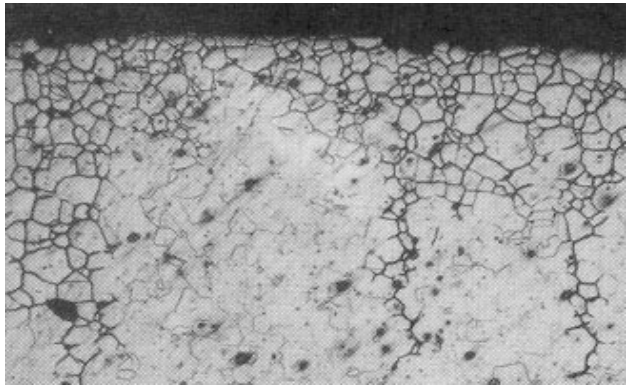
8. Intergranular Corrosion (IGC)

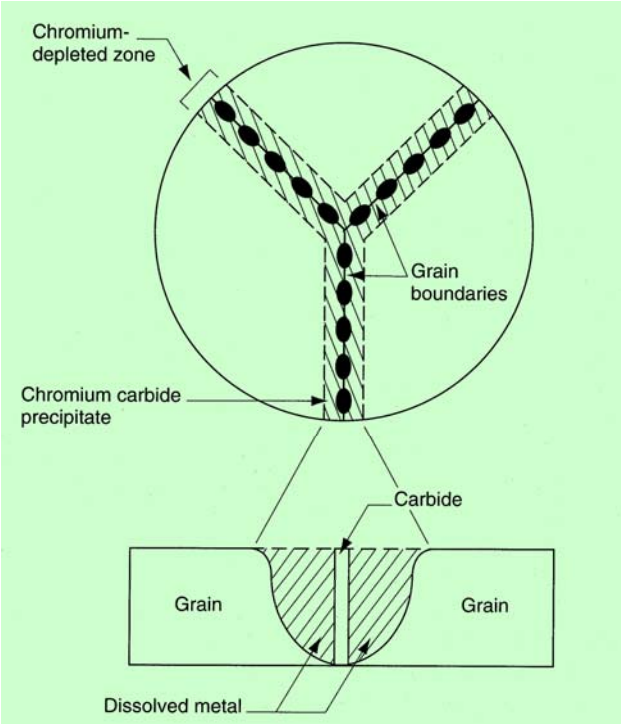
Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains. The alloy, sensitive to IGC, disintegrates and/or loses its strength when exposed to environments.



