SELECTIVE LEACHING ("Dealloying", "Parting")

Corrosion in which one constituent of an alloy is preferentially removed, leaving behind an altered (weakened) residual structure.

Can occur in several systems.

Combinations of alloys and environments subject to dealloying and elements preferentially removed

Alloy	Environment	Element removed
Brasses	Many waters, especially under stagnant conditions	Zinc (dezincification)
Gray iron Aluminium bronzes	Soils, many waters Hydrofluoric acid, acids containing Chloride	Iron (graphitic corrosion) Aluminium (dealuminification
Silicon bronzes	High-temperature steam and acidic species	Silicon (desiliconification)
Tin bronzes Copper nickels	Hot brine or steam High heat flux and low water velocity (in refinery condenser tubes)	Tin (destannification) Nickel (denickelification)
Copper-gold single crystals Monels	Ferric chloride Hydrofluoric and other acids	Copper Copper in some acids, and nickel in others
Gold alloys with copper or silver High-nickel alloys	Sulfide solutions, human saliva Molten salts	Copper, silver Chromium, iron, molybdenum and tungsten
Medium-and high-carbon steels	Oxidizing atmospheres, hydrogen at high temperatures	Carbon(decarburization)
Iron-chromium alloys	High-temperature oxidizing atmospheres	Chromium, which forms a protective film
Nickel-molybdenum alloys	oxygen at high temperature	Molybdenum

Dezincification

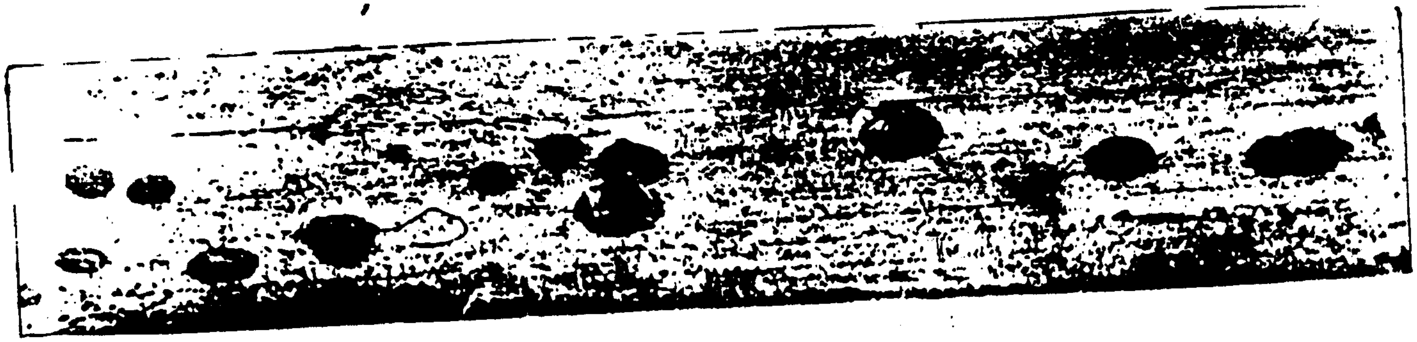
An Cu-Zn alloys (Brasses) containing > 15% Zn are susceptible . . .

e.g. common "yellow" brass . . . 30Zn 70Cu, "dezincifies" to red copper-rich structure. Dezincification can be uniform...

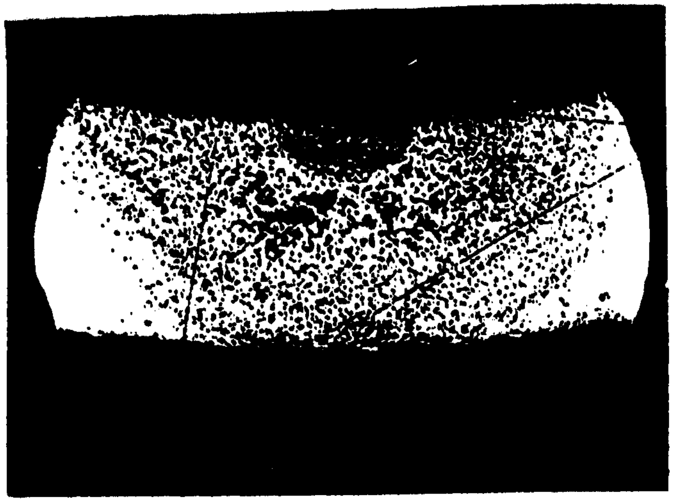
- potable water inside

Uniform dezincification of brass pipe.

