UMET
Unité Matériaux Et Transformations

Chimie Lille
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE

STAINLESS STEELS

Jean-Bernard VOGT

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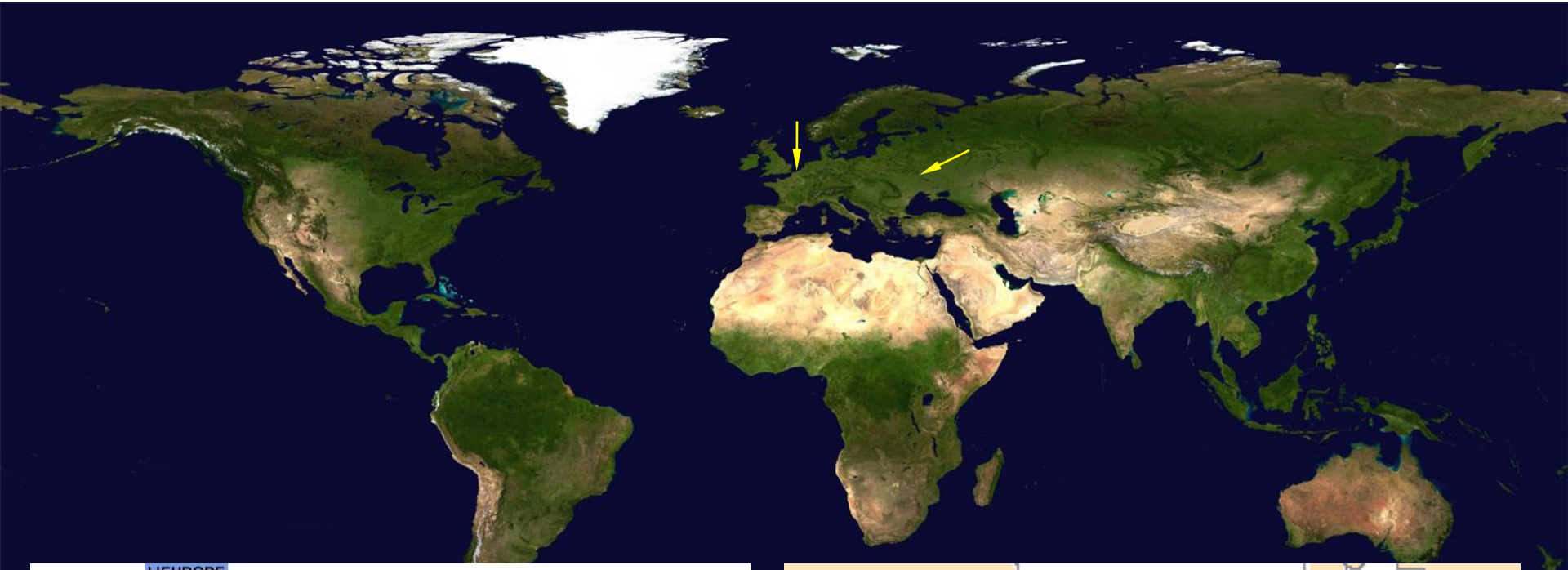


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Paris

Lille

Very close to Lille

My Gradutae school: ENSCL: fact and figures

Located on the campus of Lille University of Sciences and Technologies

Founded in 1894

Master's degree

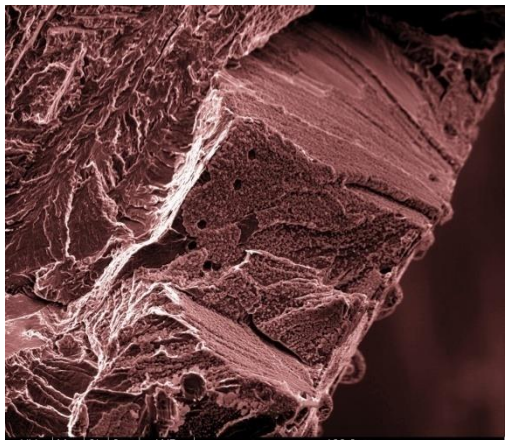
400 students

3500 alumni students

140 professors and assistant professors

(40 from industry)

2 internationally recognized research laboratories



MMATENG

Chimie Lille
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE

Tempus

January 21, 2015 the MMATENG group at the main entrance of the school

21.01.2015 master classes, visit of laboratories and visit of Lille

Unité Matériaux et Transformations

Materials and Processing Laboratory

CNRS UMR 8207 –
Université Lille 1 et Ecole Nationale Supérieure de Chimie de Lille

umet.univ-lille1.fr

UMET

Director : Prof. Alexandre Legris

Université de Lille 1 SCIENCES ET TECHNOLOGIES

cnrs dépasser les frontières

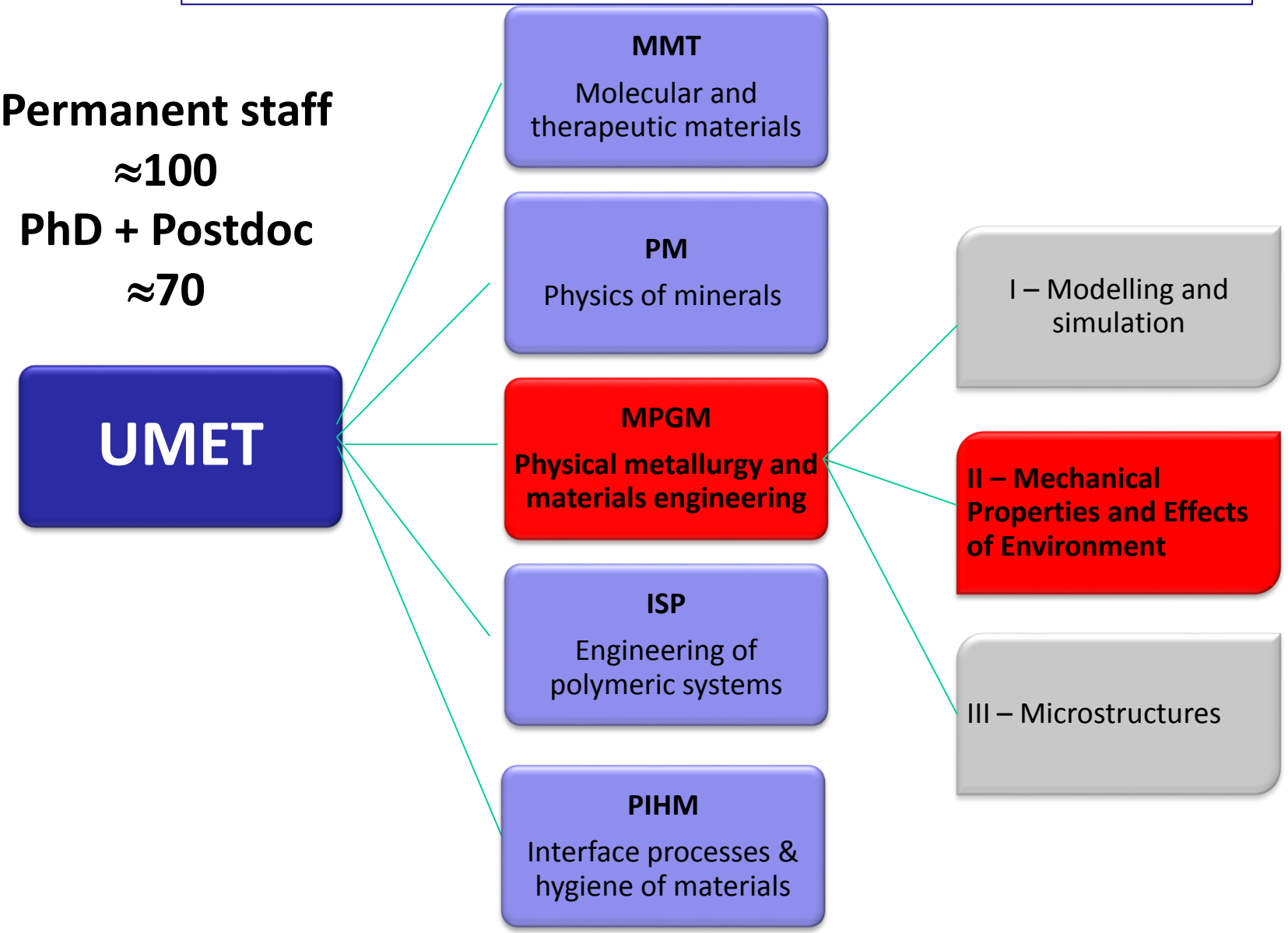
Chimie Lille ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE

54 Assistant professors and professors, 12 researchers CNRS et 24 technicians

Team: Physical Metallurgy and Engineering Materials

17 professors and assistant professors, 4 technicians et administrative , 8 PhD

Permanent staff
≈100
PhD + Postdoc
≈70



II – Mechanical Properties and Effects of Environment

Jean-Bernard VOGT (prof.), Ingrid PRORIOL-SERRE (researcher),
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Damien CRETON (tech.)
PhD candidates: Claire SCHAYES, Carla CARLE,
Maxime DELBOVE, Hassine KACEM, Gulzar SEIDAMETOVA

TOPICS *(Mechanical Properties and Effects of Environment group of UMET-MPGM)*

Mechanisms of cyclic plasticity of structural alloys:
- Role of nitrogen in stainless steels
- Partition of cyclic plasticity in dual phased microstructure steels
- Ultra fine grained stainless steels
- Fatigue induced phase transformation
- Fatigue of ODS copper
- Fatigue of coated material

Environment-deformation interactions:
- Liquid metal embrittlement
- Liquid metal accelerated damage
- Hydrogen embrittlement (stainless steel single crystal)
- Oxidation effect on fatigue resistance

