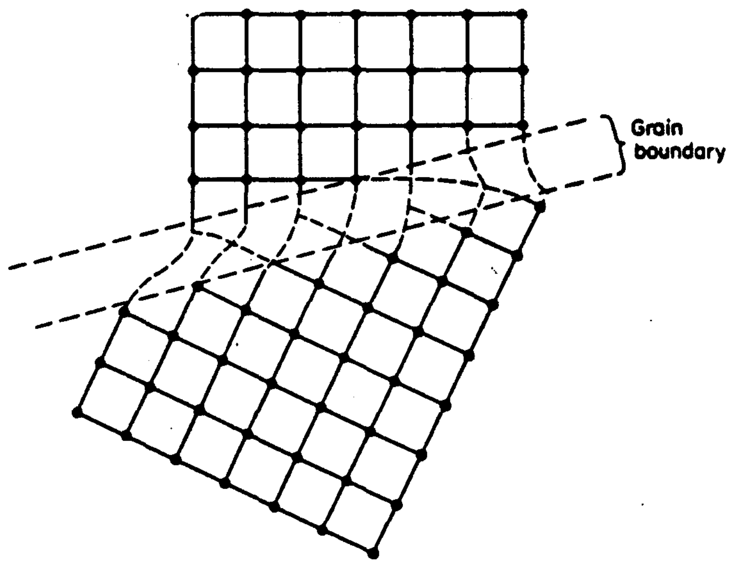
INTERGRANULAR CORROSION

(INTERGRANULAR ATTACK.. "IGA")

Metals are usually "polycrystalline" . . . an assemblage of single-crystal grains separated by grain boundaries.



Grain boundary in a polycrystalline metal (two-dimensional representation).

The atoms in the grain boundaries are in a distorted lattice (i.e., disordered).

The higher energies of grain boundary atoms make them slightly more reactive than grains.

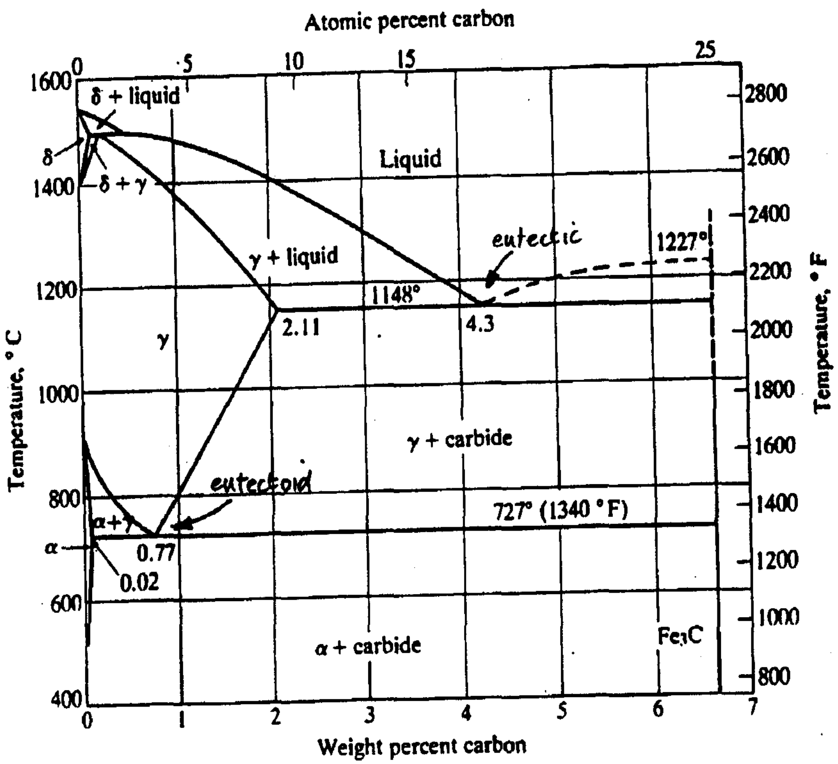
BUT: difference is NOT NOTICEABLE in general corrosion.

