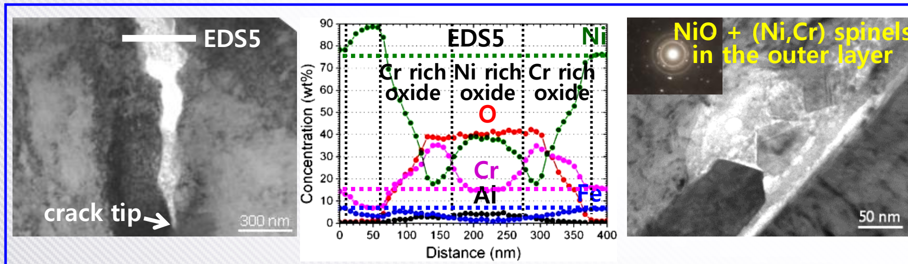


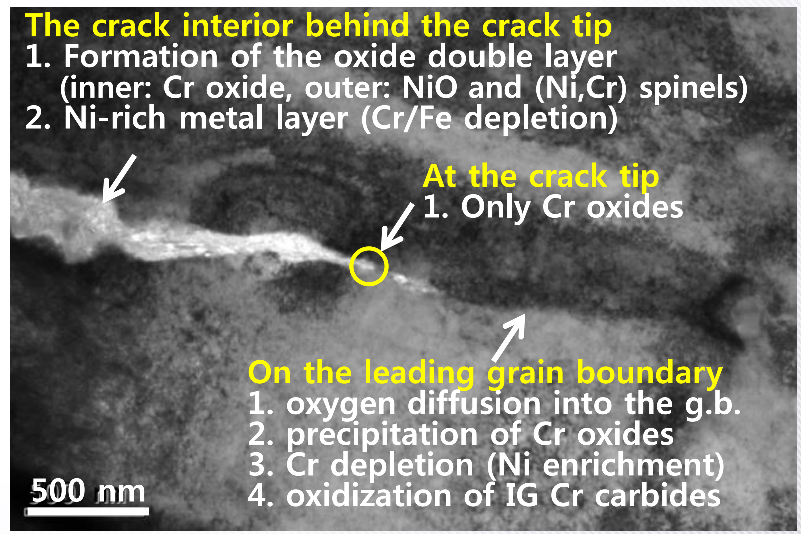
Cr/Fe depletions on the boundary with precipitation of Cr oxides



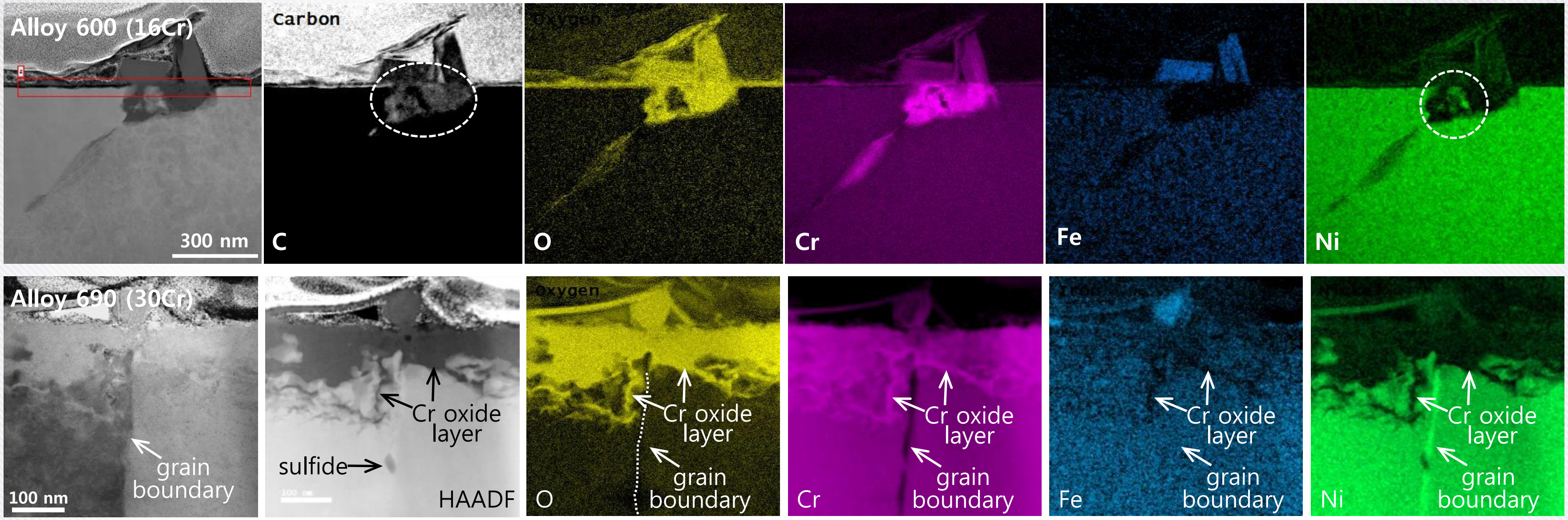
Precipitation of (Si,Al) oxide and tiny Cr oxides. The penetration depth of oxygen was ~ 600 nm







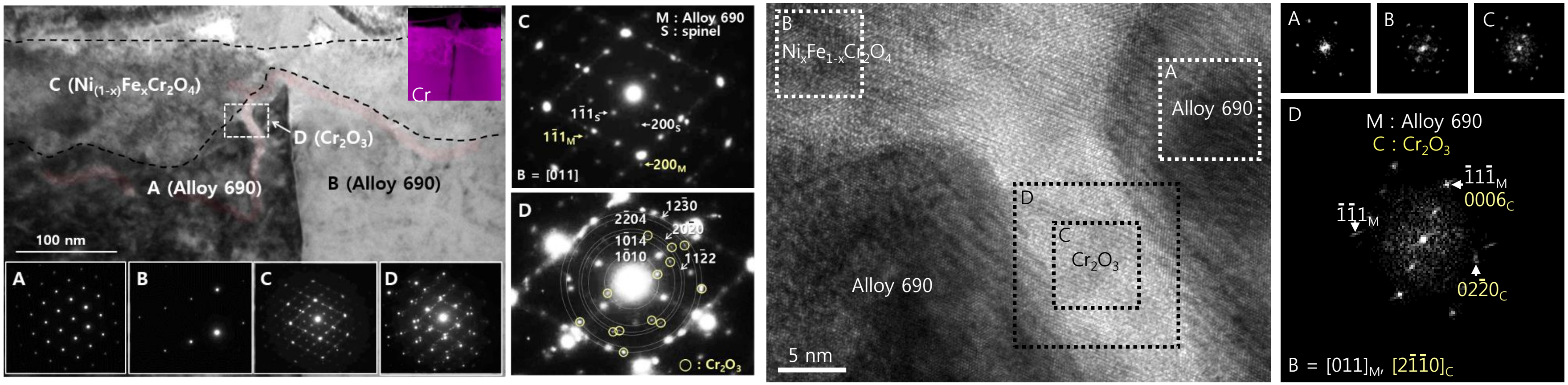
04 Influence of Cr conc. on internal and IG oxidation of Ni-base alloys



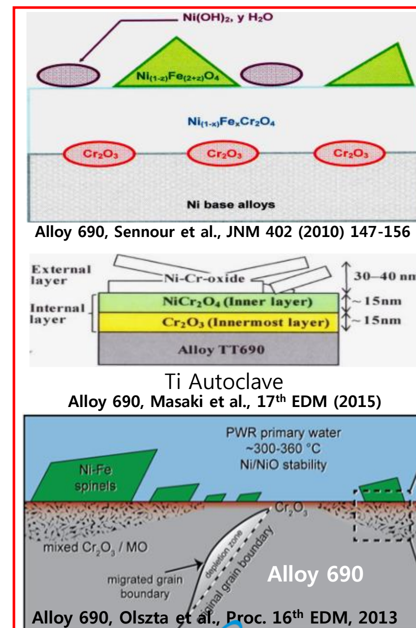
- Internal and IG oxidation phenomena in Alloys 600 and 182 are nearly identical, possibly because of the similar Cr concentrations.
- The internal oxidation layers (possibly, continuous Cr-rich oxide) are very thin, and Cr oxides formed (IG oxidation occurred) with Ni depletion in the oxidized grain boundary.