8.1 Causes of intergranular corrosion

A. Segregation of impurities at the grain boundary
   ex) Fe in Al alloys.

B. Enrichment of one of the alloying elements or depletion of one of these elements in the grain boundary areas.



8.2 Intergranular Corrosion of stainless steels and nickel based alloys

Exposed temperature : 425 ^{o}C to 815 ^{o}C

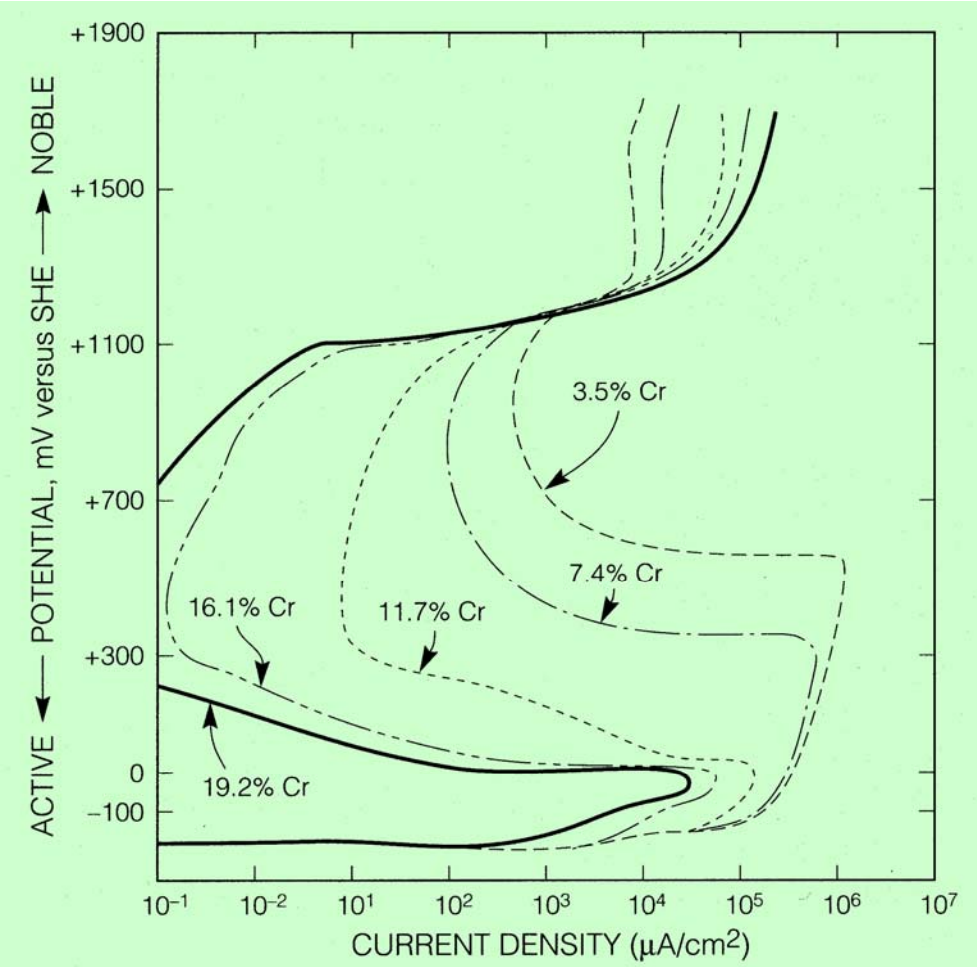
↓

Sensitization

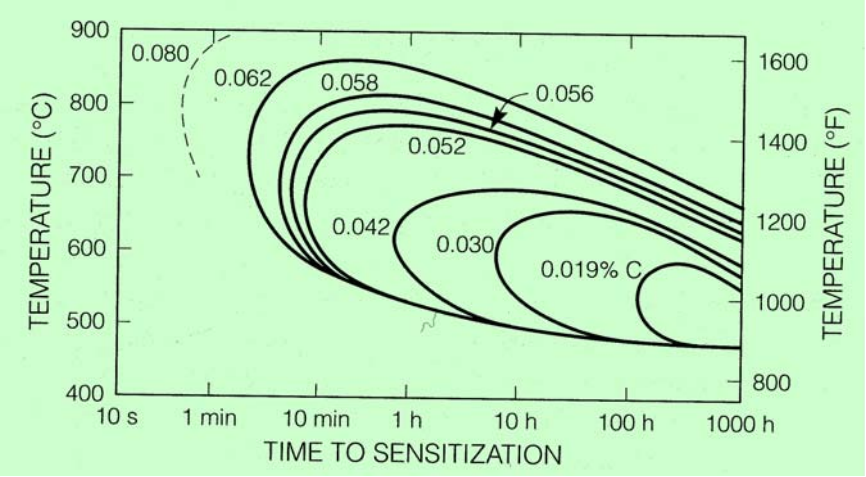
↓

This results from the preferential attack of Cr– depleted zone due to precipitation of $Cr_{23}C_6$ at grain boundary.