SOMETIMES . . . grain boundaries can become highly reactive:

- **by concentration of impurity atoms (e.g., Fe in Al has low solubility, segregates in grain boundaries which corrode more rapidly than grains, and intergranular attack results);**
- **by enrichment of an alloying element (e.g., Zn in brass);**
- **by depletion of an alloying element (e.g., Cr in SS).**

IGA (Intergranular Attack) in Austenitic SS (Stainless Steel)

What is austenite? Consider phase diagram for iron and carbon:



Fe-Fe$_3$ Phase Diagram. The lower-left corner receives prime attention in heat-treating of steels. (In calculations, 0.77 percent is commonly rounded to 0.8 percent.)

Nomenclature

- **cast iron / CS . . . . > 2%C / < 2% C;**
- **δ - iron ("δ - ferrite" not to be confused with ferrite oxides).. is BCC**
- **α - iron ("ferrite") is also BCC;**
- **carbide ("cementite") is Fe_3C;**
- **γ - iron ("austenite") is FCC.**

austenite

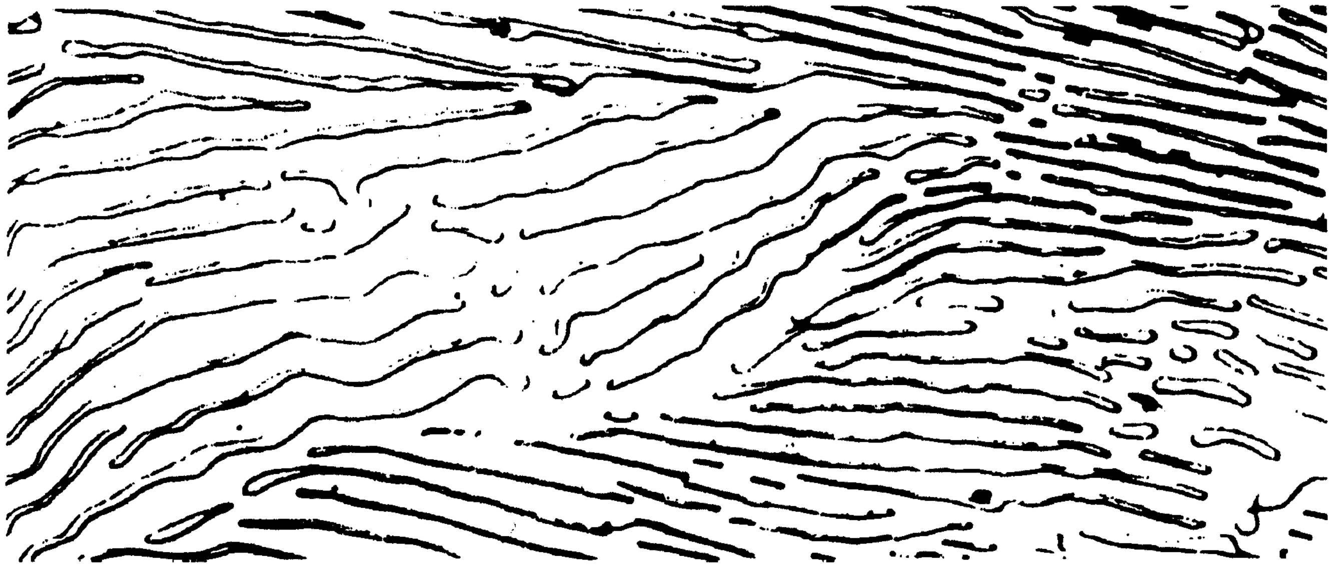
- **is non-magnetic;**
- **is unstable below 727°C**

decomposes on slow cooling to ferrite + pearlite if hypoeutectoid;