- Internal and IG oxidation phenomena in Alloys 690 and 152 were nearly identical, possibly because of the similar Cr concentrations.
- The internal oxidation layers were much thicker than those of Alloys 182 and 600.
- IG oxidation did not occur, in contrast to Alloys 600 and 182. And there is a band-shaped continuous Cr-rich oxide layer below the thick internal oxidation layer.
- The grain boundary below the internal oxide layer was severely Cr depleted and Ni enriched, in contrast to Alloys 600 and 182.

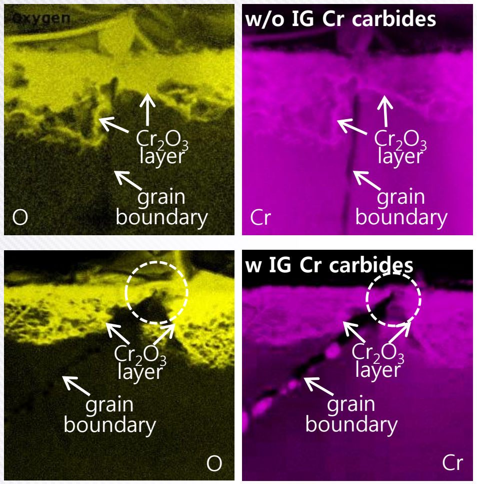
04 Influence of Cr conc. on internal and IG oxidation of Alloy 690

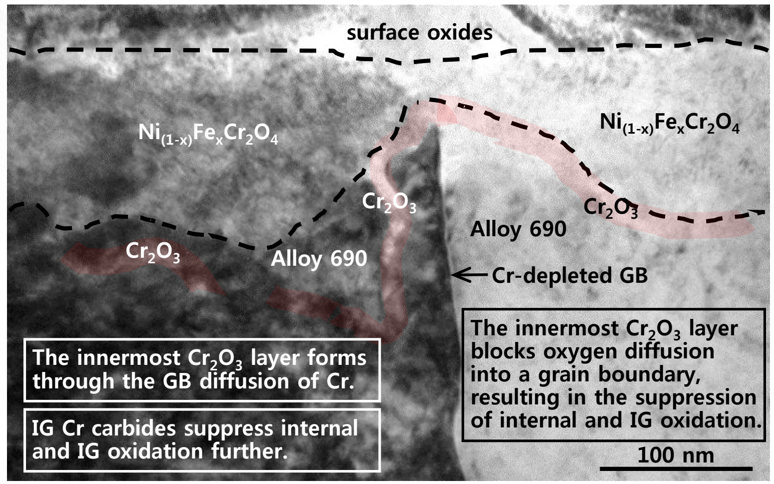


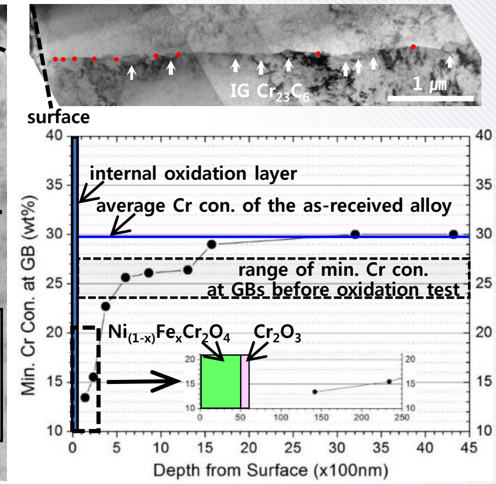
- The upper internal oxidation was identified as $Ni_{(1-x)}Fe_xCr_2O_4$, and it has a cube-cube orientation relationship with the Alloy 690 matrix, such as $[100]_{A690}//[100]_{spinel}$ and $(100)_{A690}//(100)_{spinel}$
- The band-shaped innermost Cr oxide was indexed as a hcp structure with a = 0.4597 nm and c = 1.3592 nm, which means that it is Cr_2O_3. It also has an orientation with the Alloy 690 matrix, such as such as $(\bar{1}1\bar{1})_M//(0006)_C$ and $[011]_M//[2\bar{1}\bar{1}0]_C$
- Therefore, the internal oxidation layer of Alloy 690 consists of the upper $Ni_{(1-x)}Fe_xCr_2O_4$ and the band-shaped continuous innermost Cr_2O_3 layers.
- The band-shaped innermost Cr_2O_3 layer suppresses internal and IG oxidation by preventing the inward diffusion of oxygen.



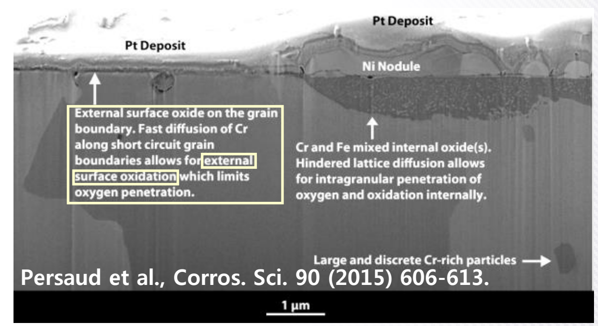
04 The Suppression of IG Oxidation and Its Implication with regard to PWSCC Resistance of Alloy 690





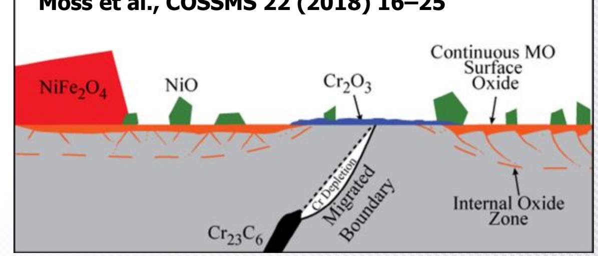


- The innermost Cr_2O_3 layer suppresses internal and IG oxidation in Alloys 152 and 690.
- IG fractures readily occur even with a small amount of applied stress when the grain boundaries are oxidized because of its intrinsic weakness.
- Therefore, the absence of IG oxidation in Alloys 152 and 690 provides the reason why they have higher resistance to PWSCC compared to those of Alloys 182 and 600 from the standpoint of IG oxidation.
- As a result, the different IG oxidation phenomena appear to lead to the different cracking resistance capabilities and cracking behaviors in Ni-base alloys.