Effects of Cr content on the anodic polarization behavior of Fe-Cr alloy



Effects of % C on senitization time of 304

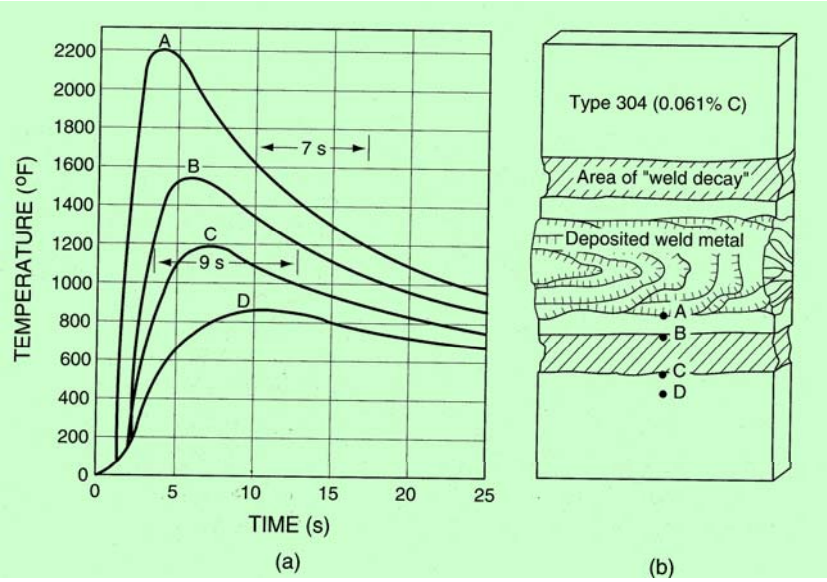


8.3 Weld Decay and Knifeline Attack(KLA)

An intergranular attack in welded structures. The weld decay zone is within the heat affected zone(HAZ) somewhat removed from the weld bead itself. At position B In Fig.3-29, the alloy is in the critical temperature range for sufficient time to produce sensitization. KLA is a highly localized form of IGC that occurs for only a few grain diameters immediately adjacent to the weld bead in Type 321 and 347 austenitic stainless steels.

TABLE 9.1 Temperature Ranges for Sensitization to Intergranular Corrosion in Austenitic Stainless Steels

Temperature	Metallurgical Reactions	Remarks: Unstabilized Nb/Ti Absent (Type 304)	Remarks: Stabilized Nb/Ti Present (Type 321, 347)
Melting Point			
A	All carbides dissolve.	Rapid cooling prevents IGC.	Rapid cooling and reheating to *C* causes KLA. Reheating to *B* prevents KLA.
1230°C (2250°F) *B*	Niobium carbide precipitates. Chromium carbide dissolves.	Rapid cooling prevents IGC.	IGC prevented by precipitating dissolved carbide uniformly.
815°C (1500°F) *C*	Chromium carbide precipitates at grain boundaries.	Sensitization to IGC caused.	No sensitization. Nb/Ti Carbides precipitated at *B*.
425°C (800°F) *D*	No reactions.	Temperature too low for adequate diffusion.	



8.4 Control of IGC

1) Metallurgical measures :

a) Solution annealing : heating the alloy to 1050 C where all Cr-carbides are dissolved, followed by rapid cooling.

b) Low-carbon alloy modifications : lower the carbon content to below 0.03% for austenitic stainless steels(304L, 316L) or to below 50ppm for ferritic stainless steels.

c) Stabilization treatment : add strong carbide former(Ti, Nb) in melt:Types 347 and 321 stainless steels.

2) Environmental measures : lower acidity and less oxidizing conditions will generally reduce the susceptibility to IGC.

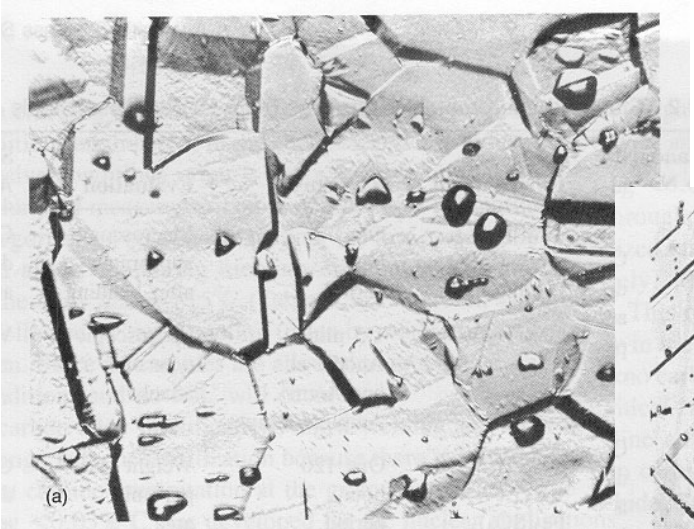
8.5 Tests for detecting sensitization of stainless steels