→ Materials for energy and Materials for transportation

Industrial collaborations

CEA (nuclear), Valeo (Car equipment), ARC international (glass manufactory), BEKAERT, LBI, INOFORGE, EDF (electricity), ESRF (synchrotron), ARCELOR MITTAL (steel), European Union (Gen IV)…

STAINLESS STEELS

INTRODUCTION
MICROSTRUCTURE *vs* ALLOYING ELEMENTS
MAIN FAMILIES OF STAINLESS STEELS
ISSUES AND SOLUTIONS
EXEMPLES
IMPROVEMENT OF PROPERTIES

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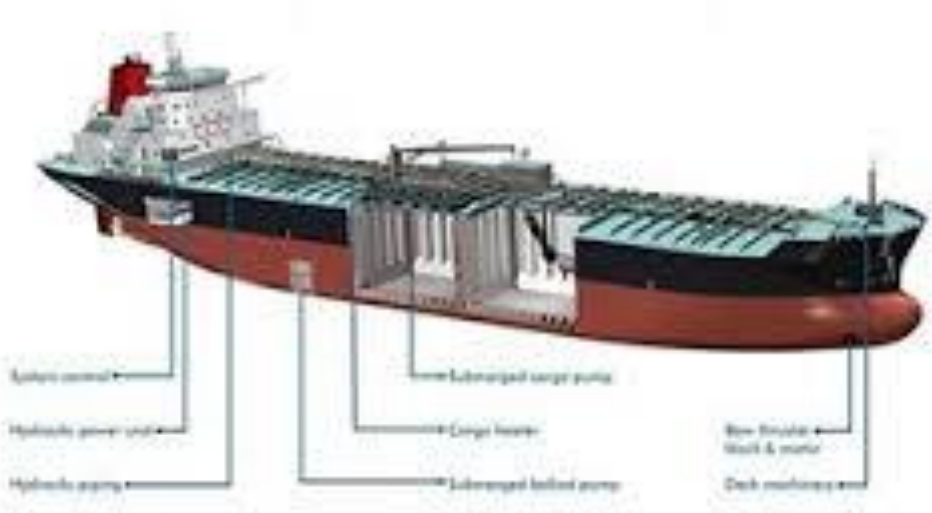
IMPROVEMENT OF PROPERTIES

Which applications bring to mind when stainless steel is mentioned ?



http://www.azalea-maritime.com/site/chemical-tanker-operations-course

Arcelor brochure

1. Stainless steel

- discovered by accident in 1913 by a Sheffield chemist - Harry Brearley when trying to solve the problem of rapid wear → tested a high Cr steel.

Routine analysis of steel at that time involved dissolving it in nitric acid. → The high Cr steel would not dissolve and also stayed shiny when left around in the lab

- Nevertheless already in 1820 Faraday (England) and Berthier (France) noticed the properties of Fe-Cr. They elaborated Fe-Cr alloys and noticed that these were more resistant to air environment than plain carbon steels

Fe+Cr exposed to oxygen→ Cr reacts to form an oxide.

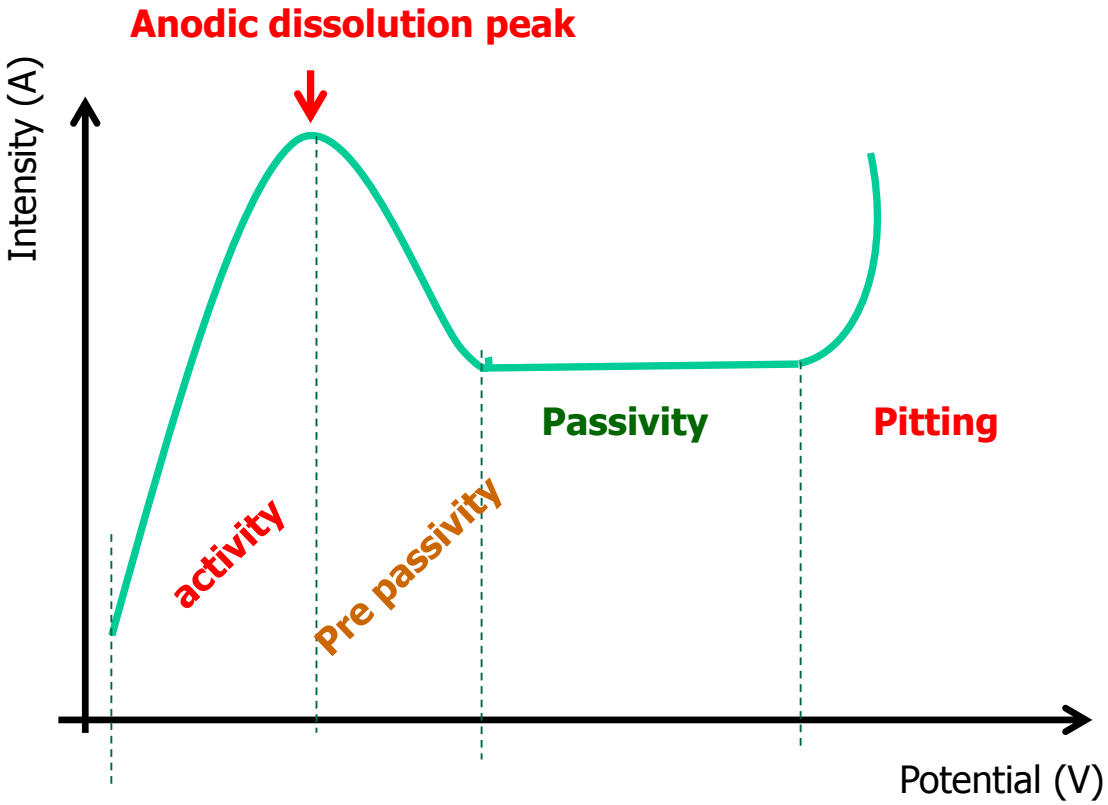
• If high Cr content → very thin layer of chromium(III) oxide as soon as the surface is exposed to the oxygen in the atmosphere

• Layer of oxide : very thin → the metal can still shine through it, but it is thick enough to prevent the oxygen and water attacking the metal underneath → no corrosion takes place

• Protection is permanent because even if the protective layer is scratched, the chromium in the steel will react with oxygen in the air to immediately re-form the protective layer.

Criterion : stainless steel if **%mass. Cr ≥ 10.5 and %mass.C ≤ 1.2**

European standard: **EN10088-1 (1995) 83 grades**



Pitting resistance equivalent numbers (PREN): theoretical way of comparing the pitting corrosion resistance of various types of stainless steels, based on their chemical compositions. The most commonly used version of the formula is

PREN = Cr + 3.3Mo + 16N or PREN = Cr + 3.3(Mo +0.5W) + 16N

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2 INFLUENCE OF ALLOYING ELEMENTS ON MICROSTRUCTURES

Recall :