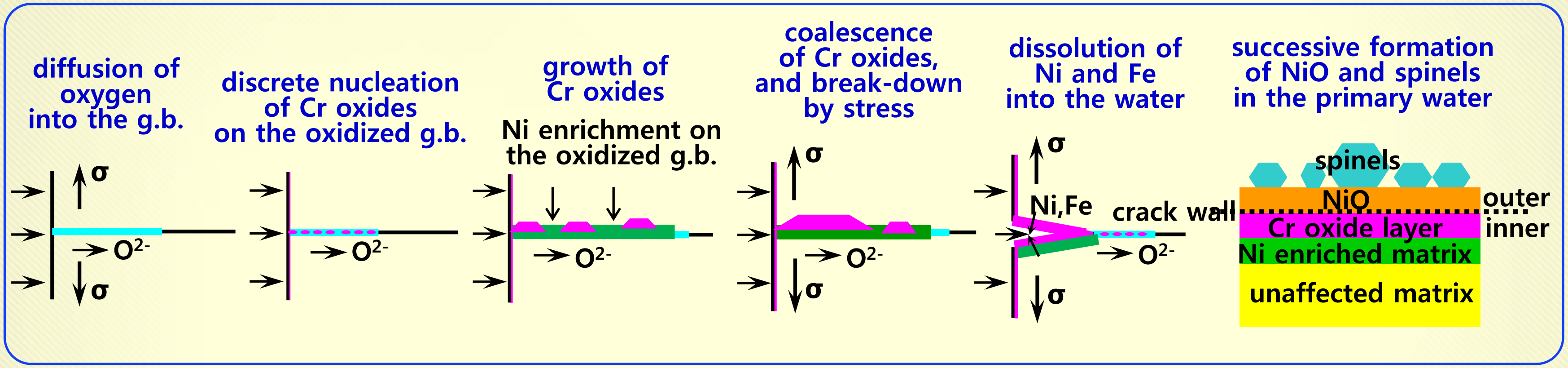
Persaud et al., Corros. Sci. 90 (2015) 606-613.

Moss et al., COSSMS 22 (2018) 16–25

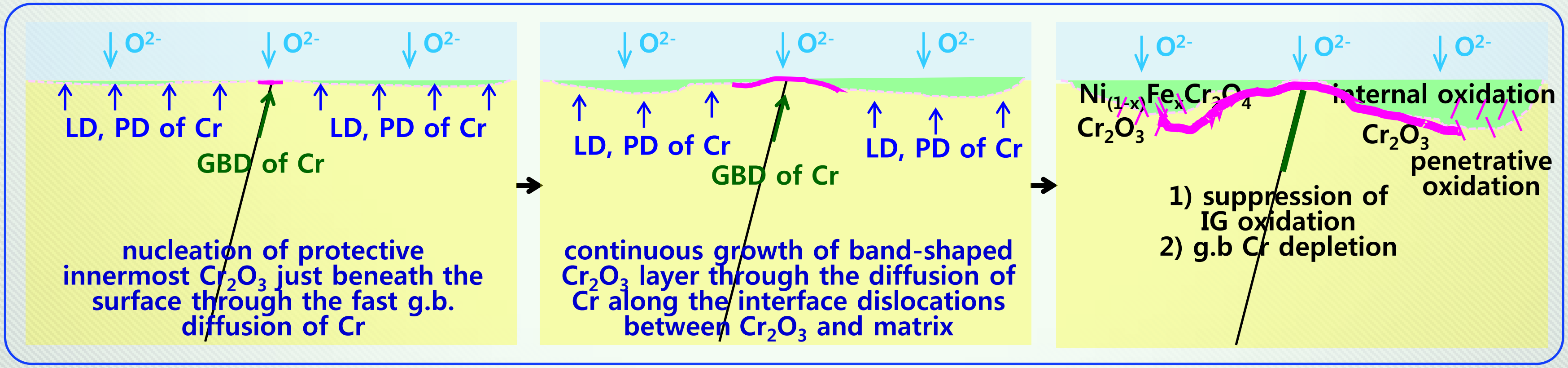


04 Influence of Cr concentration on internal/IG oxidation and the resultant resistance to crack initiation of AR Alloys 600 and 690

IG oxidation and IG cracking of Alloys 600 and 182 (325 ℃, 30 cm³ H_2/kg H_2O)
- from the analysis of PWSCC crack tips and IG oxidation layers -



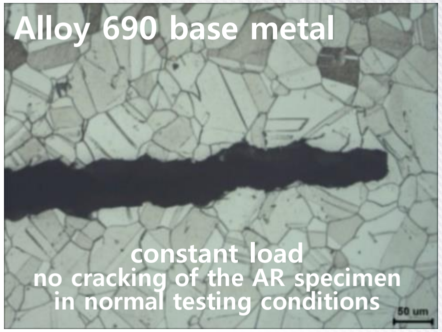
Suppression of IG oxidation of Alloys 600 and 182 (325 ℃, 30 cm³ H_2/kg H_2O)
- from the analysis of internal and IG oxidation layers -



04 Several methods for PWSCC initiation of Alloy 690

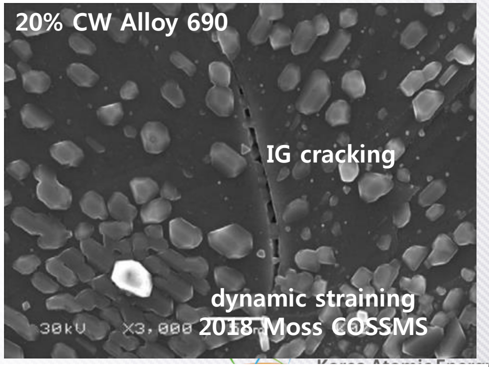
(advantages and drawbacks of some techniques for crack initiation)

- **There has been no evidence of PWSCC of Alloy 690 in steam generators since its introduction.**
- Given the past experience with the long incubation time to crack initiation in Alloy 600, **there is also concern that SCC could eventually occur in Alloy 690.**
- **However, the difficulties associated with generating cracks in Alloy 690 have been an impediment to the study of the mechanisms of SCC initiation.**