TABLE 9.2 Standard Intergranular Corrosion Tests for Stainless Steels

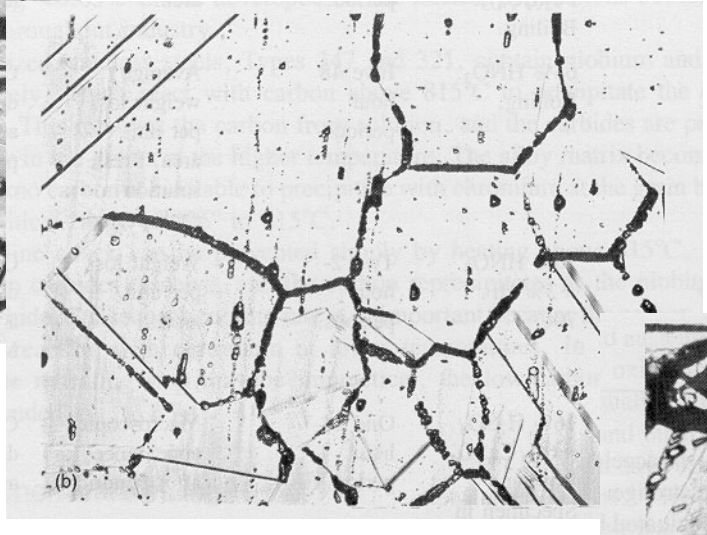
ASTM Standard (Common Name)	Environment	Exposure	Evaluation	Species Attacked
A708-86 (Strauss)	16% H_2SO_4 +6% $CuSO_4$. Boiling.	One 72-hour period.	Macroscopic appearance after bending.	Chromium-depleted area
A262-86 Practice A (Oxalic Etch)	10% $H_2C_2O_4$.	1.5 min. Anodic at one A/cm^2. Ambient temp.	Microscopic type of attack.	Various carbides.
A262-86 Practice B (Streicher)	50% H_2SO_4 +2.5% $Fe_2(SO_4)_3$. Boiling.	One 120 hour period.	Weight loss per unit area.	Chromium-depleted area.
A262-86 Practice C (Huey)	65% HNO_3. Boiling.	Five 48 hour periods.	Average weight loss per unit area. Fresh solution each period.	Chromium-depleted area, σ phase and carbides.
A262-86 Practice D (Warren)	10% HNO_3 +3% HF. 70C	Two 2-hour periods.	Weight loss per unit area.	Chromium-depleted area in Mo bearing steels.
A262-86 Practice E (Copper Accelerated Strauss)	16% H_2SO_4 +6% $CuSO_4$. Boiling. Specimen in contact with copper metal.	One 24-hour period.	Macroscopic appearance after bending.	Chromium-depleted area.

1) Oxalic acid test

Polishing of specimen → Etch the specimen for 1.5 min. at 1.0 A/cm^2 in oxalic acid → Determine the type of surface morphology :

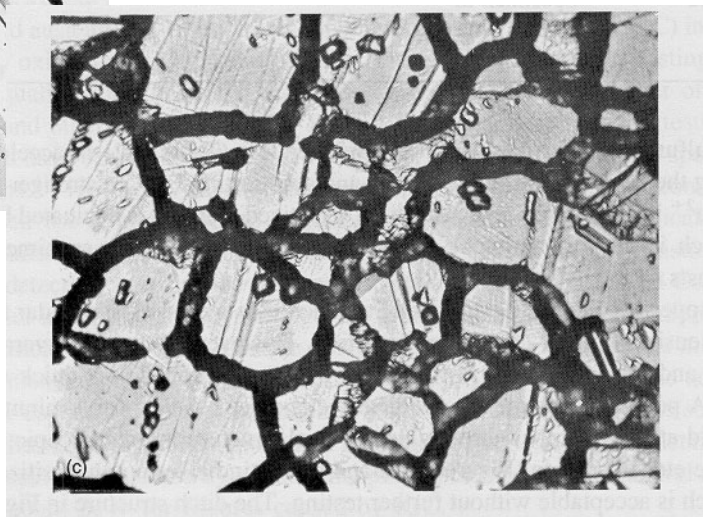


▲ Step



▲ Dual

▼ Ditch



2) Electrochemical Potentiokinetic Reactivation(EPR) Test

A. Single loop test

For 304 stainless steel in 0.5M H_2SO_4 + 0.01M KSCN solution in which the E_{corr} is -400mV,$_{SCE}$.

a. Polarize the alloy to the passivation range or +200mV,$_{SCE}$ and hold there for 2 min.

b. Reverse scan at 6V/hr (1.67mV/sec) to E_{corr}. Obtain E vs. log (current) curve from which electric charge Q during the reactivation process is measured. The Q (the shaded area under the reactivation peak) depends on the total area of the Cr-depleted zone.