α– Iron (BCC) : 0°C to 910°C

γ– Iron (FCC) : 910°C to 1390°C

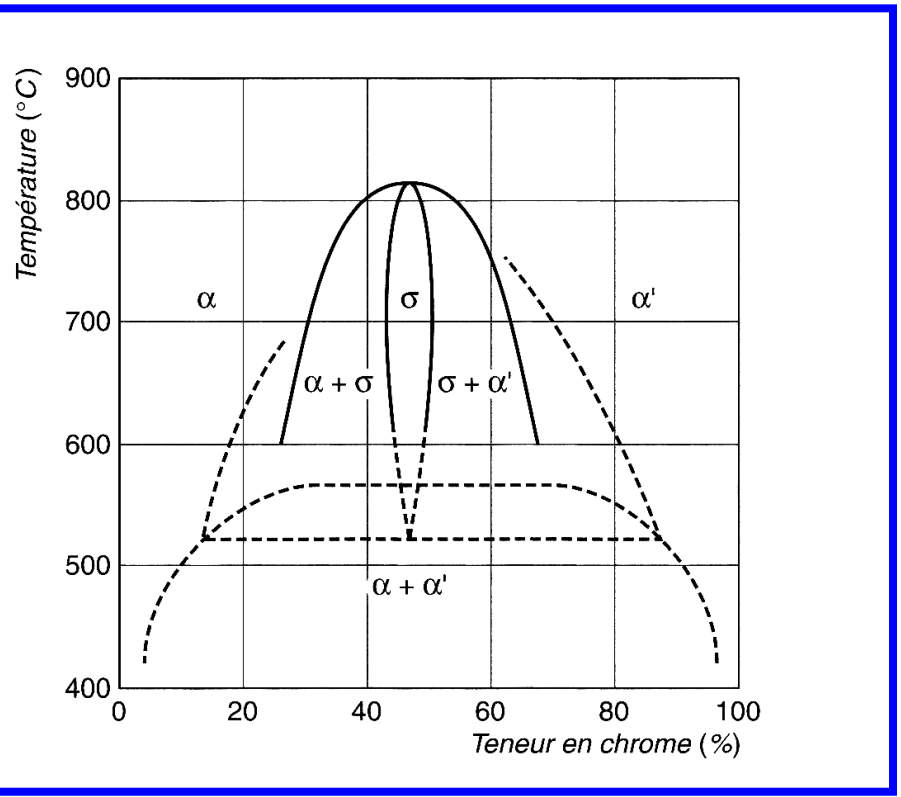
δ– Iron (BCC) : 1390°C to 1539°C

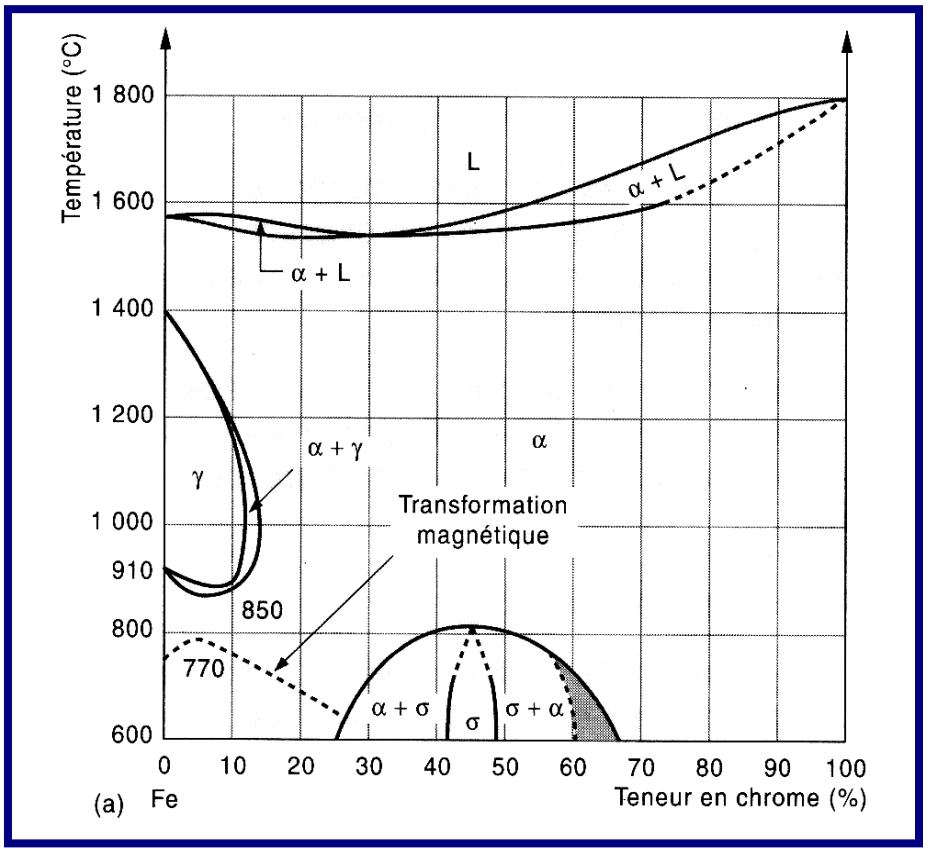
Basic alloying elements in Fe : C, Cr, Ni

Effect of Cr : see Fe-Cr diagramme

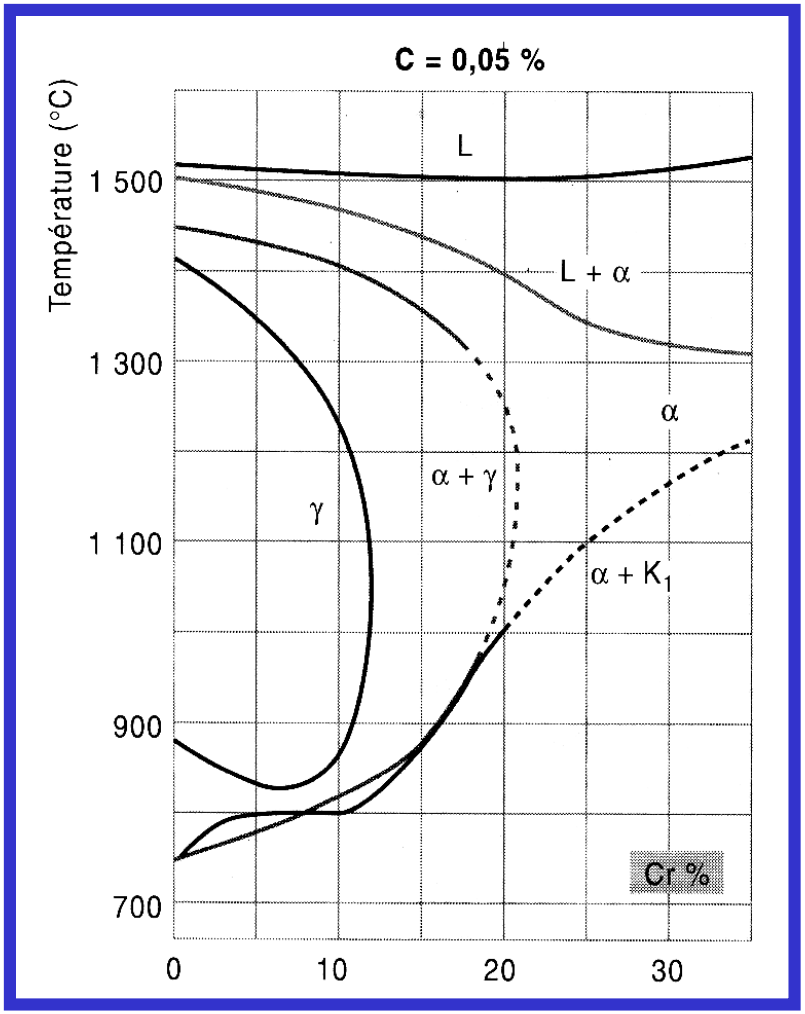
- ↓ T_f up to 25%Cr
- stabilises α–phase, closes γ domain
- fully ferritic if Cr>13%
- ordered phase: σ (tetragonal) forms very slowly in the range 820°C→ 600°C for Cr≈30 à 60%

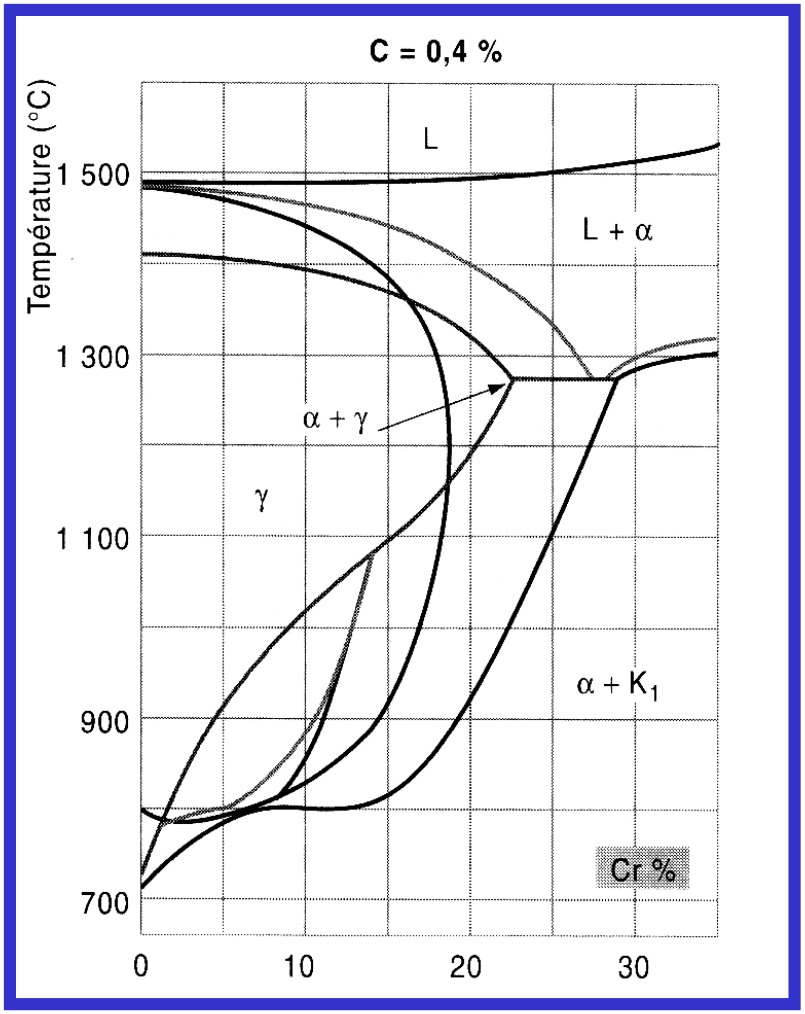
σ induces brittleness of the steel





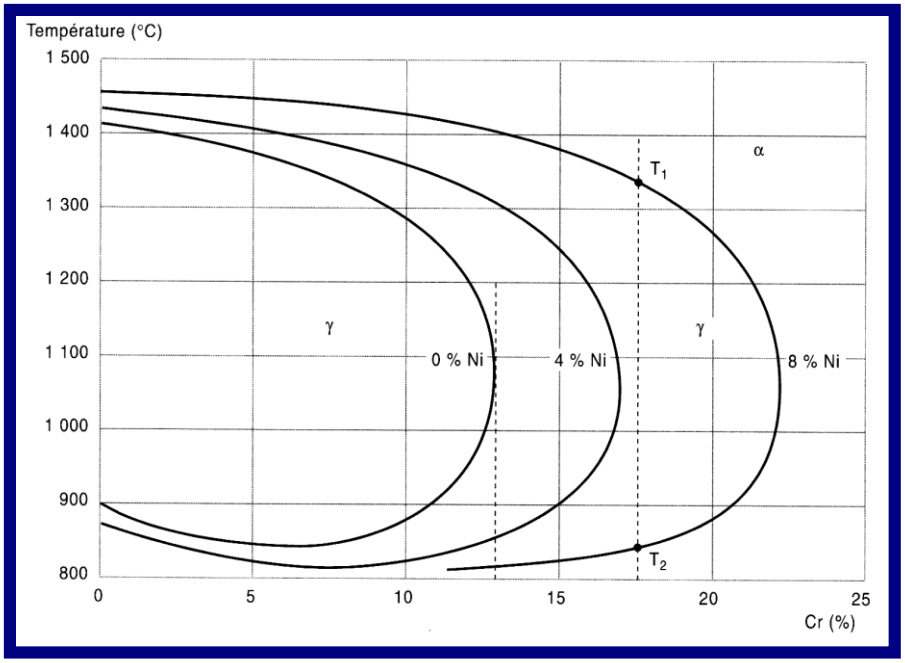
Action of C : see diagrams Fe-Cr with 0.05%C and 0.4%C