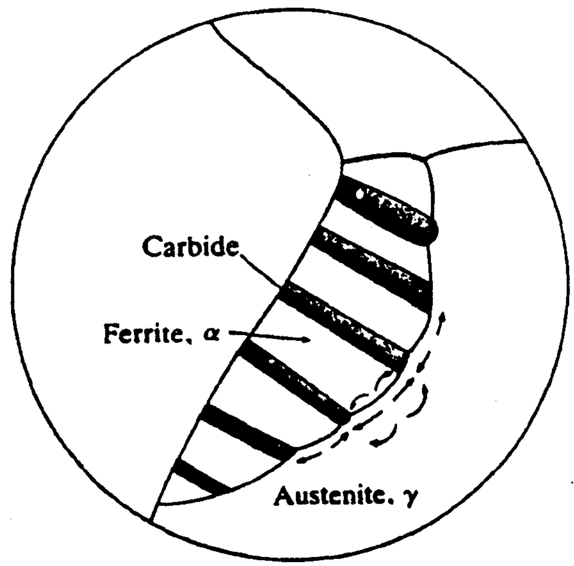
pearlite + eutectic if hyperentectoid

(N.B. "pearlite" is the lamellar mixture of ferrite and carbide that forms on cooling austenite of eutectoid composition . . . 0.8% C).

Pearlite. This microstructure is a lamella mixture of ferrite (lighter matrix) and carbide (darker). Pearlite forms from austenitic of eutectoid composition. Therefore, the amount and composition of pearlite are the same as those of eutectoid austenite.



Pearlite Formation. Carbon must diffuse from the eutectoid austenite (~0.8 percent) to form carbide (6.7 percent). The ferrite that is formed has negligible carbon.



AUSTENITE decomposes on rapid cooling below 727°C (i.e., "quenching") to:

"MARTENSITE" - a metastable forced solution of C in ferrite that is very hard, has BCT (body-centered-tetragonal) structure.

N.B. IN STAINLESS STEELS, THE THREE MAJOR CARBON STEEL PHASES (FERRITE, AUSTENITE, MARTENSITE) CAN ALSO BE FORMED.

Also:

- **"ferritic-austenitic" ("duplex")**
- **"precipitation-hardened".**

Stability and mechanical/physical properties depend on combination of alloying elements.

austenite stabilizers: C, N, Mn, Ni, (q.v. Ni alloys);

ferrite stabilizers: Si, Cr, Mo, Nb (Columbium"- Cb - ugh!), Ti.

Selection of a steel/alloy for a particular application depends on mechanical or physical property considered to be most important.

Unified Numbering System

n. Iron & Steel Inst.