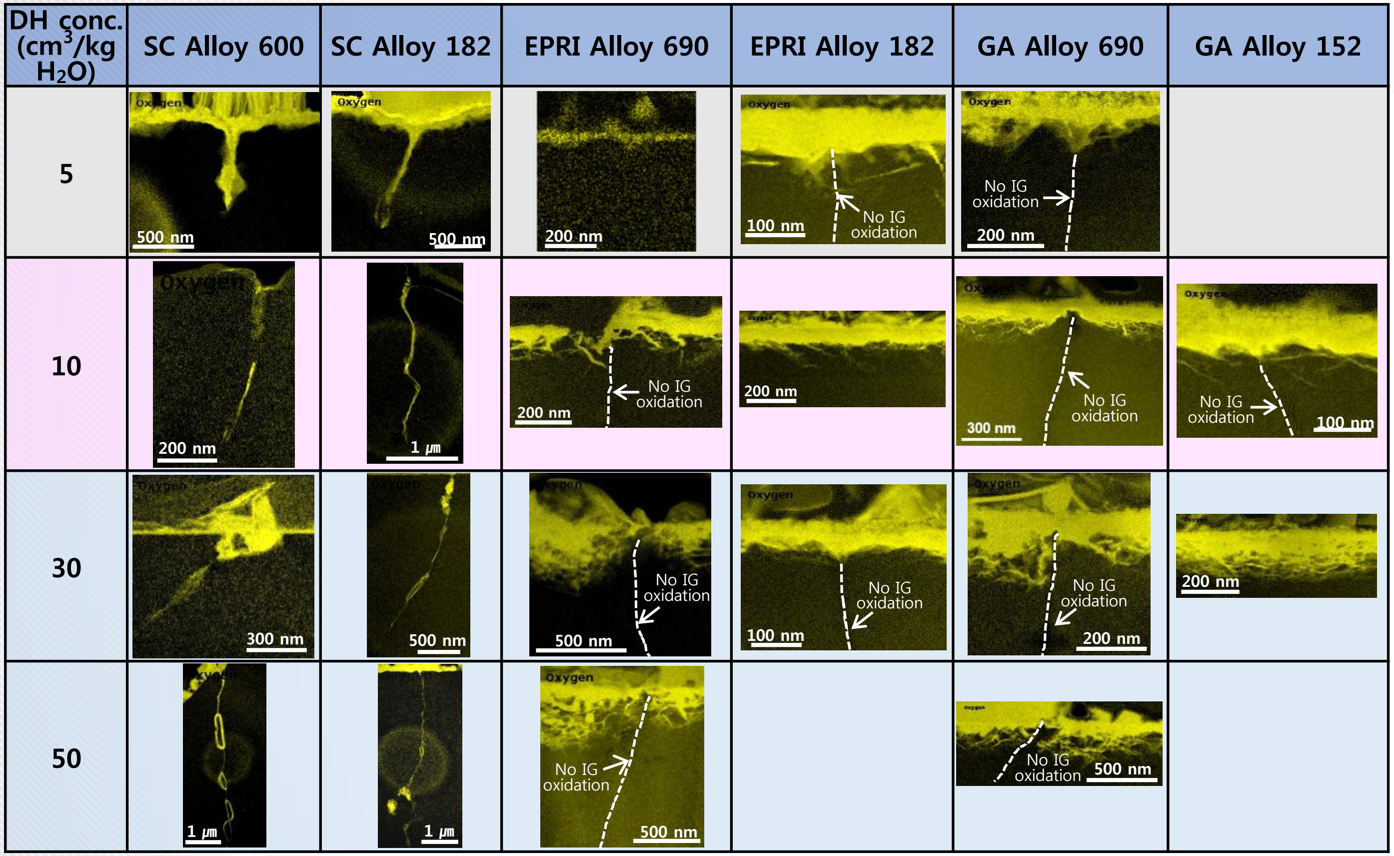
technique	specimens	straining	advantage	drawback	Crack initiation	remarks
constant strain (deflection)	U-bend, C-ring	static	easy to implement	Stress relaxation occurs with time at high temp.	very hard	Crack initiation occurs only when the samples undergo extensive plastic deformation
constant load	tensile, blunt notched CT (BNT)	static	most realistic	Crack initiation is not easy for resistant materials	very hard	Extensive period of time is needed to initiate cracks
constant extension rate tensile (CERT)	**(tapered) tensile**	**dynamic**	**accelerated test for resistant materials**		**easy**	**Only the CERT test can consistently initiate cracks on the resistant materials**

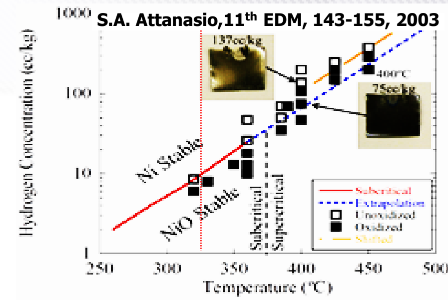
- **The IG oxidation weakens the grain boundary strength and allows a crack to propagate upon application of stress.**
- **After repeated cycles (dynamic straining) of oxide fracture followed by repair, the grain boundary becomes further depleted in Cr** and migrates further from its original position.
- At some point, the grain boundary is no longer able to supply enough Cr to form a protective surface film, exposing the grain boundary to the environment, **resulting in IG and subsequent crack nucleation by fracture along the oxidized boundary**.

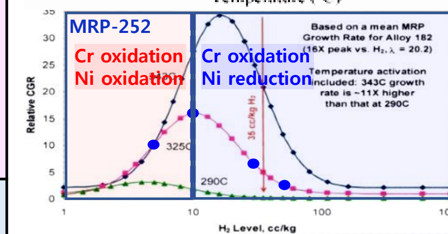


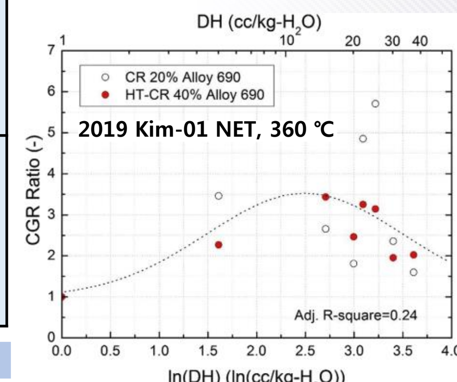
[2] Moss et al., Stress corrosion crack initiation in Alloy 690 in high temperature water, Current Opinion in Solid State and Materials Science, 22 (2018) 16-25

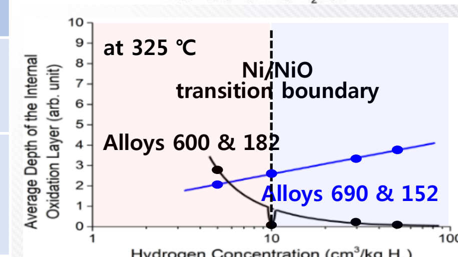
04 Influence of hydrogen concentration on internal and IG oxidation of Ni-base alloys