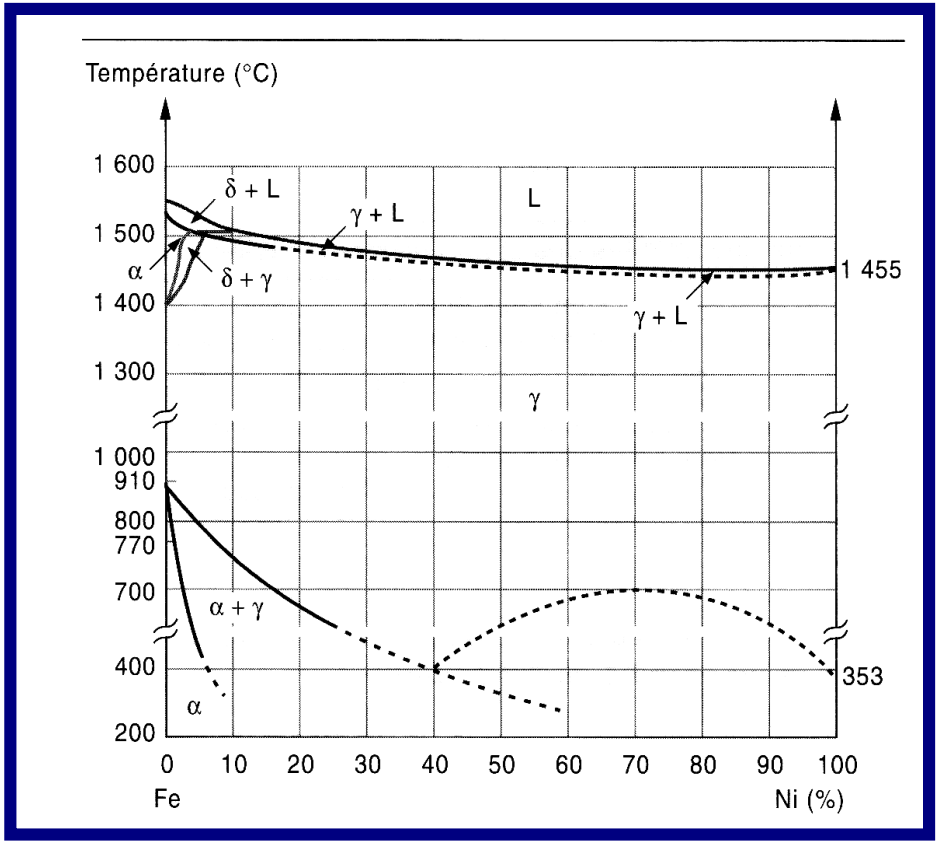




- ↓ T_f
- stabilises γ phase, enlarges γ domain
- more abundant precipitation of carbides $K_1 = M_{23}C_6$

Action of Ni: see diagrams Fe-Ni





- ↓ T_f
- considerably enlarges the austenitic domain :

Ni: the base element for elaboration of austenitic stainless steels

Combined effect of C, Ni and Cr

- There is a competition between the α-promoter element and the γ-promoter one
- According to their relative quantity, cooling the liquid metal follows the following steps:

liquid → liquid+α → α up to RT

ex. Alloy with 0.05%C/22%Cr

or liquid → liquid+α → liquid+α+γ → liquid+γ→ γ

ex. Alloy with0.4%C/12%Cr

→ occurrence of γ domain : quenching effects are possible

→ ferritic et martensitic steels

Effect of Alloying on Structure and Properties

Chromium: Increases strength of this passive layer Prompts the formation of ferrite

Nickel: Improves general corrosion resistance, Prompts the formation of austenite

Molybdenum (and Tungsten): Increases resistance to both local (pitting, crevice corrosion, etc) and general corrosion; Mo added to martensitic stainless steels improves high temperature strength. Mo promotes σ phase

Nitrogen: Increases strength and enhances resistance to localised corrosion.

Copper: Increases general corrosion resistance to acids

Carbon: Enhances strength (especially, in hardenable martensitic stainless steels), but may have an adverse affect on corrosion resistance by the formation of chromium carbides.

Titanium (and Niobium & Zirconium): may be used to stablise stainless steel against intergranular corrosion as Ti, Nb, Zr carbides are formed in preference to chromium carbide

Sulphur: Improves machinability but reduces corrosion resistance.

Cerium: Improves the strength and adhesion of the oxide film at high temperatures.

Manganese: Austenite former; increases the solubility of nitrogen in the steel and may be used to replace nickel in nitrogen-bearing grades.

Silicon: Improves resistance to oxidation

Role of other alloying elements

Mo, W, Ta, Nb, Si,V, Al : α-formers

Mn, Co, Cu, Pb, N : γ-formers

Prediction of stainless steel class:

SCHAEFFLER diagram (RT microstructure of weld joints rapidly solidified

$\%Cr_{équi}$: %Cr + %Mo + 1.5%Si + 0.5%Nb

$\%Ni_{équi}$: %Ni + 30%C + 0.5%Mn

Attention :several formulas !

→ de Delong diagram**: takes into account nitrogen:**

Ni (eq) = Ni + (30 x C) + (0.5 x Mn) + (30 x N)

→ Pryce and Andrews **: rolled steels, structure at 1100°C**

Role of other alloying elements

Mo, W, Ta, Nb, Si,V, Al : α-formers
Mn, Co, Cu, Pb, N : γ-formers

Prediction of martensitic transformation temperature

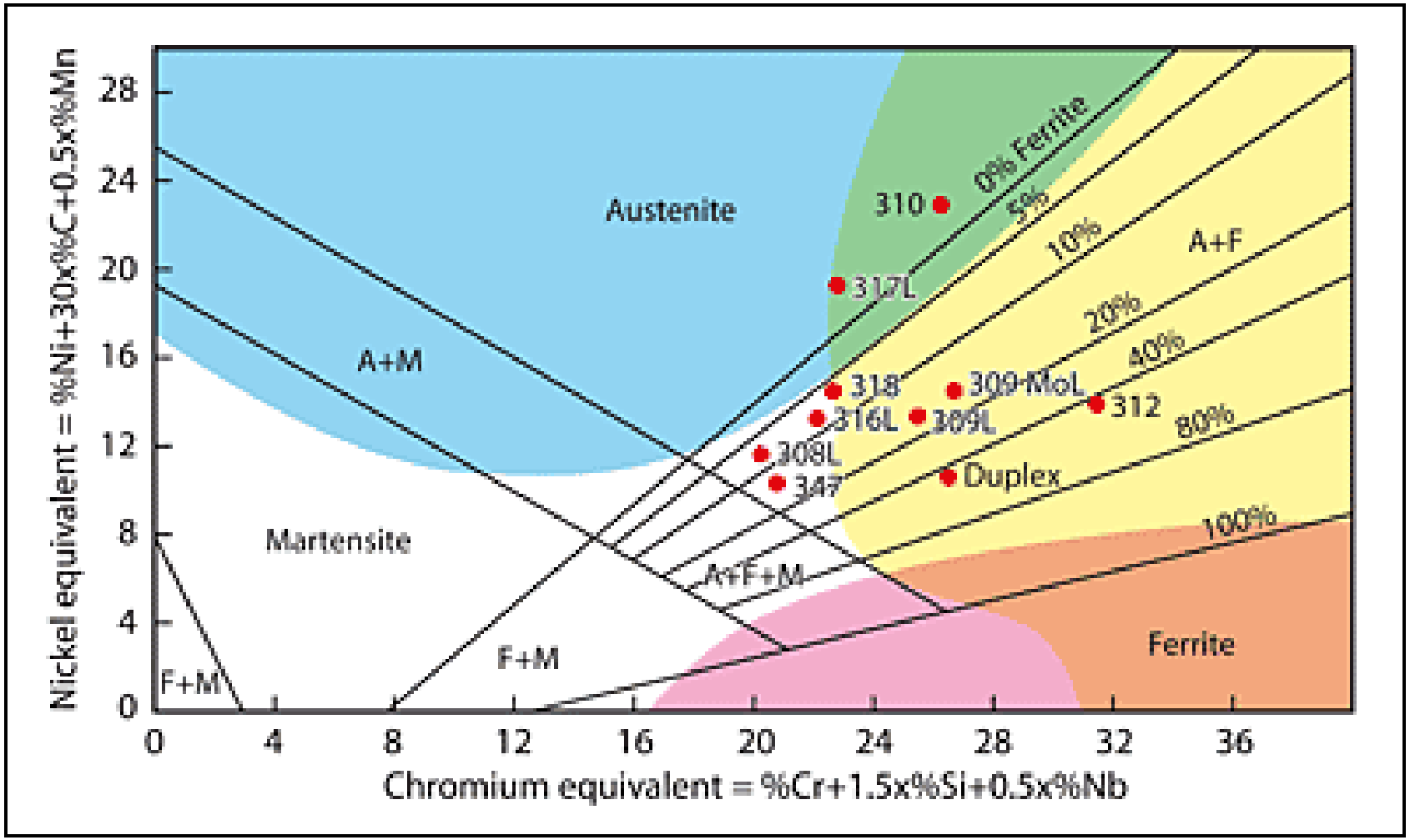
M_s (°C): start temperature of martensitic transformation upon cooling

M_s(°C) : 1302 – 1667(C+N) – 33(Mn) – 42(Cr) –61(Ni) – 28(Si)