- or "plug-type".... (boiler water inside, combustion gases outside)



Plug-type dezincification.



Section of one of the plugs shown before

Overall dimensions of original material tend to be retained . . . residual is spongy and porous . . . often brittle.

Can go unnoticed, especially if covered with dirt/deposit, etc.

<u>Uniform dezincification</u>...

- usually found in high brasses (high[Zn]), acid environments;

<u>Plug-type dezincification</u>...

- usually found in low brasses, alkaline, neutral or slightly acid environments.

Mechanism

(1) Zn atoms leave lattice sites . . .

"are leached into the environment selectively"

Discuss . . . w.r.t. last picture.

(2.) Generally accepted . . .

- brass dissolves;
- Zn stays in solution;
- Cu re-deposits.

Discuss . . . w.r.t. last picture.

N.B. possibility for local anode-cathode couples .. Cu deposits accelerate attack.

N.B. dezincified areas generally 90-95% Cu; some Cu_2O/CuO present if O_2 in the environment.

Prevention

- Make environment less aggressive (e.g., reduce O_2 content);
- Cathodically protect;
- Use a better alloy (common cure - above not usually feasible)...
  - "red" brass (15% Zn) almost immune
  - Admiralty Brass. . . 70 Cu, 29 Zn, 1 Sn;
  - arsenical Admiralty. . . 70 Cu, 29 Zn, 1 Sn, 0.04 As

    (Sn and Sn-As in deposited films hinder redeposition of Cu).
- For very corrosive environments likely to provoke dezincification, or for critical components, use . . .
  - cupronickels 70-90 Cu, 30-10 Ni.

"Graphitization" (misnomer . . . graphitization is the breakdown of pearlite to ferrite + C at high Temperature)

"Gray" cast iron is the cheapest engineering metal . . . 2-4% C, 1-3% Si.

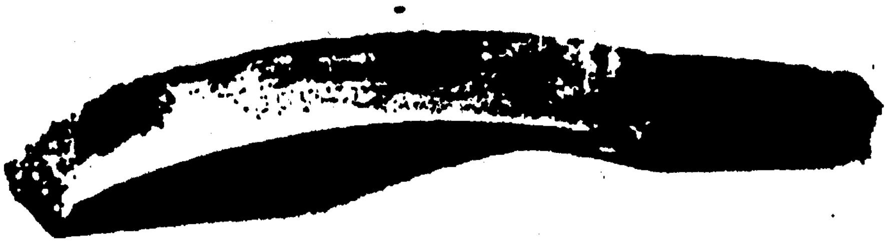
Hard, brittle, easily cast; carbon present as microscopic flakes of matrix graphite within microstructure.

Microstructure of gray cast iron.