Chemical composition of stainless steels

AISI type	UNS number	%C	%Cr	%Ni	% other elements	Remarks
			Group I Martensitic chromium steels			
410	S 41000	0.15 max	11.5–13.5	—	—	Turbine blades, valv trim
416	S 41600	0.15 max	12–14	—	Se, Mo, or Zr	"Free" machining
420	S 42000	0.35–0.45	12–14	—	—	Cutlery
431	S 43100	0.2 max	15–17	1.25–2.5	—	Improved ductility
440A	S 44002	0.60–0.75	16–18	—	—	Very hard; cutters
			Group II Ferritic nonhardenable steels			
405	S 40500	0.08 max	11.5–14.5	0.5 max	0.1–0.3 Al	Al prevents hardenir
430	S 43000	0.12 max	14–18	0.5 max	—	Auto trim, tablewar
442	S 44200	0.25 max	18–23	0.5 max	—	Resists O and S at h temperatures
446	S 44600	0.20 max	23–27	0.5 max	0.25*N* max	
			Group III Austenitic chromium-nickel steels			
201	S 20100	0.15 max	16–18	3.5–5.5	5.0–7.5 Mn 0.25*N* max	Mn substitute for N
202	S 20200	0.15 max	17–19	4–6	7.5–10 Mn 0.25*N* max	Mn substitute for N
301	S 30100	0.15 max	16–18	6–8	2 Mn max	Strain hardens
302	S 30200	0.15 max	17–19	8–10	2 Mn max	Architectural uses
302B	S 30215	0.15 max	17–19	8–10	2–3 Si	Si for high-temp. oxidation
304	S 30400	0.08 max	18–20	8–12	1 Si max	Continuous 18-8S
304L	S 30403	0.03 max	18–20	8–12	1 Si max	Very low carbon
308	S 30800	0.08 max	19–21	10–12	1 Si max	"High" 18-8
309	S 30900	0.2 max	22–24	12–15	1 Si max	25-12, heat resistan
309S	S 30908	0.08 max	22–24	12–15	1 Si max	Lower carbon
310	S 31000	0.25 max	24–26	19–22	1.5 Si max	25-20, heat resistan
310S	S 31008	0.08 max	24–26	19–22	1.5 Si max	Lower carbon
314	S 31400	0.25 max	23–26	19–22	1.5–3.0	Si for high-temp. oxidation
316	S 31600	0.10 max	16–18	10–14	2–3 Mo	18-8S Mo
316L	S 31603	0.03 max	16–18	10–14	2–3 Mo	Very low carbon
317	S 31700	0.08 max	18–20	11–14	3–4 Mo	Higher Mo
321	S 32100	0.08 max	17–19	8–11	Ti 4 × C(min)	Ti stabilized
347	S 34700	0.08 max	17–19	9–13	Cb + Ta 10 × C(min)	Cb stabilized
Alloy 20*	J 95150	0.07 max	29	20	3.25 Cu, 2.25 Mo	Best corrosion resis
			Group IV Age-hardenable steels*			
322	—	0.07	17	7	0.07 Ti, 0.2 Al	
17-7PH†	S 17700	0.07	17	7	1.0 Al	
17-4PH†	S 17400	0.05	16.5	4.25	4.0 Cu	
14-8MoPH†	S 13800	0.05 max	14	8.5	2.5 Mo, 1% Al	
AM350†	S 35000	0.10	16.5	4.3	2.75 Mo	
CD4MCu‡	—	0.03	25	5	3.0 Cu, 2.0 Mo	

*Typical compositions

†Commercial designations

‡Cast form only

Sensitization:

Cr is added to steels to make them "stainless". The Cr-rich oxide film (based on Cr_2O_3) is thin, adherent and very protective.

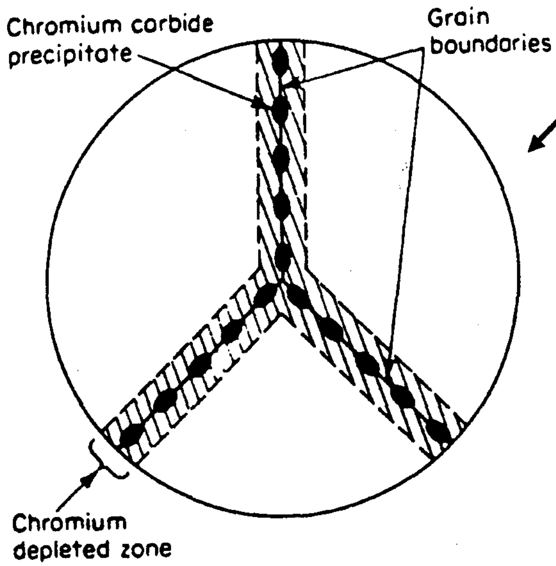
BUT if heated into range 510-790°C, the steels "sensitize" and become prone to IGA.

Sensitization involves the precipitation of Cr carbide ($Cr_{23}C_6$) at the grain boundaries; at the high temperature its solubility is virtually zero.

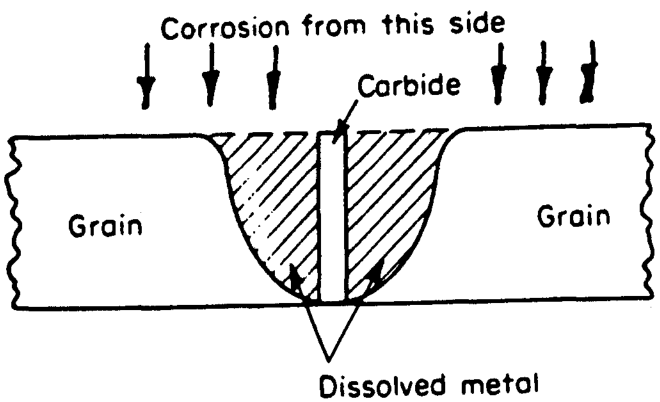
The C diffuses readily, and the disorder in the boundaries provides nucleation sites.