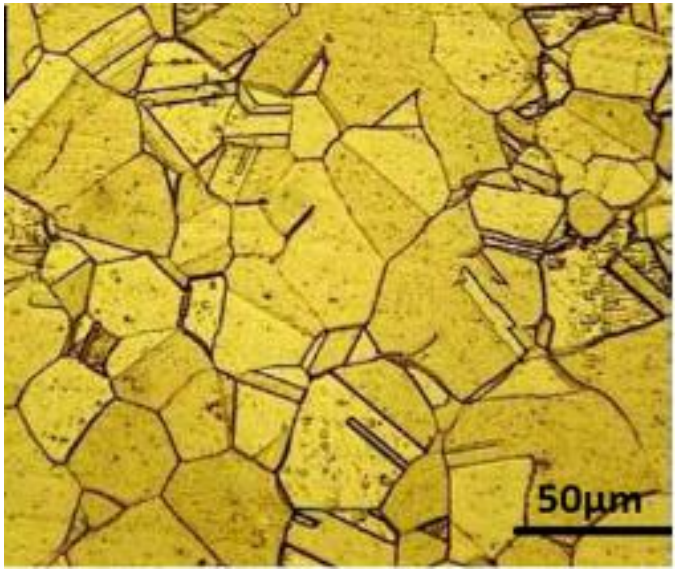
M_{d30} : temperature at which 50% of α' martensite is obtained in a tension test for a true deformation of 0.3

M_{d30}(°C) : 413 – 462(C+N) – 8.1(Mn) – 13.7(Cr) – 18.5(Mo) –9.2(Si)-9.5(Ni)

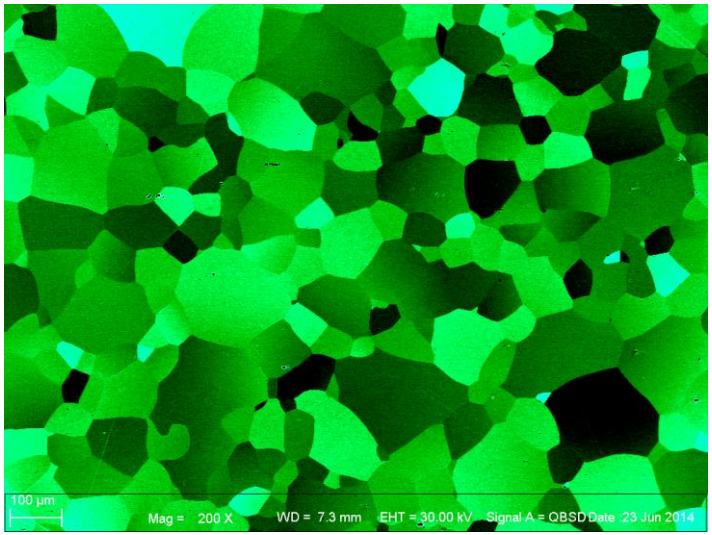
diagram SCHAEFFLER



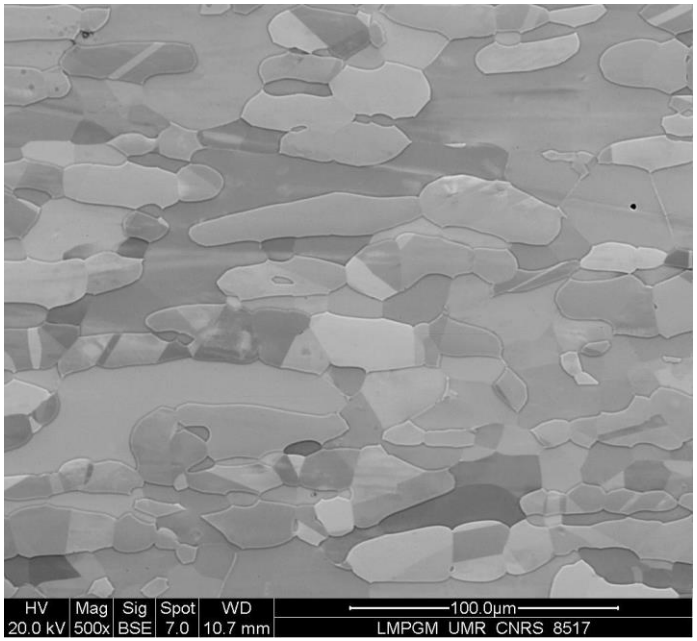
Stainless steels- Microstructure vs Alloying Elements



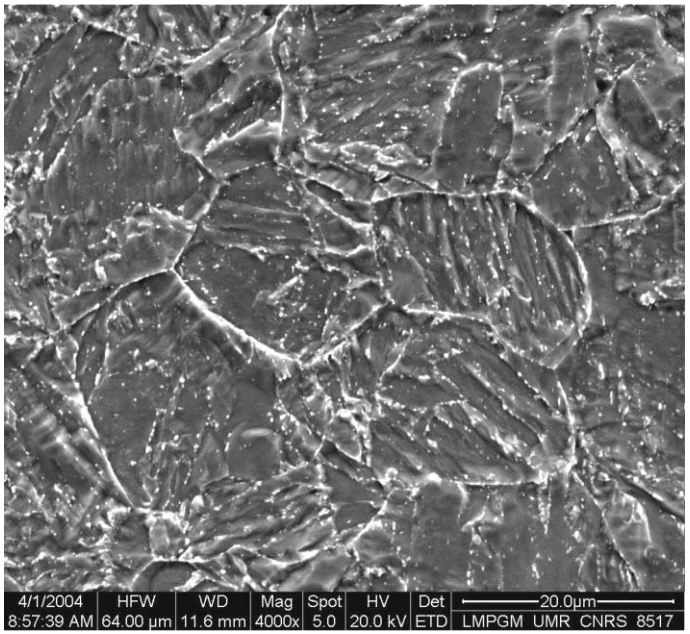
Austenitic



ferritic



austeno-ferritic (duplex)



martensitic

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IMPROVEMENT OF PROPERTIES

3.1 Ferritic stainless steels: High Cr content

STANDARD FERRITIC STEELS

Group 1: 10-14%Cr
type 409/410L): very basic steel

Group 2: 14-18%Cr, C<0,08%

e.g. AISI 430 the most widely used of ferritic steels
To increase ductility, %C is in the range of 0.02% to 0.05

Group 3: 14-18%Cr + Ti, Zr, Nb as stabilization elem.

e.g. AISI 430Ti, 439, 441 → fully ferritic steel

SPECIAL FERRITIC STEELS

Group 4: 10-18%Cr and Mo> 0,5%
e.g. AISI 434, 436, 444

For extra corrosion resistance → fully ferritic steel and fully stabilized
This grade is more sensitive to intermetallic precipitations (σ, χ)

Group 5: Cr>18% up to 30%Cr and Mo> 0.5%
e.g. AISI 445, 447:
25%<Cr<29% and 3%Mo, extra low C and N, 2%<Ni<4%
→ superferritic

For extra corrosion resistance → fully ferritic steel and fully stabilized
sensitive to embrittlement by intermetallic precipitations and difficult to weld
For most severe corrosion resistance to replace Ti alloys

FERRITIC STAINLESS STEELS

- cannot be quench hardened because of the absence of the austenitic domain

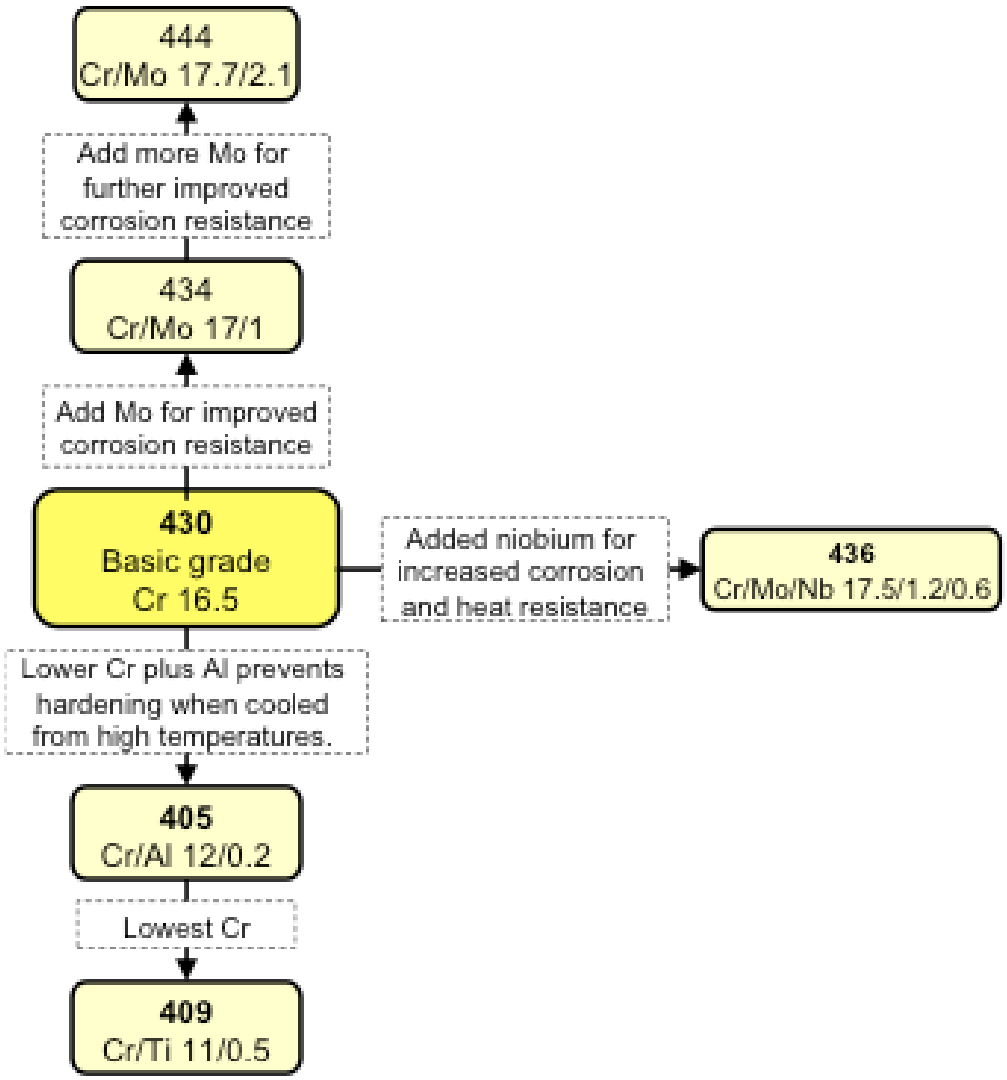
- Heat treatment: solution treated at 750°C-900°C and then air cooled