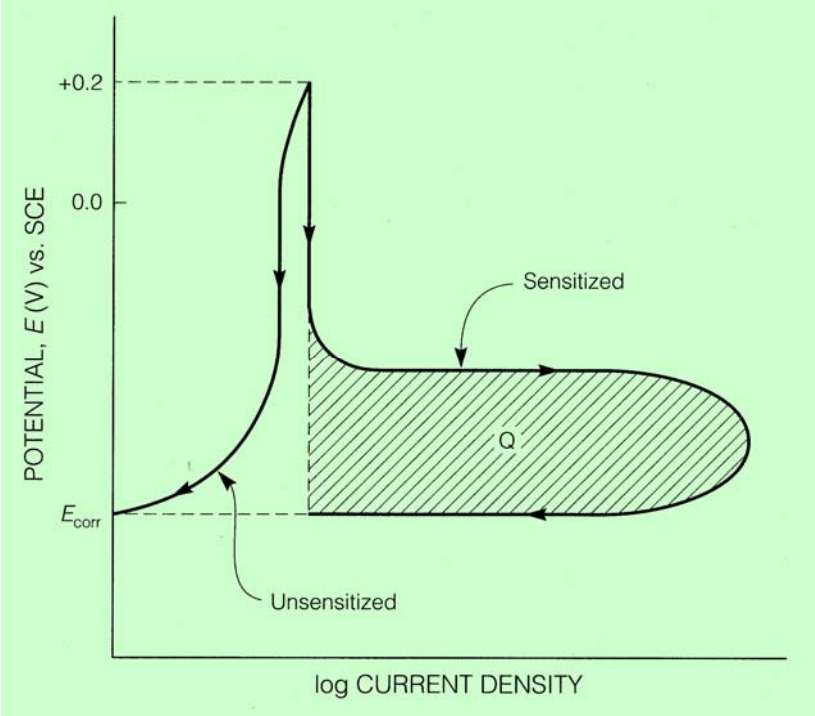
c. A measure of sesitization :

Pa = Q/GBA, Coul/cm^2

GBA(grain boundary area) is calculated from the following eq.

GBA = $A_s[\ 5.095 \times 10^{-3} \exp(0.347x)]$, where A_s is the sample area in cm^2 and x is the ASTM grain size at 100 magnification.

P_a Value	General Interpretation
<2	Unsensitized microstructure, no pitting
2–5	Slightly sensitized microstructure; Pitting and limited intergranular attack
5–15	Sensitized microstructure; Pitting and attack of entire grain boundaries
>15	Heavily sensitized; Strong grain boundary attack

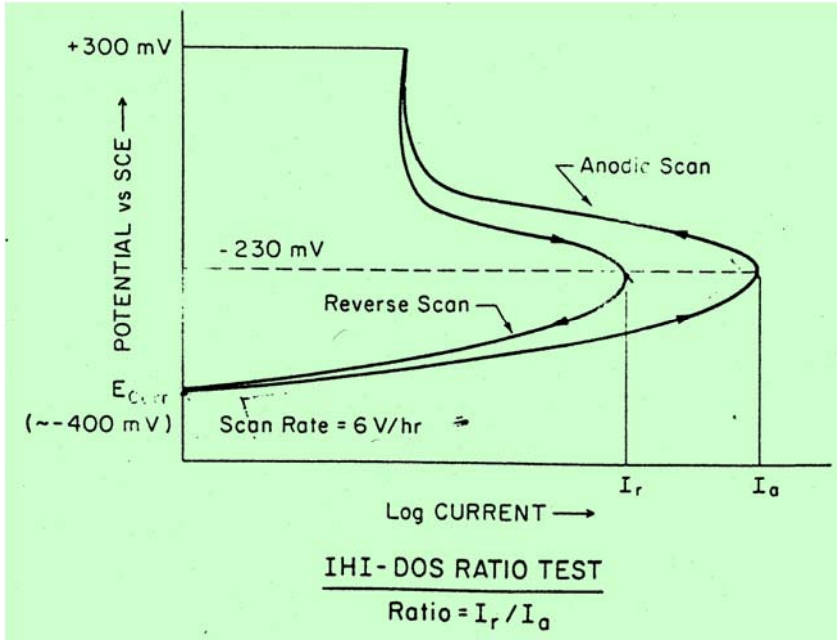


B. Double Loop Test

The testing solution, temperature and cell components are the same as those in the single loop test.