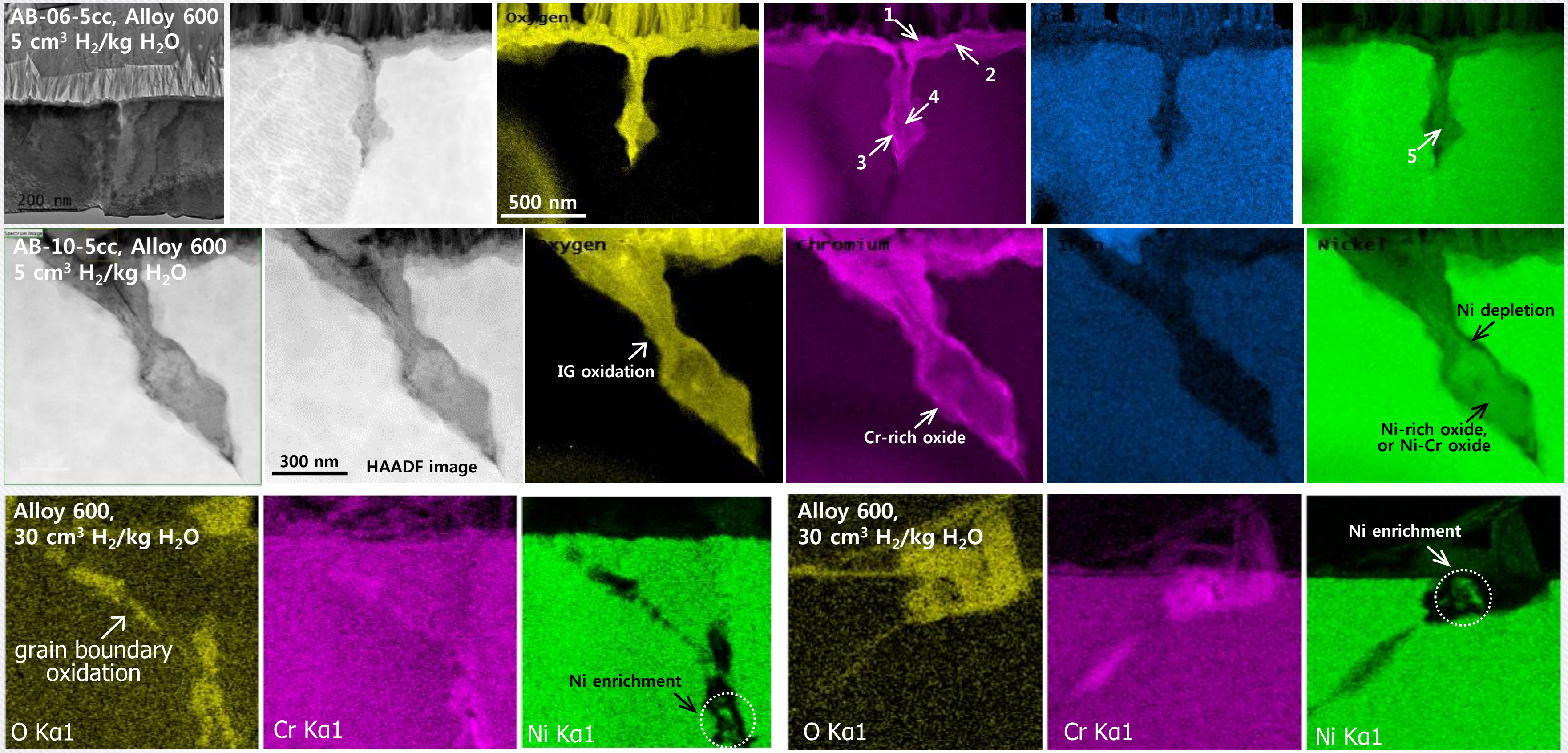




Internal and IG oxidation phenomena depending on the hydrogen concentration		
	Alloys 600 and 182	Alloys 690 and 152
independent phenomena	1. IG oxidation and related phenomena 2. duality of the internal oxidation layer	1. no IG oxidation and related phenomena 2. duality of the internal oxidation layer 3. DIGM and its related phenomena
dependent phenomena	1. needle Ni-rich oxide on the surface 2. Ni enrichment (or Ni oxidation) of the IG oxidation region 3. change of the int. oxi. layer thickness	1. presence of Ni nodules on the surface 2. Ni enrichment (or Ni oxidation) of the internal layer 3. change of the int. oxi. layer thickness

04

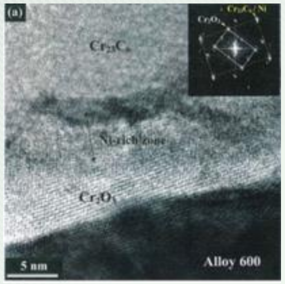
Influence of hydrogen concentration on internal and IG oxidation of Alloy 600

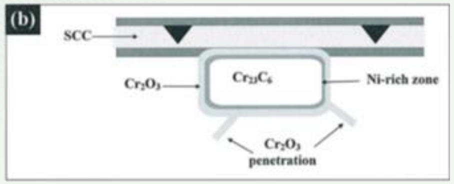


- The Cr concentrations at the interface (1) and interior (2) of the internal oxidation layer/matrix, and interface (3) and interior (4) of the oxidized grain boundary/matrix are quite different, which means that the types of oxides are different, and therefore oxide layer consists of a dual layer.
- Ni enrichment was found when the hydrogen conc. was 30 cm^3 H_2/kg H_2O (metallic state of Ni), however, Ni oxide formed when the hydrogen conc. was 5 cm^3 H_2/kg H_2O (oxidizing state of Ni).

04 Influence of IG Cr carbides on internal/IG oxidation and the resultant resistance to crack initiation of Ni-base alloys

Alloy 600 LTMA → Alloy 600 HTMA → Alloy 600 TT → Alloy 690





(2009 Sennour JNM) superficial oxidation or entire transformation of the IG carbide into Cr_2O_3 oxide

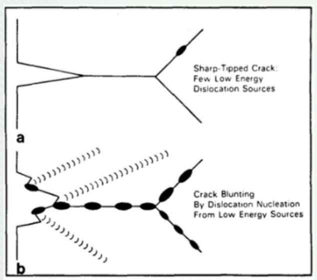
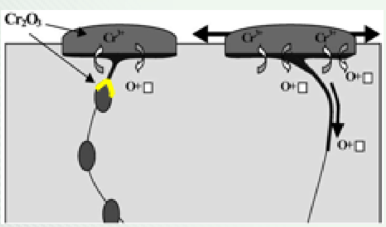


FIGURE 8. Grain boundary carbides promoting crack blunting because of their effectiveness as a dislocation source.

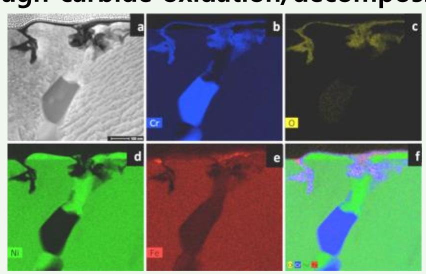
(2017 Langelier 2017) grain boundary pinning

(1988 Bruemmer Corros.) crack tip blunting as a dislocation source.

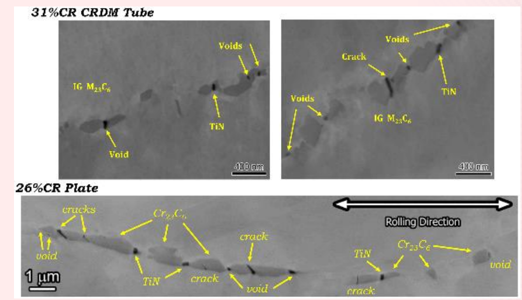


(Panter 2006 JNM) oxygen trap and impeding the penetration of oxygen

(2017 Bertali CS) a reservoir of Cr for the formation of a protective Cr-rich oxide through carbide oxidation/decomposition



(2015 Bruemmer IGC-EAC Meeting) grain boundary voids and cracked carbides in highly CR Alloy 690



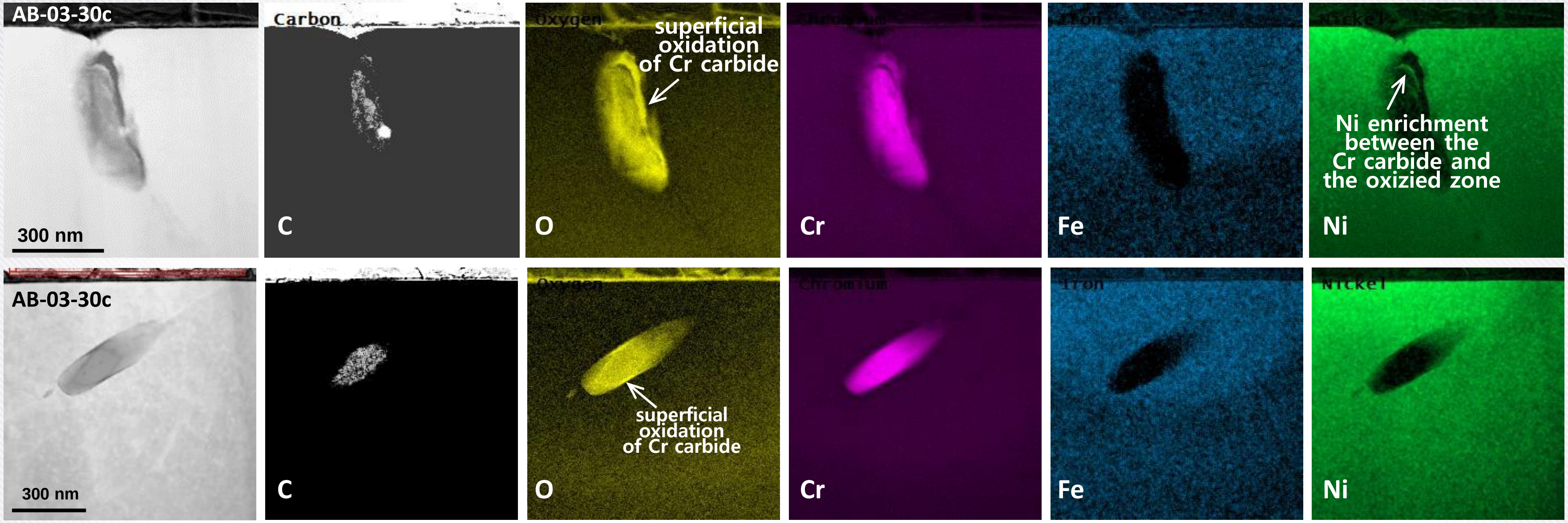
Alloy 690 becomes susceptible to IGSCC in the highly deformed (≥~15% CW) condition.