- BCC structure → DBTT, which depends on %Cr :
  11.5%<Cr<13.5 → 0°C<TT<20°C
  16% <Cr<18% → TT>50°C

→ Thin products (groupes 1, 2 and 3) : biaxial state

- beware of long time holding between 550°C et 800° (steel >20%Cr) → σ phase and near 475°C → spinodal decomposition de α → α'

Stainless steels- main families: ferritic stainless steels



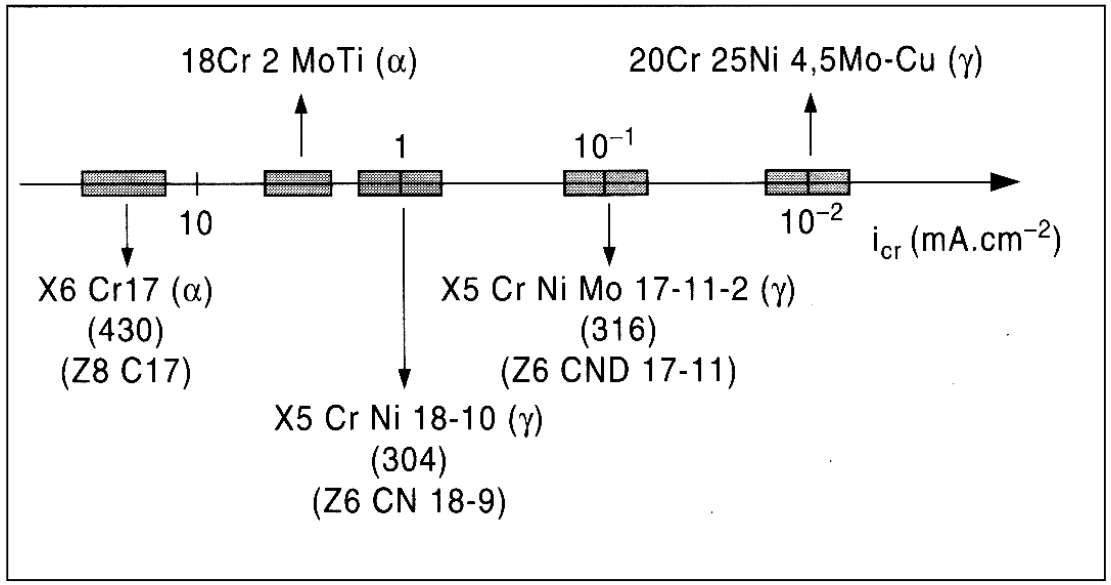
Ferritic stainless steels family

3.2 Austentic stainless steels: High Cr, High Ni

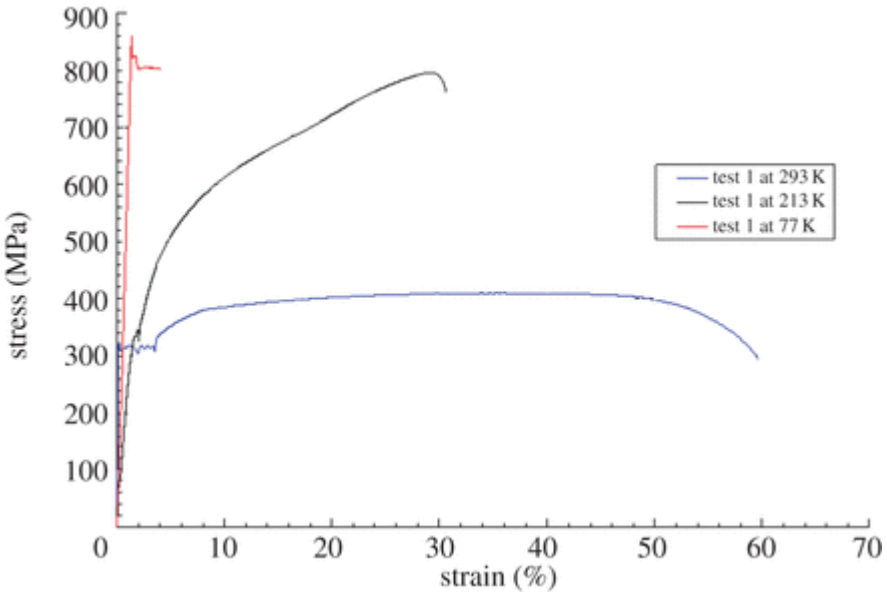
Grades for severe corrosion

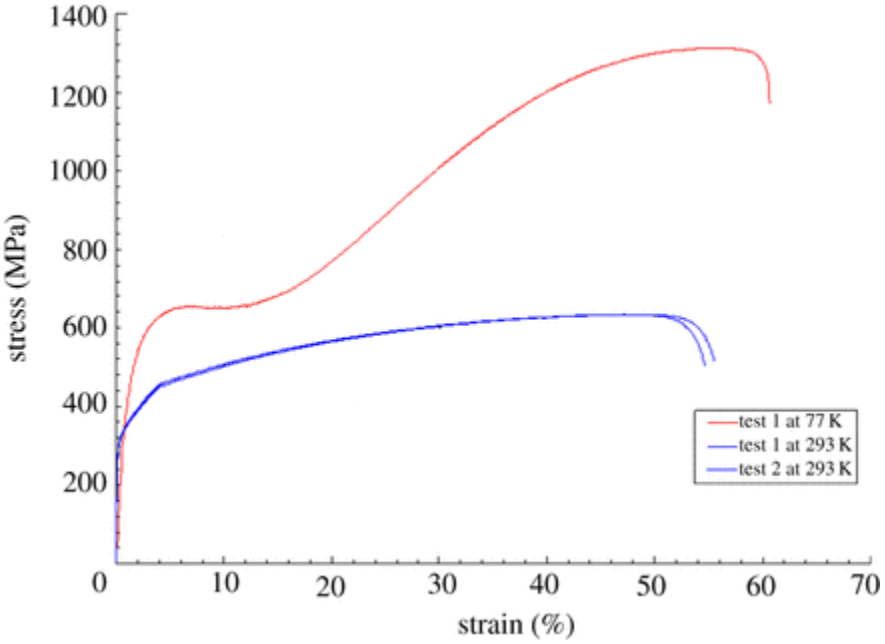
Grade 18-10	***Grade 17-12-Mo***	***Grade 25-20-Mo-Cu*** ***superausténitique***
X5CrNi18-10 Z6C18-09- AISI 304	X2CrNiMo17-12-2 Z2CND17-12- AISI 316L	X1NiCrMoCu31-27-4 Z2NCDU31-27
Sensitive to intergranular except if C is low (~0.02%) or if Ti is added		
HNO_3 (up to boiling , conc. 50%) **H_3PO_3** **Sodium and Potassium hydroxide (NaOH and KOH)** **Up to 100°C**	**HNO_3 (up to boiling, conc. 70%)** **H_3PO_3, whatever conc. up to 80°C** **HCl up to 2-3% at 20°C**	**HNO_3 (up to boiling, high concentration)** **H_3PO_3, with presence of Cl^-, HF, H_6SiF_6** **HCl if conc.> 2-3%** **Sodium and Potassium hydroxide (NaOH and KOH)** **Up to 150°C**

Austenitic stainless steels



- Heat treatment: solution heat treatment at 1050°C-1150°C followed by quenching (hypertrempe)
- FCC structure CFC at RT due to large amount of Ni → application in cryogenics
- Possible destabilisation of γ phase assisted by mechanical stress $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ or $\gamma \rightarrow \alpha'$
- γ phase: non magnetic