This depletes the boundaries of Cr.

Sensitization (continued)



Diagrammatic representation of a grain boundary in sensitized type 304 stainless steel.



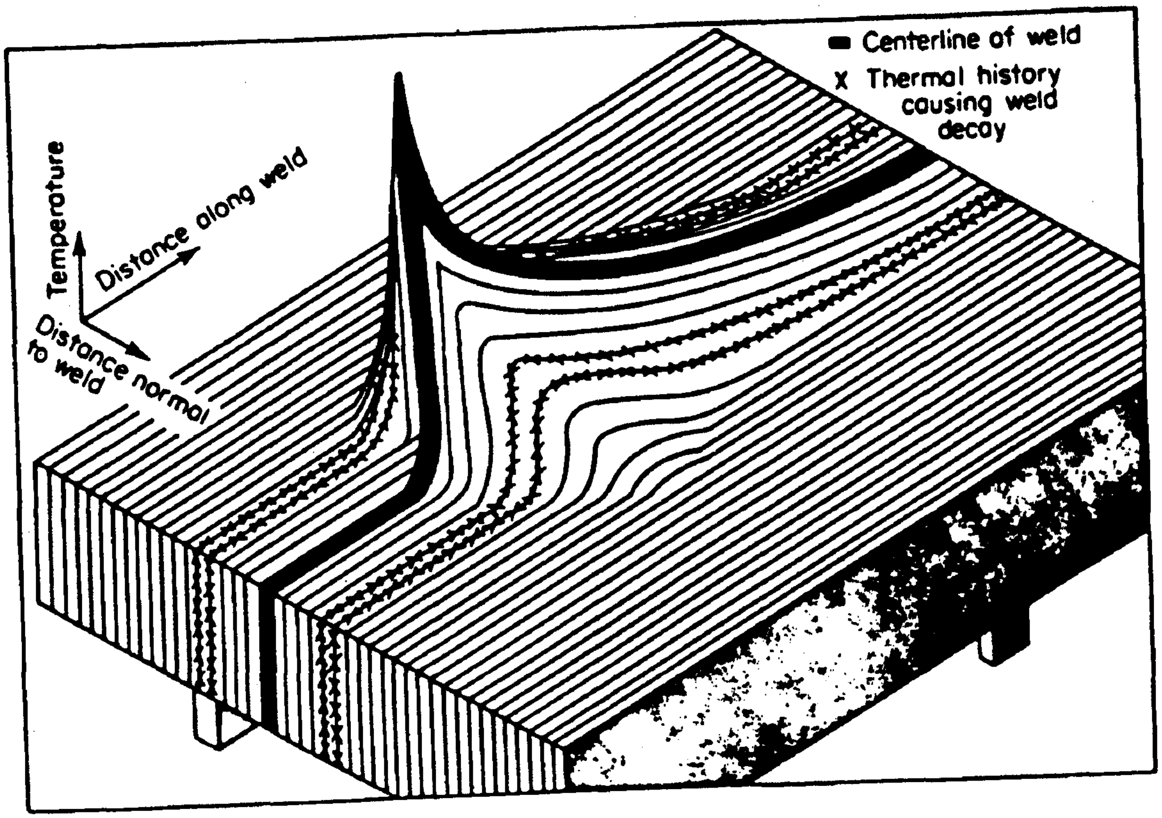
Cross section of area shown above.

Electron photomicrograph of carbides isolated from sensitized type 304 stainless steel.