IG Cr carbides can be a source of voids and micro-cracks in the severely cold-worked Alloy 690, which is detrimental to IGSCC resistance by promoting IG oxidation.

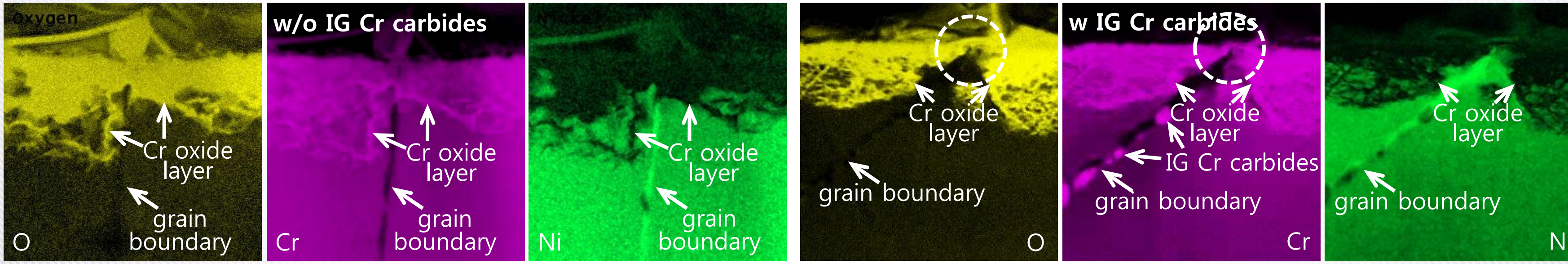
beneficial — degree of cold working — detrimental

~ 30 %

04 Influence of IG Cr carbides on internal and IG oxidation of Ni-base alloys

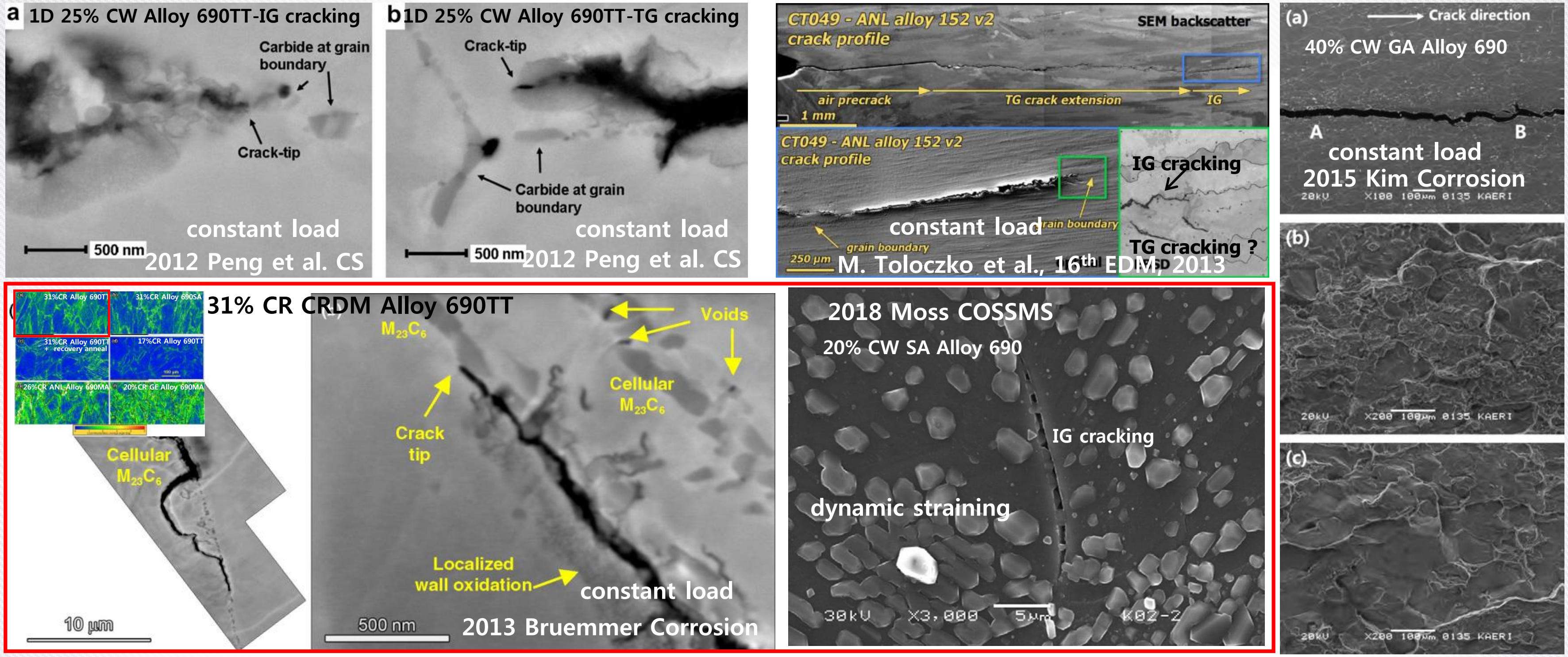


- oxygen which diffuses into a grain boundary of Alloy 600 caused superficial oxidation or the entire transformation of the IG carbide into Cr oxide, leaving a Ni-enriched zone between the IG carbide and the transformed Cr oxide layer.



- IG Cr carbides suppress internal and IG oxidation further, because they can act as another Cr source for the formation of the innermost Cr_2O_3 layer in the early stage of the internal oxidation process.

04 Influence of cold working on internal and IG oxidation of Alloy 690



- IG/TG cracking issue : There are many conflicting results on the cracking behavior of the cold worked Alloy 690. The cold worked Alloy 690 shows IG cracking, and TG cracking as well.

IG cracking of Alloy 690

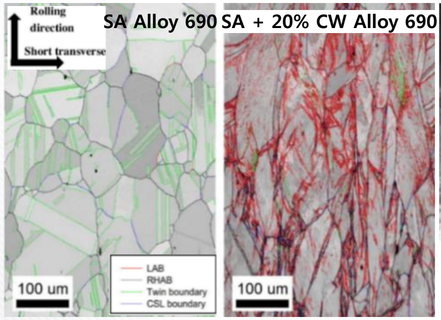
- Moss' discussion: After repeated cycles of oxide fracture and repair during **dynamic straining**, the grain boundary becomes Cr-depleted and migrates from its original position, finally resulting in grain boundary oxidation and subsequent crack nucleation by fracture along the oxidized boundary.
- Bruemmer's discussion: The results indicate that **localized grain boundary strains and stresses by cold working** promote IGSCC susceptibility and not the cracked carbides and voids.