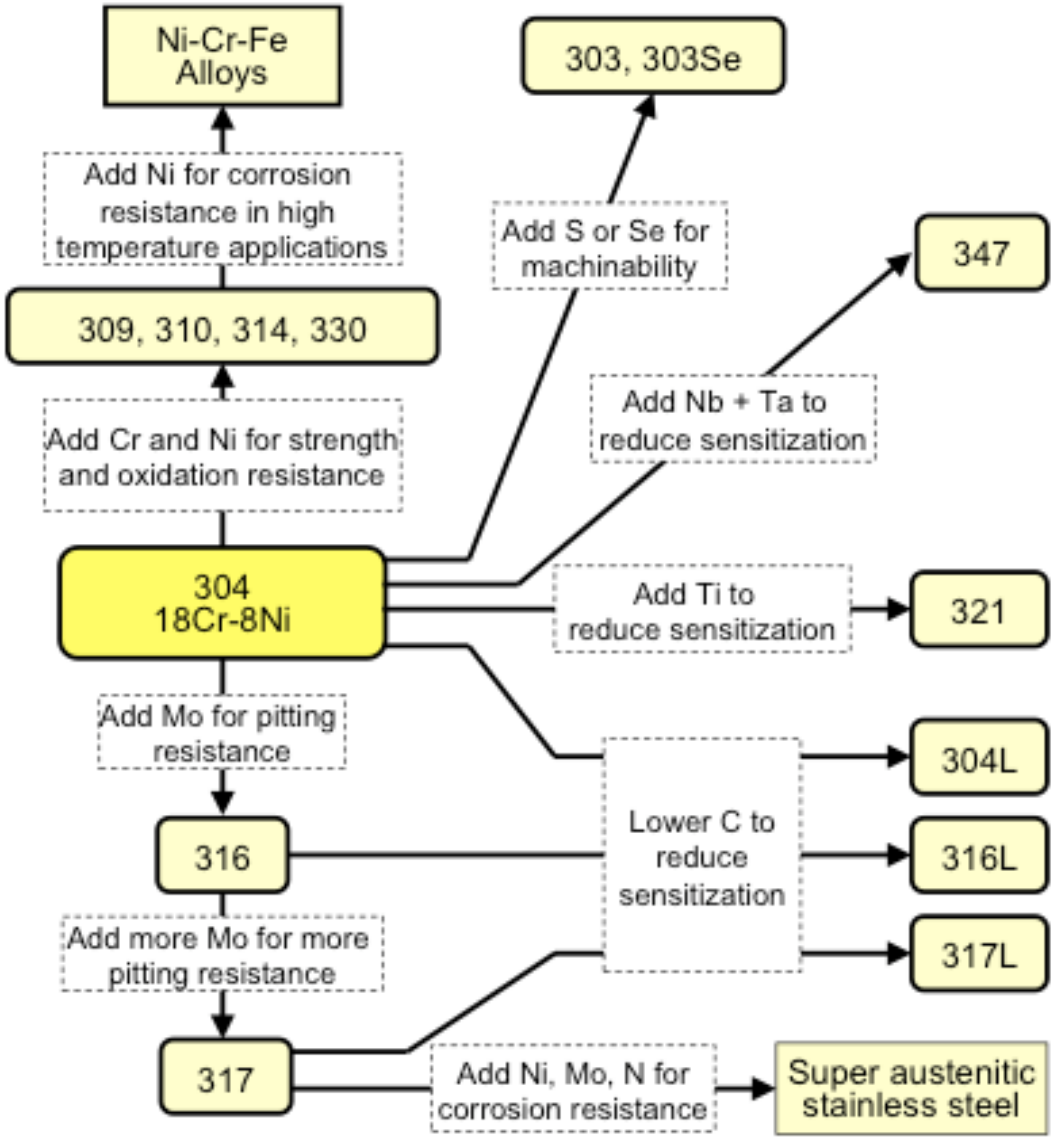


Mild steel

From Laribou et, Proc. Royal Society, November 2012
Volume: 468 Issue: 2147

316L

Stainless steels - main families: austenitic stainless steels



Austenitic stainless steels family

3.3 AUSTENO FERRITIC STAINLESS STEELS or<u>DUPLEX</u> : high Cr, low Ni, low C , high N

Lean Duplex: low Ni and **no Mo** and N

C~0.03 % Cr : 21-23% Ni: 1.5 -4% N: 0.12% -0.22%

2101, 2102, 2202, 2304

Duplex SS: moderate Ni and Mo

C~0.03 % Cr: 20-24% Ni: 3.5-5% Mo: 1.5–3% N: 0.12-0.22%

2205, 2003, 2404

Super Duplex SS: 25%Cr, higher Ni and Mo

C~0.03 % Cr ~25% Ni ~7% Mo 3-5% N: 0.2-0.3%

2507, Z100

Hyper Duplex SS: more Cr, Ni, Mo, N

C~0.03 % Cr ~ 27% Ni ~6% Mo ~5% N:0.4%

2707

Chemistry of Lean Duplex SS

Name	UNS No.	C	Cr	Ni	Mo	N	Other
2101	S32101	.04	21	1.5	0.5	.22	Mn=5
2102	S82011	.03	21.5	1.5	0.5	.21	Mn=2.5
2202	S32202	.03	22	2	0.5	.22	
2304	S32304	.03	23	4	0.5	.12	

High Cr low Ni 0.2 N and no Mo

Chemistry of *Duplex* SS

Name	UNS No.	C	Cr	Ni	Mo	N	Other
2003	*S32003*	*.03*	*20*	*3.5*	*1.7*	*.16*	
2404	*S82441*	*.03*	*24*	*3.5*	*1.5*	*.22*	*Cu*
2205	*S31803*	*.03*	*21.8*	*5*	*2.8*	*.12*	
2205	*S32205*	*.03*	*22.5*	*5*	*3.2*	*.16*	

High Cr Moderate Ni and Mo and 0.16N

Chemistry of Super Duplex SS

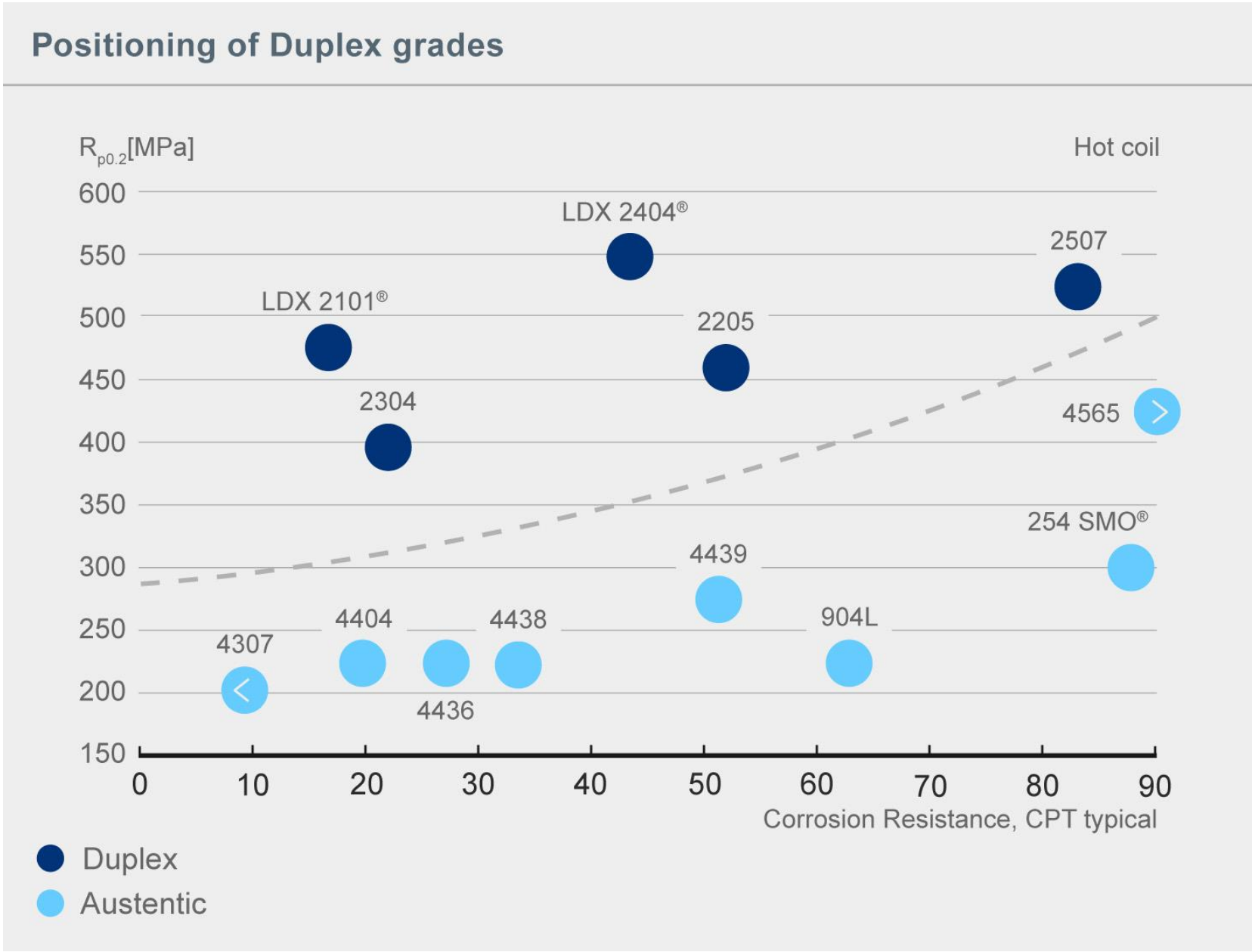
and Hyper Duplex

Name	UNS No.	C	Cr	Ni	Mo	N	Other
2507	S32750	.03	25	7	4.0	.28	Cu=.5
255	S32550	.03	25.5	5.5	3.4	.20	Cu=2.0
Z100	S32760	.03	25	7	3.5	.25	Cu=.75W=.75
2707	S32707	.03	27	6.5	4.8	.40	

Higher Cr More Ni and Mo .25+N and "others"

AUSTENO -FERRITIC STAINLESS STEELS or DUPLEX STEELS

- Cooling from $\alpha + \gamma$ domain at 1050-1150°C :
  → γ phase contains enough γ element promotors to avoid transformation
  →α phase is not affected
- Requires accurate control of chemical composition which in general optimised to give rise to obtain 50%α-50%γ
- pay attention to partition of alloying elements in each phase: partitioning coefficient
- Cooling must be rapid enough to avoid precipitation σ phase
- Long term use: be aware of spinodal decomposition in ferrite (475°C embrittlement)
  → working temperature limited to 350°C