a. Expose the specimen to the solution for about 2 min. to establish the E_{corr}(-400mV,$_{SCE}$).
b. Polarize it anodically to the passivation range of + 300mV,$_{SCE}$ at a rate of 6V/hr.
c. Reverse scan to the E_{corr} at a rate of 6V/hr.
d. Measure the maximum currents for each loop : I_a for the large anodic loop, and I_r for the smaller loop generated during reactivation.

A measure of degree of sensitization = I_r/I_a



8.5 IGC of Other Alloys

1) Ni-Cr alloys

- INCONEL600 (Ni-16Cr-9Fe) alloy fails by IGC and IGSCC in the caustic(alkaline) solutions that concentrate in the crevices.

2) Al alloys

- Al-Mg (5xxx) alloys : Mg_2Al_8 is active to the Al matrix.
- Al-Mg-Zn (7xxx) alloys : $MgZn_2$ is active to the Al matrix.
- Al-Cu (2xxx) and Al-Zn-Mg-Cu(7xxx) alloys : The copper depleted zone adjacent to grain boundary precipitates (Al_2Cu) is attacked anodically.

Predicting IGSCC susceptibility of Alloy 600 using Modified EPR test.

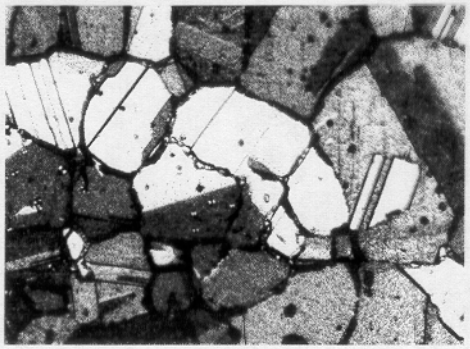
• Ref. M. K. Ahn et al. Corrosion 51(1995) p. 441

▶ IGC & IGSCC : Corrosion damages occurred most frequently in alloy 600 steam generator tubes

Condition of Standard EPR test

Conditions of Standard EPR Test

Electrolyte	0.5 M H_2SO_4 + 0.01 M KSCN
Temperature	30 °C
Vertex potential	600 mV_{SCE}
Scan rate	6 V/h (1.67 mV/s)



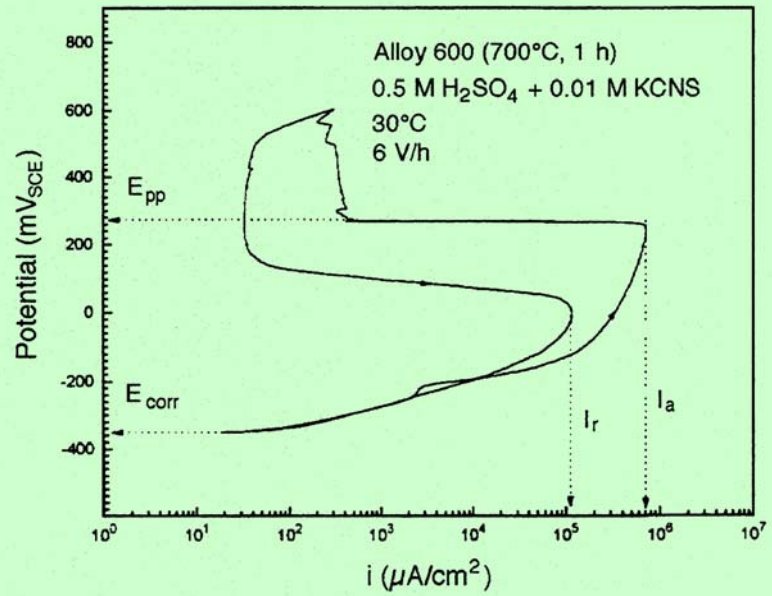


FIGURE 1. *Potentiokinetic curve for alloy 600 aged at 700°C for 1 h and measured in the standard DL-EPR test condition.*