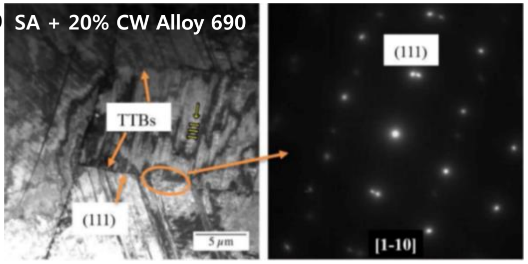
04 Influence of cold working on internal and IG oxidation of Alloy 690

In a standpoint of internal and IG oxidation

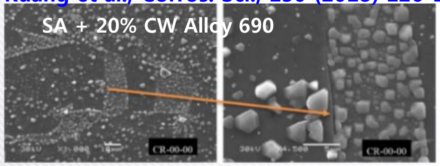
- As-received (heat-treated, not cold worked) Alloy 690 did not show IG oxidation, however, **oxygen penetrated deeply into the matrix through defects such as dislocations from the oxidation layer/matrix interface**. Dislocations act as an enhanced diffusion path for oxygen.
- Dislocations locally accumulated around a grain boundary by grain boundary strains and stress in a severely cold worked Alloy 690 can induce oxygen diffusion along the grain boundary by preventing from the formation of continuous protective Cr_2O_3 innermost layer, resulting in the IG oxidation. **The induced IG oxidation can promote IGSCC in the cold worked Alloy 690.**

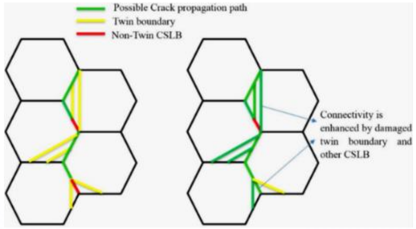
- Most of the twin boundaries were **transformed into transformed twin boundaries (TTBs) by cold rolling, which belong to random high angle boundaries (RHABs).**
- TTBs become susceptible to SCC due to the promoted outward diffusion of Cr and can enhance the connectivity of susceptible grain boundaries.

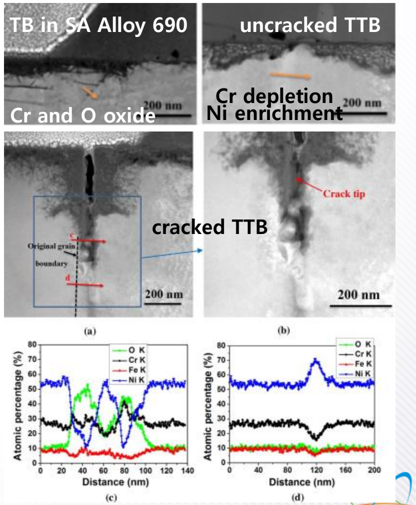




Kuang et al., Corros. Sci., 130 (2018) 126-137

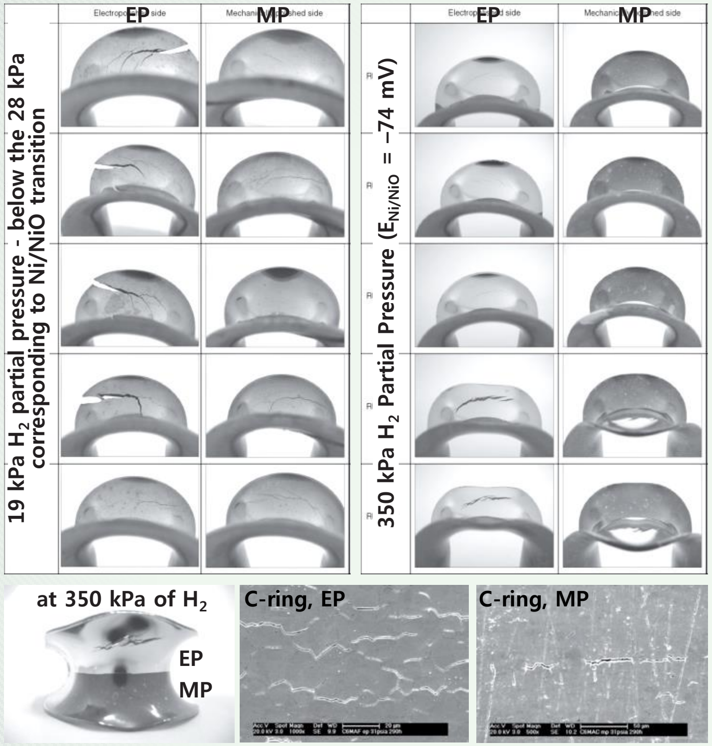






04 Influence of surface deformation on internal/IG oxidation and the resultant resistance to crack initiation of Alloy 600

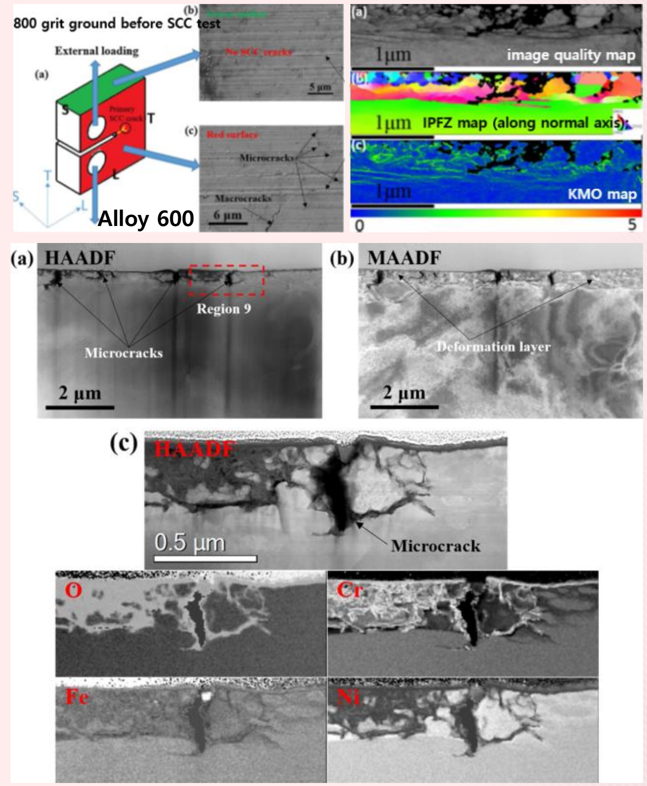
F. Scenini et al, Corrosion, 64(11) (2008) 824-835



Mecanically polished surfaces are revealed to be more resistant to SCC than electrochemically polished surfaces due to the short circuit diffusion of Cr to the surface, which promotes external protective rather than internal oxidation.

beneficial (increase of dislocation density)