Sensitization by welding, or "Weld Decay"

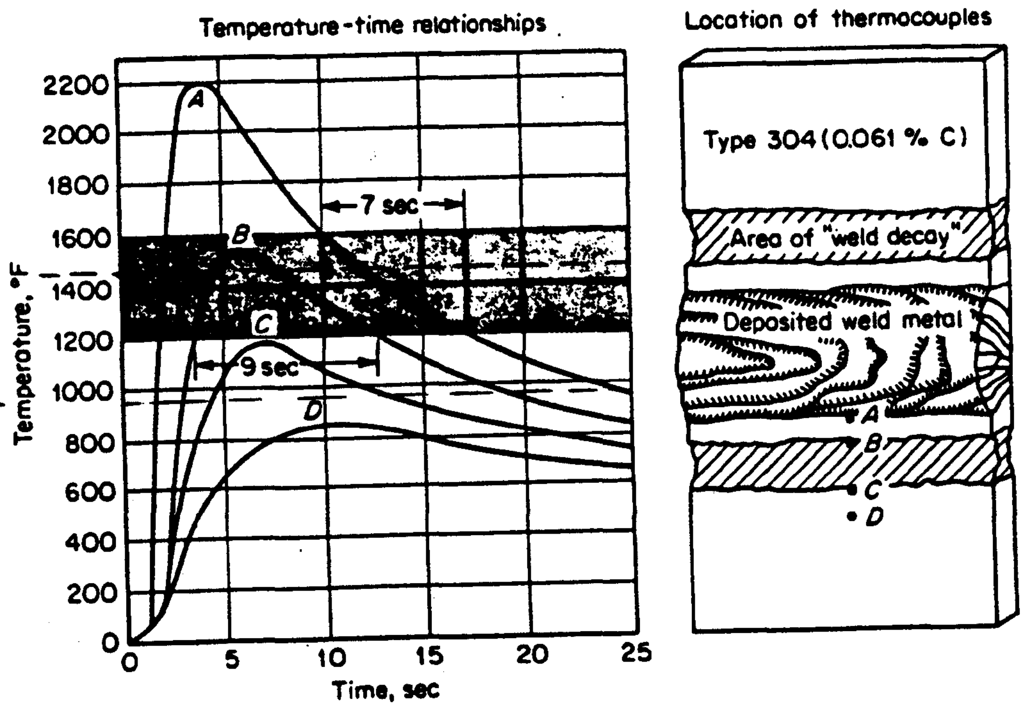
During welding, the weld "bead" and the metal on either side pass through the temperature range for sensitization.

Temperature AND time are crucial for carbide precipitation: sensitized areas are on either side of the bead.



Tablecloth analogy of heat flow and temperatures during welding. The rise and fall of each stripe represents the rise and fall of temperature in a welded plate.

sens. range should be here



(a) (b)

time within correct range ...

A 13s
B 12s
C $8\frac{1}{2}$s
D —

Temperatures during electric-arc welding of type 304 stainless steel.

Actual measurements made with thermocouples at points ABCD. Fontana says metal at and between points B and C within sensitizing range for some time.

Discuss

N.B. Sensitized SS can be used in many environments which are not too aggressive or where selective corrosion not a problem (domestic, architecture).

Minimizing IGA of SS

(1) Heat Treatment "Quench - Annealing"

or ... "Solution - Annealing"

or .... "Solution - Quenching"

Involves heating to above Cr carbide precipitation temperature to dissolve carbides, then water-quenching to cool through sensitization range rapidly.

Most austenitic SS supplied in solution-quenching condition; if welded during fabrication, must be quench-annealed to avoid weld decay during subsequent exposure to corrosive environments.

Solution-quenching of large components can be a problem.

Discuss: why not heat-treat just the weld region?