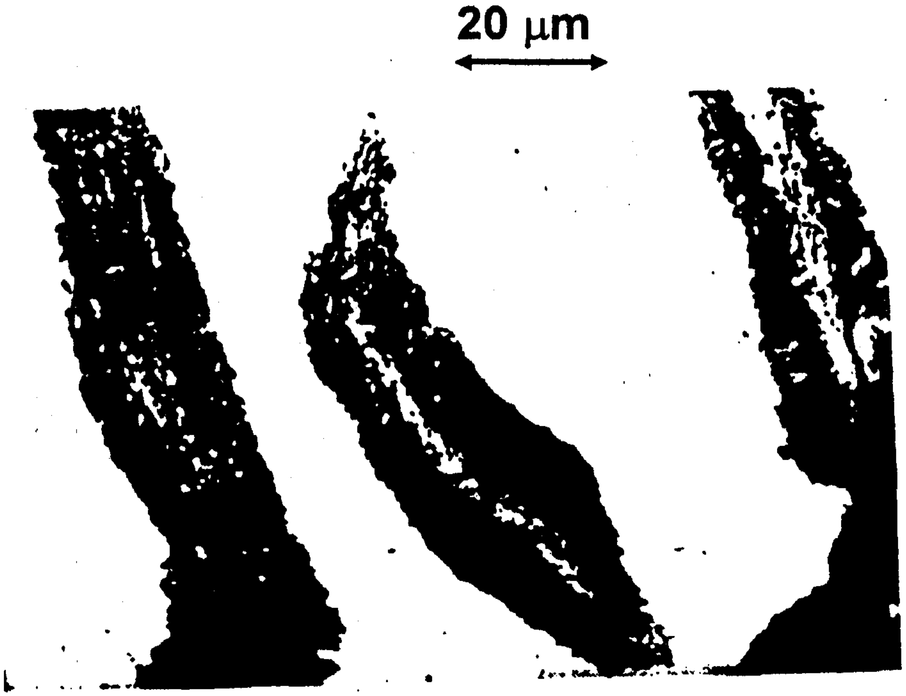
In some environments (notably mild, aqueous soils affecting buried pipe) the Fe leaches out slowly and leaves graphite matrix behind . . . appears graphitic . . . soft . . . can be cut with a knife. Pores usually filled with rust. Original dimensions are retained.

A 200-mm (8-in.) diameter gray iron pipe that failed because of graphic corrosion. The pipe was part of a subterranean fire control system. The external surface of the pipe was covered with soil; the internal surface was covered with water. Severe graphitic corrosion occurred along the bottom external surface where the pipe rested on the soil.

The small-diameter piece in the foreground is a gray iron pump impeller on which the impeller vanes have disintegrated because of graphitic corrosion.



(a) External surface (a) of the gray iron pipe exhibiting severe graphitic corrosion.



(c) Micrograph of symmetrical envelopes of graphitically corroded iron surrounding flakes of graphite.

(b) Close-up of the graphitically corroded region shown in (a).

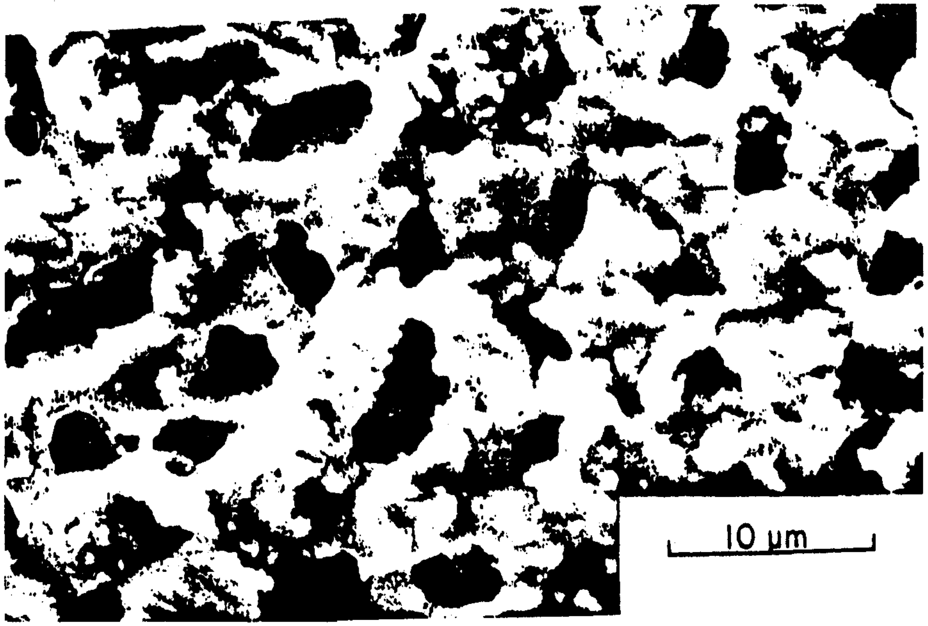
Selective Dissolution in Liquid Metals

In liquid metal coolants (LMFBR with Na or Na-K coolant), austenitic alloys can lose Ni and Cr and revert to the ferrite phase...