Problem : Severe General corrosion + pitting

Low discriminating power for DOS

→ Too Severe test condition

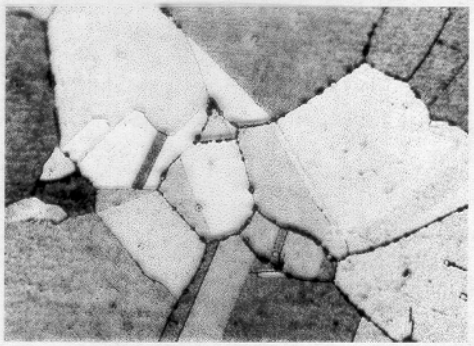
▶ Modified EPR Test

$I_r/I_a = f(\chi_{electrolyte}, T, V_{SCAN})$

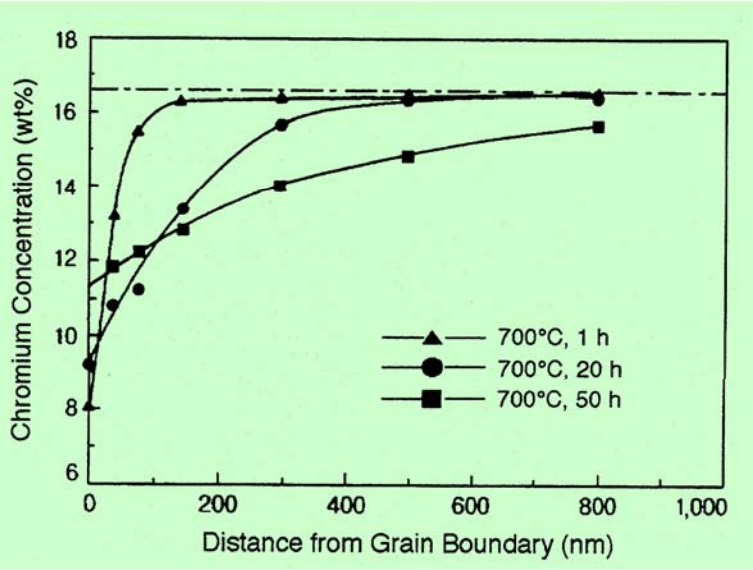
Condition of Modified EPR test

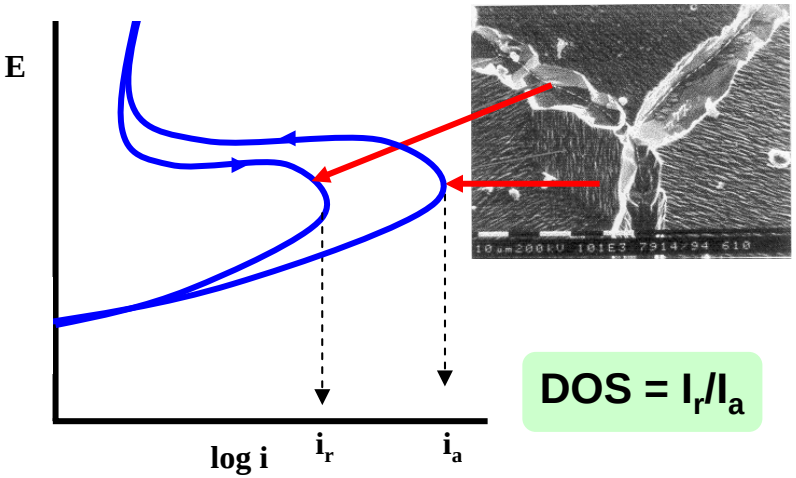
Conditions of Modified EPR Test

Electrolyte	0.01 M H_2SO_4 + 10 ppm KSCN
Temperature	25 °C
Vertex potential	600 mV_{SCE}
Scan rate	0.5 mV/s