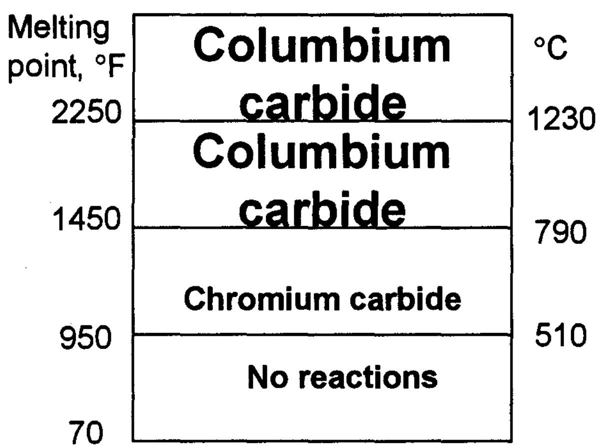
(2) Alloy "stabilization"

Elements that are strong carbide formers are added:

Nb (or Nb+Ta) $\longrightarrow$ type 34 > SS

Ti $\longrightarrow$ type 32 > SS

Important to ensure that Nb (for example) carbide has precipitated, so that Cr Carbide cannot precipitate and reduce corrosion resistance at grain boundaries (REMEMBER - it is the Cr that provides the corrosion resistance, <u>not</u> the stabilizer).



Schematic chart showing solution and precipitation reactions in type 304 and 347.

Stabilized SS from supplier usually heat-treated by quenching from ~1070°C.

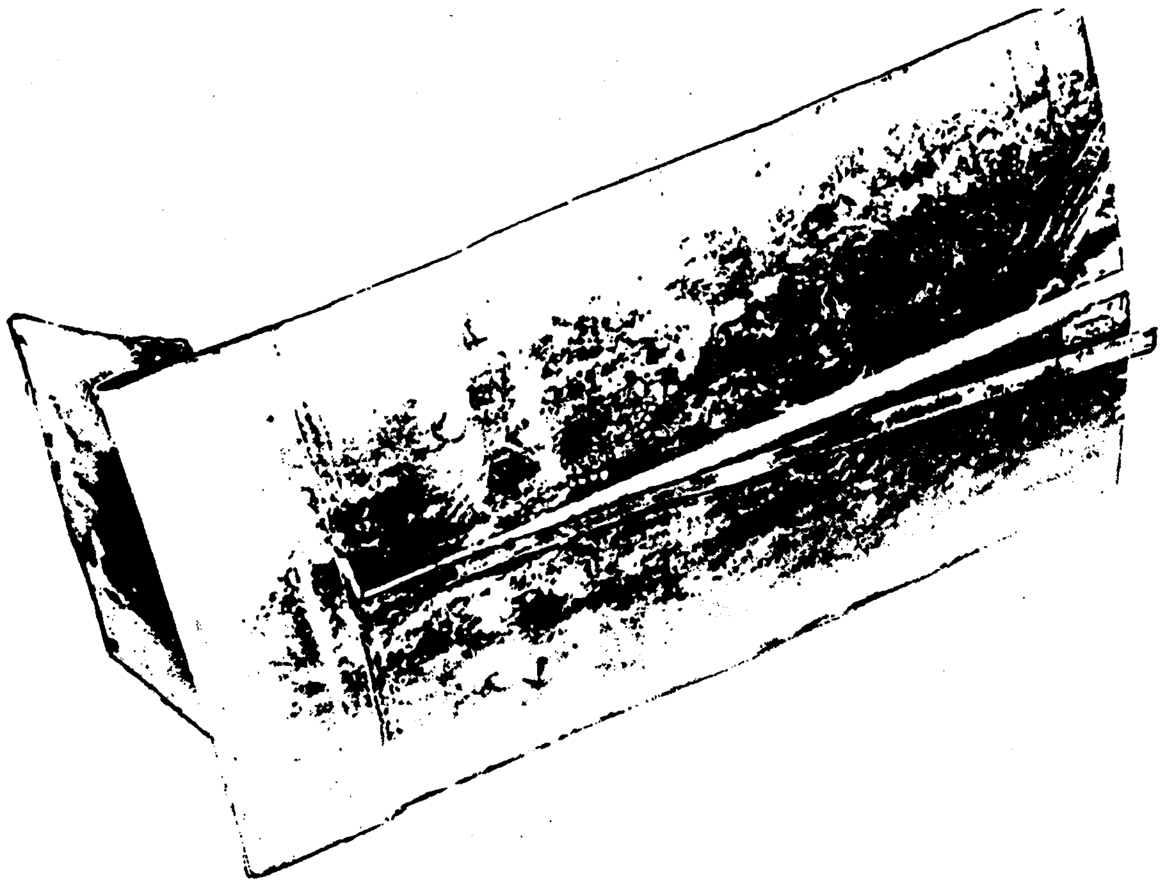
- **Nb carbide has precipitated,**
- **Cr left in solution, hence no C available for any reactions with Cr at lower temperatures.**