Corrosion of Inconel* alloy 706 exposed to liquid sodium for 8,000 hours at 700°C (1290°F); hot leg circulating system. A porous surface layer has formed with a composition of ~ 95% Fe, 2% Cr and < 1% Ni. The majority of the weight loss encountered can be accounted for by this surface degradation. Total damage depth: 45 µm. (a) Light micrograph. (b) SEM of the surface of the porous layer.

*** Alloy 706 ... 39-44% Ni, 14.5-17.5% Cr, 0.06% C.**

Also in fusion-reactor environments (Li as coolant)....

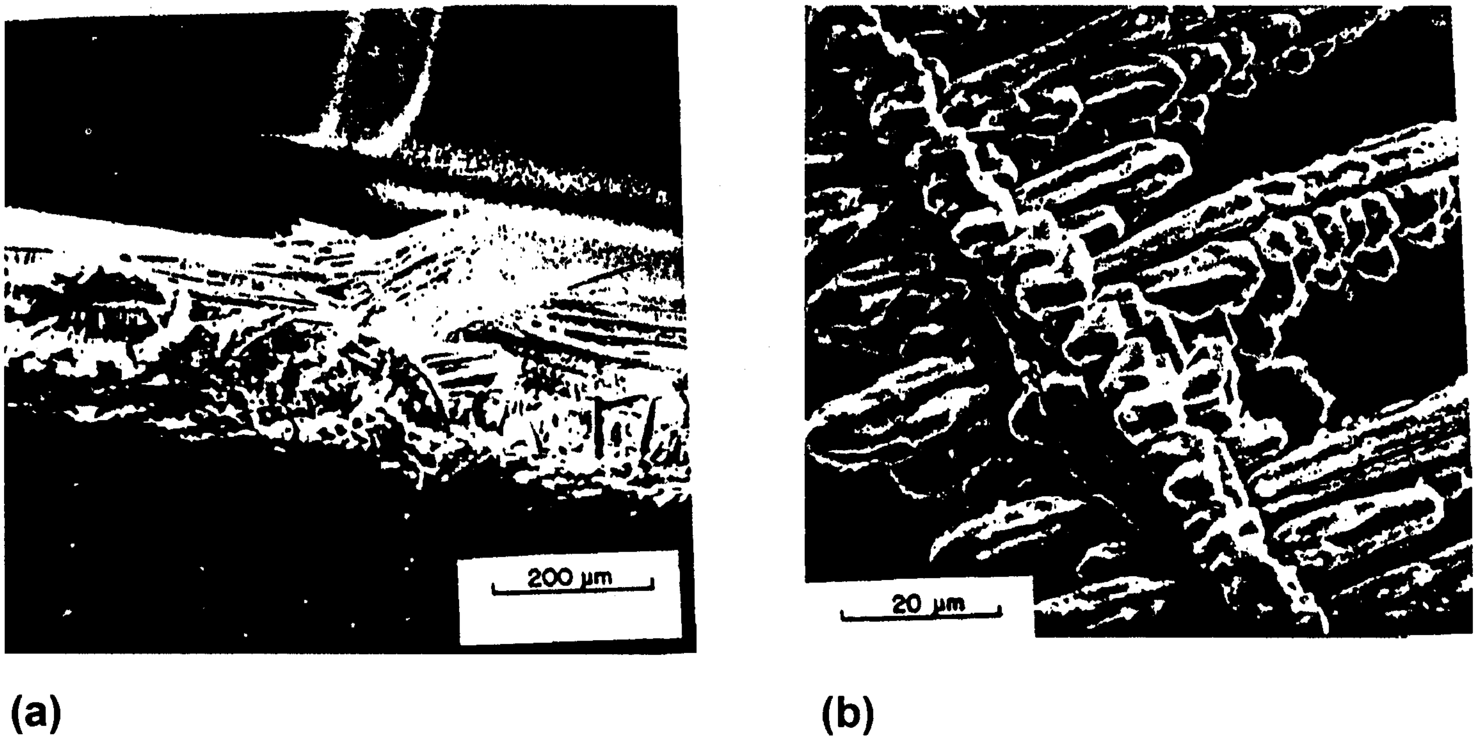


Light micrograph of cross-section.

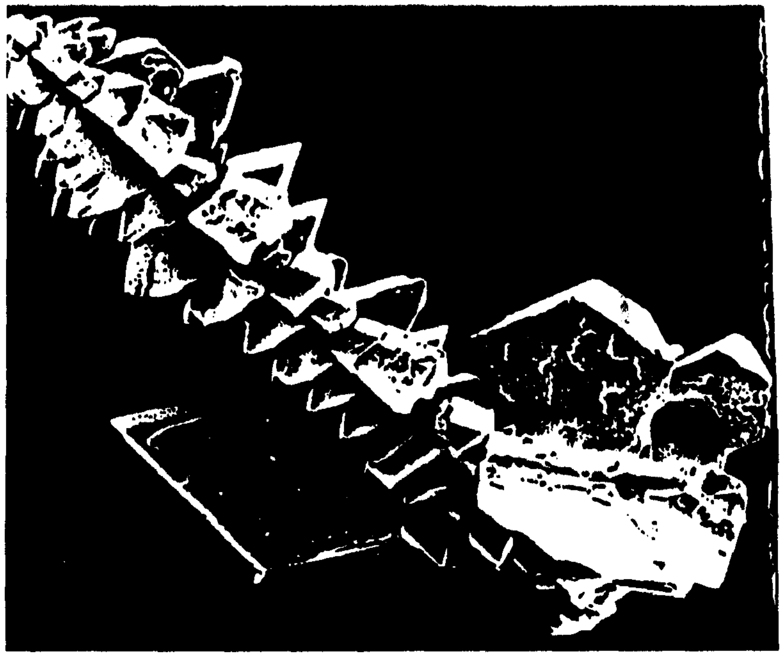
SEM of surface showing porous layer.

Corrosion of type 316 stainless steel exposed to thermally convective lithium for 7488 hours at the maximum loop temperature of 600°C.

Usually, the transport and deposition of leached elements is of more concern than the actual corrosion.



SEM micrographs of chromium mass transfer deposits found at the 460°C (860°C) position in the cold leg of a lithium/type 316 stainless steel thermal convection loop after 1700 hours. Mass transfer deposits are often a more serious result of corrosion than wall thinning. (a) Cross section of specimen on which chromium was deposited. (b) Top view of surface.



Iron crystals found in a plugged region of a failed pump channel of a lithium processing test loop.