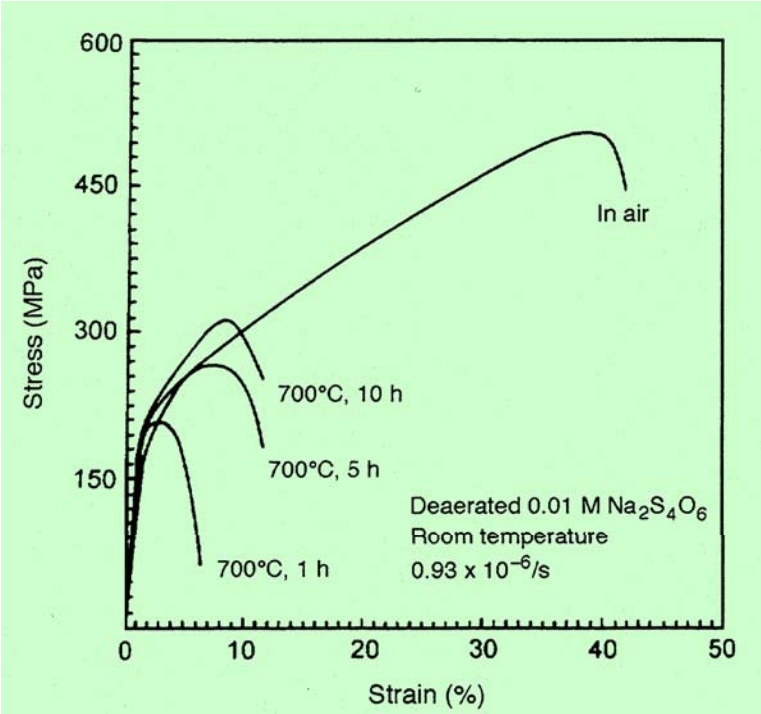
- Selective Grain Boundary attack
- High Discriminating power for DOS of alloy 600.



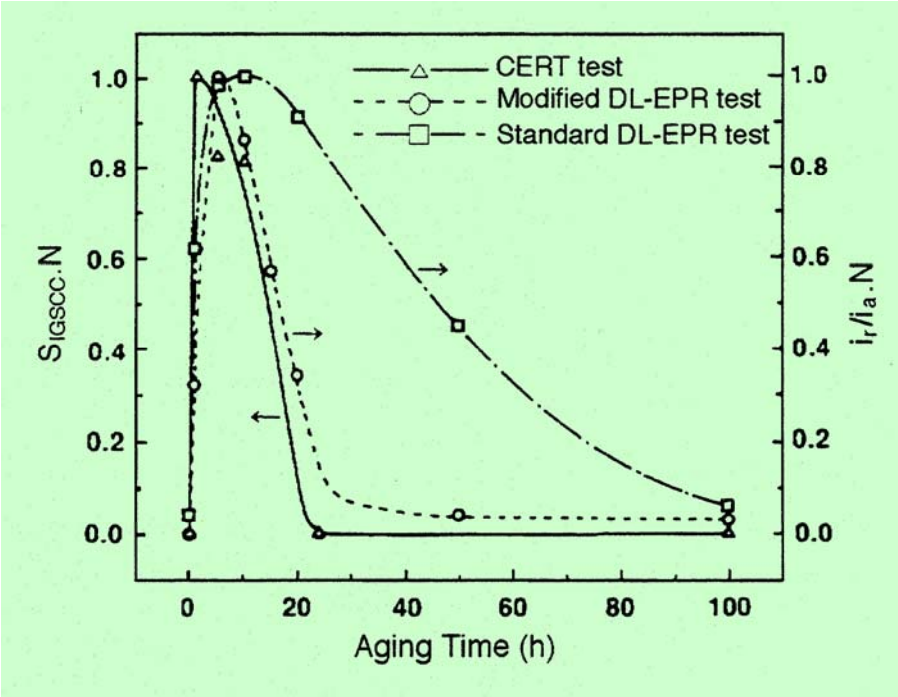


DOS = I_r/I_a

▶ Relationship between EPR test result and IGSCC susceptibility.



Stress vs. strain curves of alloy 600 aged at 700 °C



Comparison between the results of EPR tests and S_{IGSCC} of alloy 600 aged at 700 °C

The Modified DL-EPR test gave a closer correlation to S_{IGSCC} than the standard DL-EPR tests because the modified test attacks the deeper chromium-depleted region selectively, with the shallower chromium-depleted region remained immune.