HOWEVER, care is needed during welding etc.

If welding involves a <u>rapid</u> cooling of metal from temperatures just at or below the melting point (as can occur in thin sheets), BOTH Nb and Cr remain in solution.

This metal can now be sensitized if it is heated to the Cr carbide precipitation range (510 - 790°C, as might occur during a stress-relief).

"Knife-Line-Attack" (KLA) may now occur in narrow band next to weld if exposed to corrosive environment.

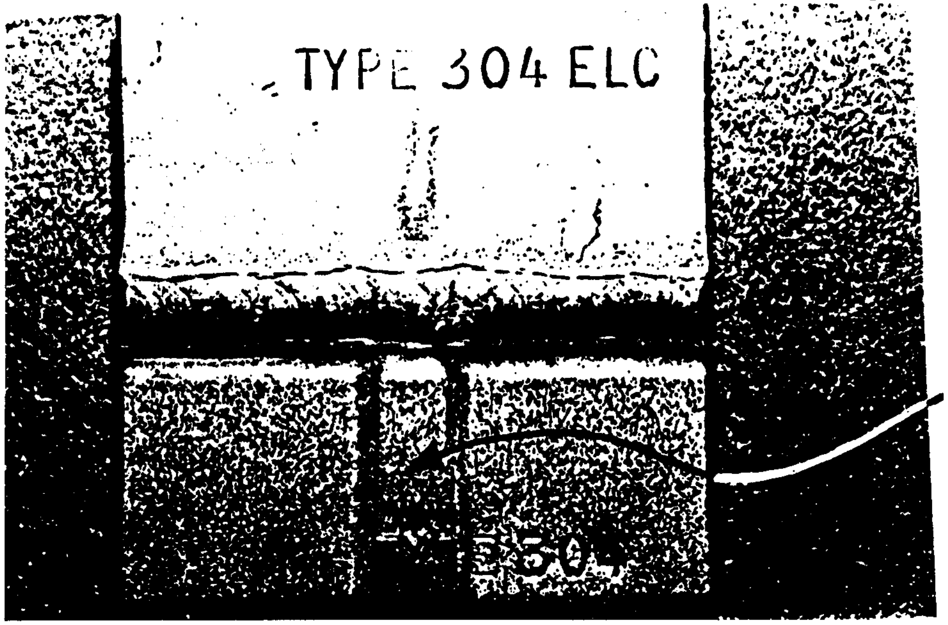


Knife-line attack on type 347 stainless steel.

Should have been heat-treated between 790 & 1230 °C (Nb carbide precipitates, Cr dissolves).

(3) Use "Low-Carbon" (< 0.03%) Alloy.

At concentrations < 0.03%, not enough C can precipitate as Cr carbide to sensitize. Get "L-Grade" or "ELC" alloys e.g., "type 304L".



Elimination of weld decay by type 304L.

weld bead at back

<u>N.B.</u> Must take care to avoid C contamination during casting, welding, etc.

<u>Other Alloys and IGA</u>

Alloy with precipitated phases may also show IGA:

- **Duralumin(um) Al-Cu can precipitate $CuAl_2$ and deplete Cu locally;**
- **Die-cast Zn alloys containing Al... IGA in steam, marine environments;**
- **Minor IGA effects in many Al alloys.**