SEM

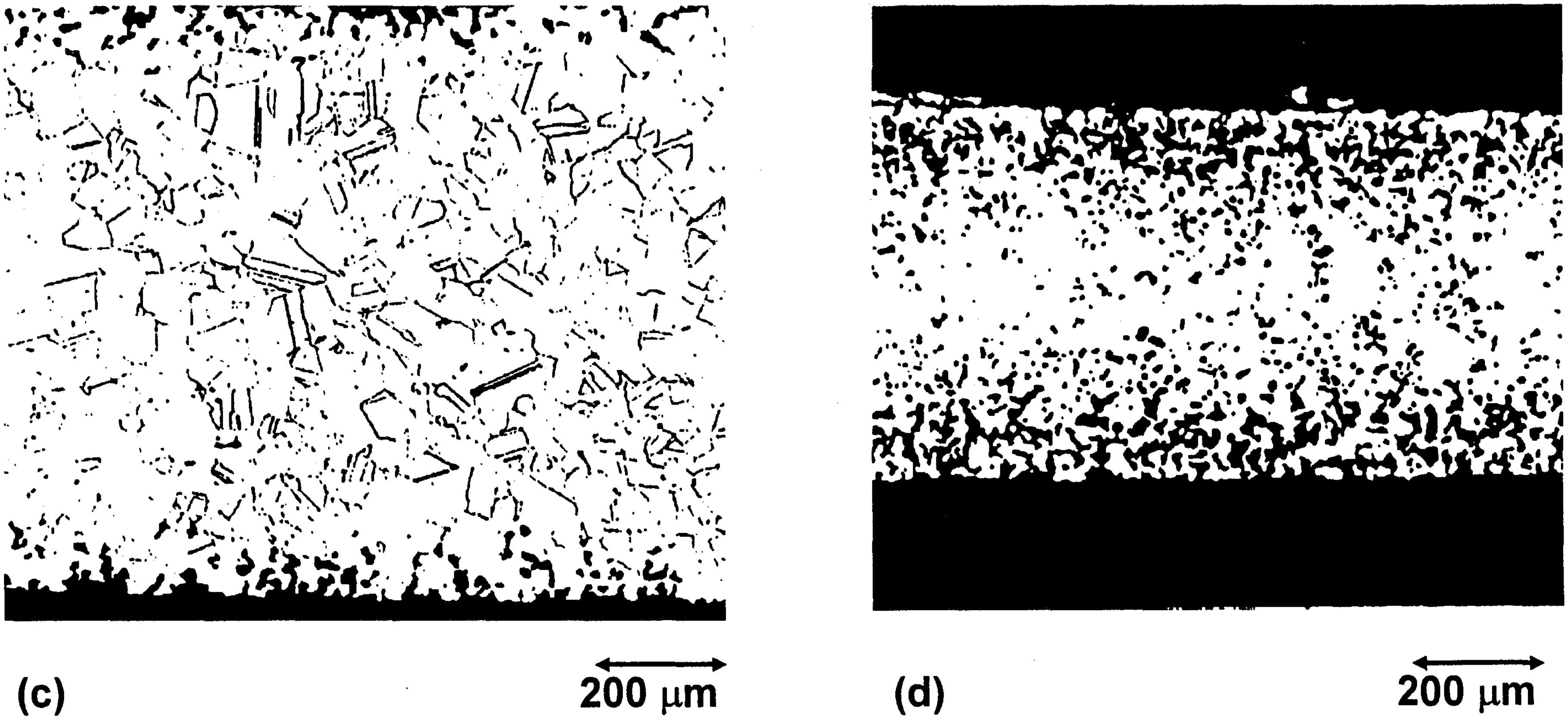
100 μm
⟷

Selective Leaching in Molten Salts

Molten salts are ionic conductors (like aqueous solutions) and can promote anodic-cathodic electrolytic cells . . . they can be aggressive to metals.

ALSO . . . some molten salts (notably fluorides) are "Fluxes" and dissolve surface deposits that would otherwise be protected:

dealloying of Cr from Ni-base alloys and stainless steels can occur in the surface layers exposed to molten fluorides; the vacancies in the metal lattice then coalesce to from subsurface voids which agglomerate and grow with increasing time and temperature.



(c) microstructure of type 304L SS exposed to LiF-BeF$_2$-ZrF$_4$-ThF$_4$- UF$_4$ (70-23-5-1-1 mole % respectively) for 5700 hours at 688°C.

(d) microstructure of type 304L SS exposed to LiF-BeF$_2$-ZrF$_4$-ThF$_4$- UF$_4$ (70-23-5-1-1 mole % respectively) for 5724 hours at 685°C.