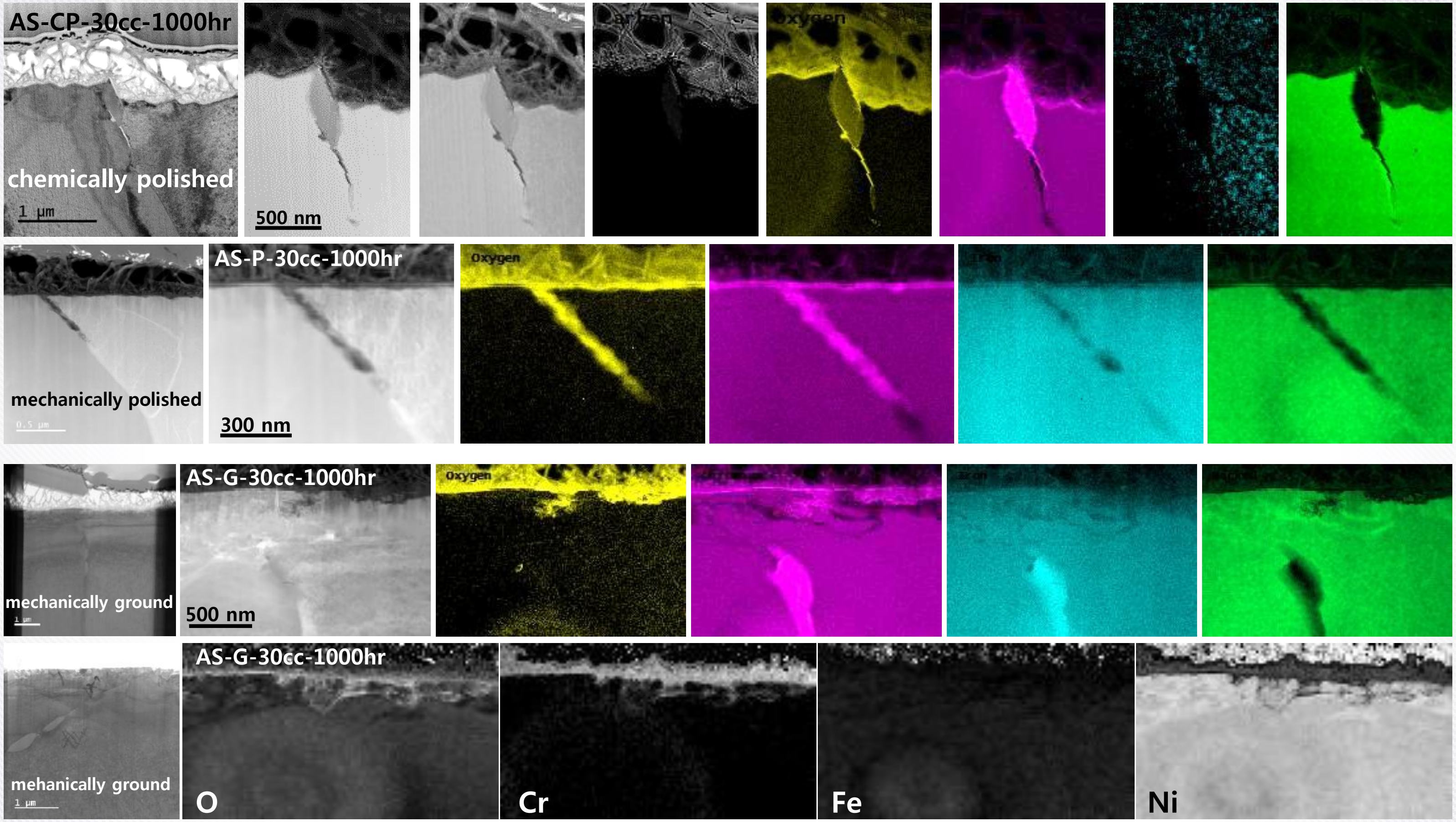
Z. Shen et al., Corros. Sci. 152 (2019) 82–92



Mechanical polishing introduced a thin recrystallization layer on the specimen surface, which lead to the crack initiation along highly deformed recrystallization grain boundaries.

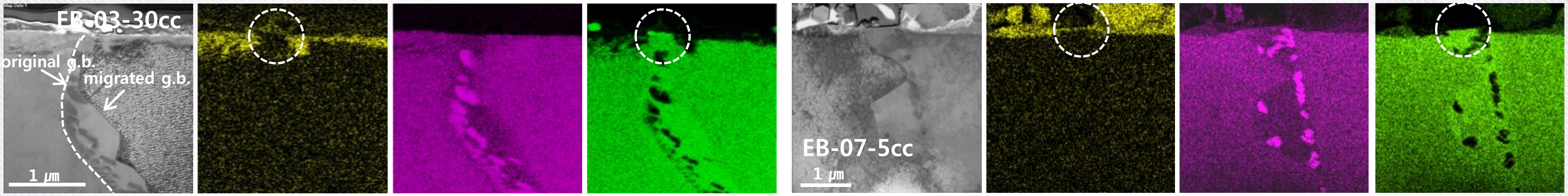
detrimental (recrystallization)

04 Influence of surface deformation on internal and IG oxidation of Alloy 600



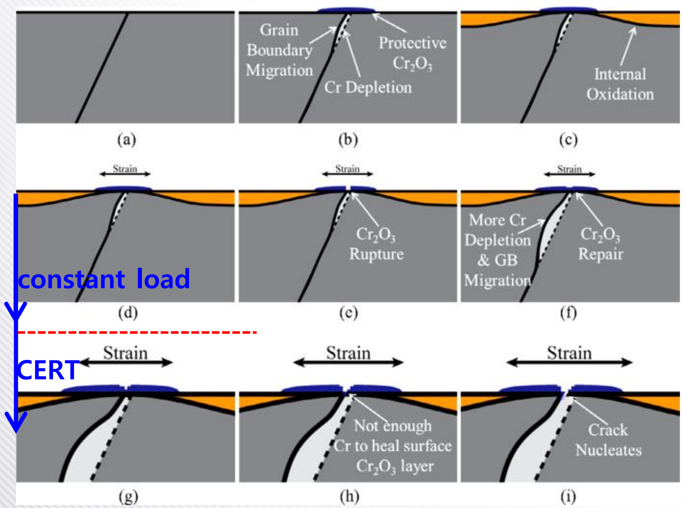
- The internal oxidation layers were similar and IG oxidation was found in the mechanically polished (P) and chemically polished (CP) specimens.
- However, IG oxidation was not found in the mechanically ground (G) specimens with a thick and complicated deformed internal oxidation layer.

04 Influence of diffusion induced grain boundary migration (DIGM) on internal and IG oxidation of Alloy 690



- DIGM commonly occurred in Alloy 690 irrespective of the concentration of dissolved hydrogen, and the swept region by DIGM was characterized by Cr depletion and Ni enrichment.
- The internal oxidation layers of the swept region were much thinner than those of the surroundings, and there were Ni nodules on the swept surfaces.

T. Moss, G.S. Was, Stress corrosion crack initiation in Alloy 690 in high temperature water, Current Opinion in Solid State and Materials Science, 22 (2018) 16-25



The crack initiation process **during dynamic straining** is composed of three stages; **an oxidation stage** in which a protective film of Cr_2O_3 is formed on the surface over the grain boundaries, **an incubation stage** in which successive cycles of oxide film rupture and repair depletes the grain boundary of Cr, and **a nucleation stage** in which the **Cr depleted grain boundary is no longer able to support formation of a protective Cr oxide layer**, exposing the grain boundary to the water environment and subsequent formation and rupture of oxides down the grain boundary.
Only the dynamically strained (not constant load) samples can go through the full stages of crack initiation.

05

Conclusions

1. Alloys 600 and 182 showed IG cracking with high CGRs in normal testing conditions simulating PWR primary water. However, Alloys 690 and 152 showed the different tendencies.
2. The grain boundaries of Alloys 600 and 182 were oxidized due to the oxygen diffusion into the specimen. However, IG oxidation of Alloys 690 and 152 was suppressed by a continuous protective band-shaped Cr_2O_3 layer.
3. The differences in cracking property and susceptibility between Alloys 600 and 182, and Alloys 690 and 152 can be attributed to the different IG oxidation behavior of the alloys. The main reason for these differences is thought to be the different chemical compositions, especially the different Cr contents in these two alloy groups.
4. The metallurgical factors (Cr content, hydrogen concentration, IG Cr carbides, grain boundary migration, cold working and surface deformation) significantly affect the internal and IG oxidation, and the resultant SCC properties of Ni-base alloys.

THANK YOU