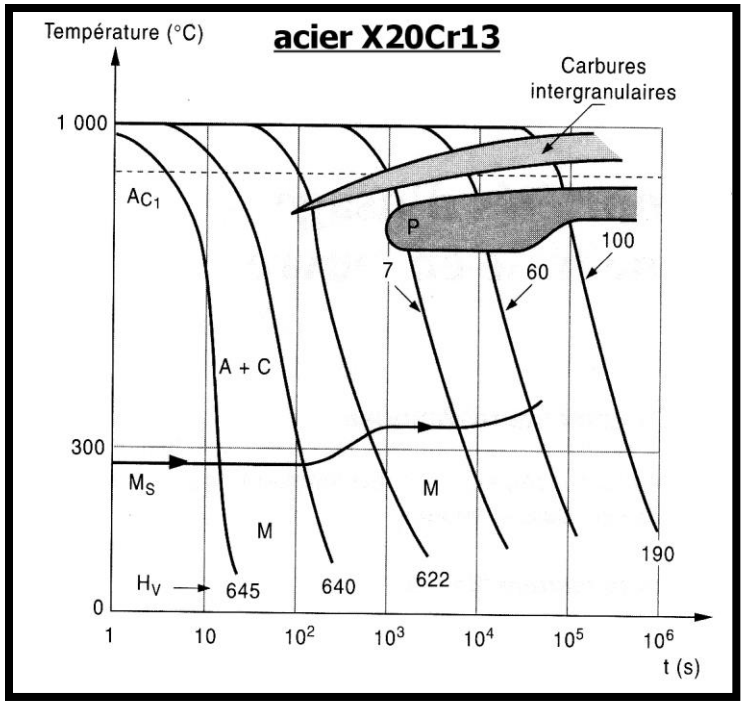

Positioning of Duplex grades
$R_{p0.2}$[MPa]
Hot coil
600
550
500
450
400
350
300
250
200
150
LDX 2404®
2507
LDX 2101®
2205
2304
4565
254 SMO®
4439
4404
4438
904L
4307
4436
0
10
20
30
40
50
60
70
80
90
Corrosion Resistance, CPT typical
Duplex
Austentic

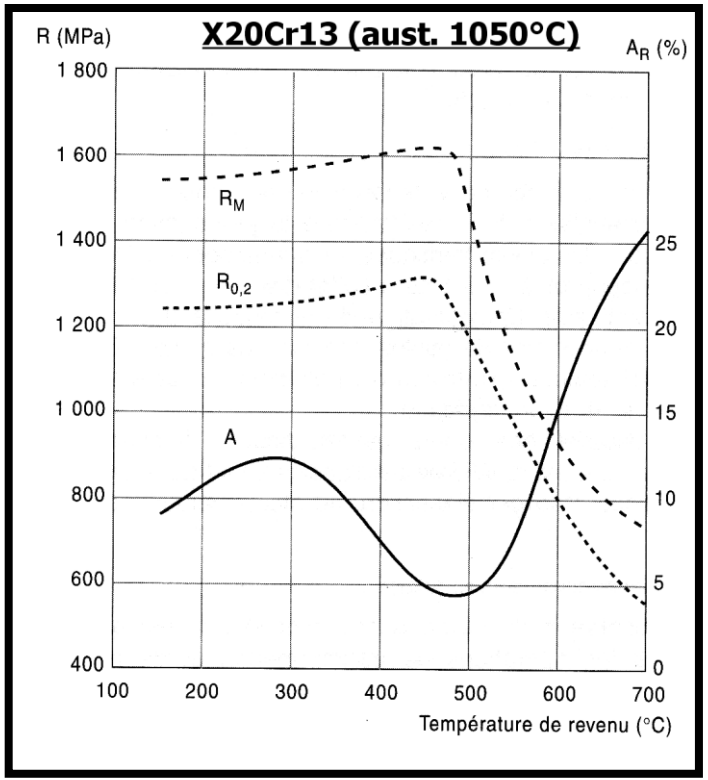
3.4 MARTENSITIC STAINLESS STEELS : high Cr and high C

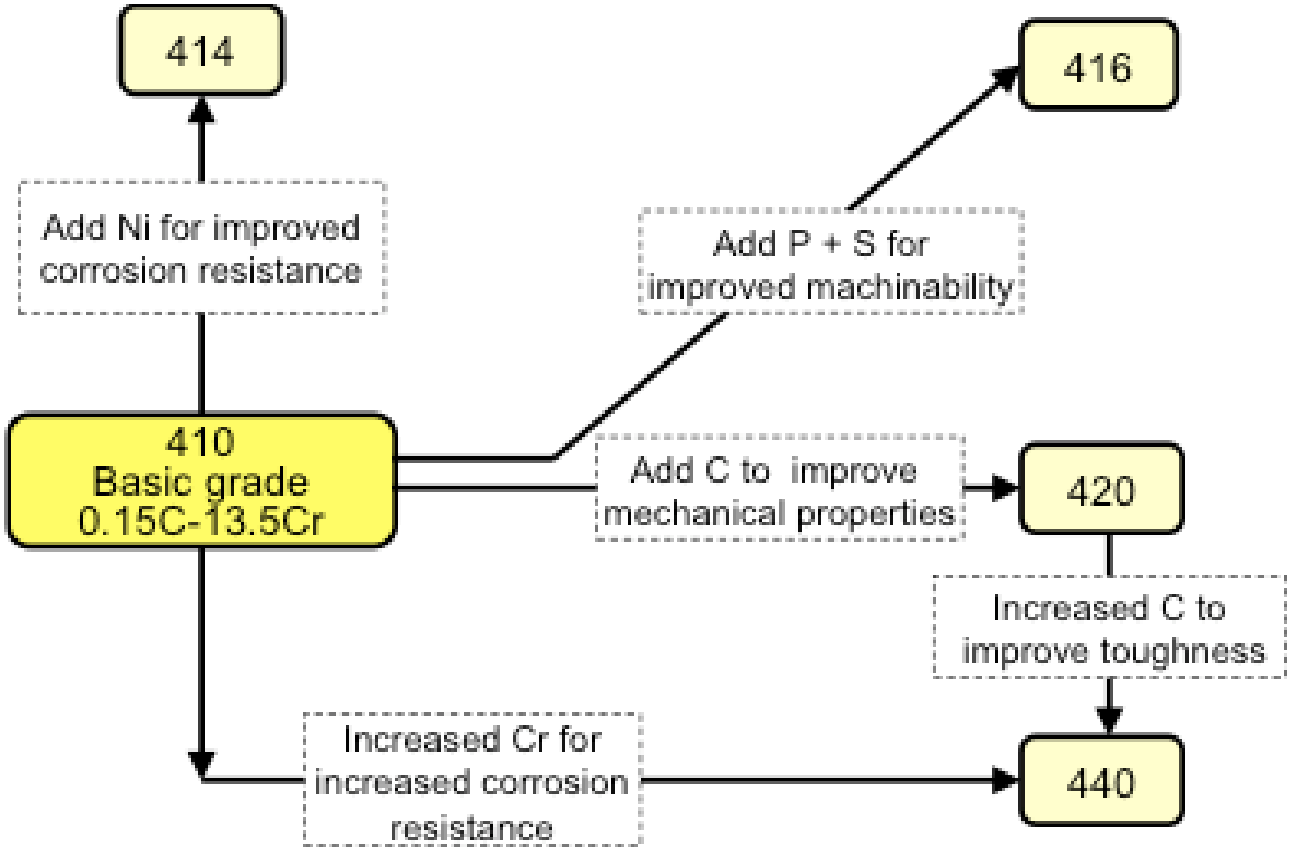
Group 1 **C~0.15% Cr : 11.5-13.5%** X12Cr13 - Z10C13 - AISI410	R_m= 600-900MPa Limited Corrosion resistance Weldable	Valves, fittings, scew and bolts …
Group 2 **C:0.2-0.4% Cr :12.5-14.5%** X20Cr13 - Z20C13 - AISI420	R_m=900-1500MPa Medium corrosion resistance Non easy weldable	Knives, forks, springs…
Group 3 **C : 0.6-1.2% Cr : 16-18**	Very hard and brittle	Surgical tools valves
Group 4 **C<0.1% Cr :16-18% Ni :2-4%** X5CrNiCu16-4 – Z7CNU17-4 **Nuance haut de gamme**	R_E= 600-800MPa Good corrosion resistance weldable	Big wrought or cast components Valves, pumps, turbines, propeller shaft…

MARTENSITIC STAINLESS STEELS

- obtained by quench from austenitic domain and further tempering
  - → Solution heat treated at: 950°C-1100°C cf equil. diag.
  - → Cooling rate: oil or water cf diag. TRC diag
  - → tempering: 150°C-350°C : relaxation of residual stresses
    550°C-750°C : softening tempering







Martensitic stainless steels family

TABLEAU DES NUANCES DES ACIERS INOXYDABLES

	AISI	NFA	Symbolique	Numérique
Austénitique	304	Z7 CN 18.09	X5CrNi18-10	1.4301
	304H	Z7 CN 18.09	X6CrNi18-10	1.4948
	304L	Z2 CN 18.10	X2CrNi19-11	1.4306
	304L	Z3 CN 19.09	X2CrNi18-9	1.4307
	321	Z6 CNT 18.10	X6CrNiTi18-10	1.4541
	321H	Z6 CNT 18.10	X6CrNiTiB18-10	1.4941
	316	Z7 CND 17.11.02	X5CrNiMo17-12-2	1.4401
	316L	Z2 CND 17.12	X2CrNiMo17-12-2	1.4404
	316L Mo sup	Z2 CND 18.14.03	X5CrNiMo18-14-3	1.4435
	316Ti	Z6 CNDT 17.12	X6CrNiMoTi17-12-2	1.4571
Austéno-Ferritique	Duplex / 318LN	Z2 CND 22.05.03	X2CrNiMoN22-5-3	1.4462
	Super Duplex	Z3 CND 25.06 Az	X2CrNiMoCuWN25-7-4	1.4501
		Z2 CN 23.04 Az		1.4362
Super Austénitique	904L	Z1 NCDU 25.20.04	X1NiCrMoCu25-20-5	1.4539
	928	Z1 NCDU 31.27.03	X1NiCrMoCu31-27-7	1.4563
Férritique	409L	Z3 CT 12	X2CrTi12	1.4512
	410S	Z8 C12	X6Cr13	1.4000
	430	Z8 C17	X6Cr17	1.4016
	434	Z8 CD 17.01	X6CrMo17-1	1.4113
Martensitique	410	Z12 C 13	X12Cr13	1.4006
	420	Z30 C13	X30Cr13	1.4028
	420	Z44 C14	X46Cr13	1.4034
Réfractaire	310S	Z8 CN 25.20	X8CrNi25-21	1.4845
	309S	Z15 CN 24.13	X12CrNi23-13	1.4833

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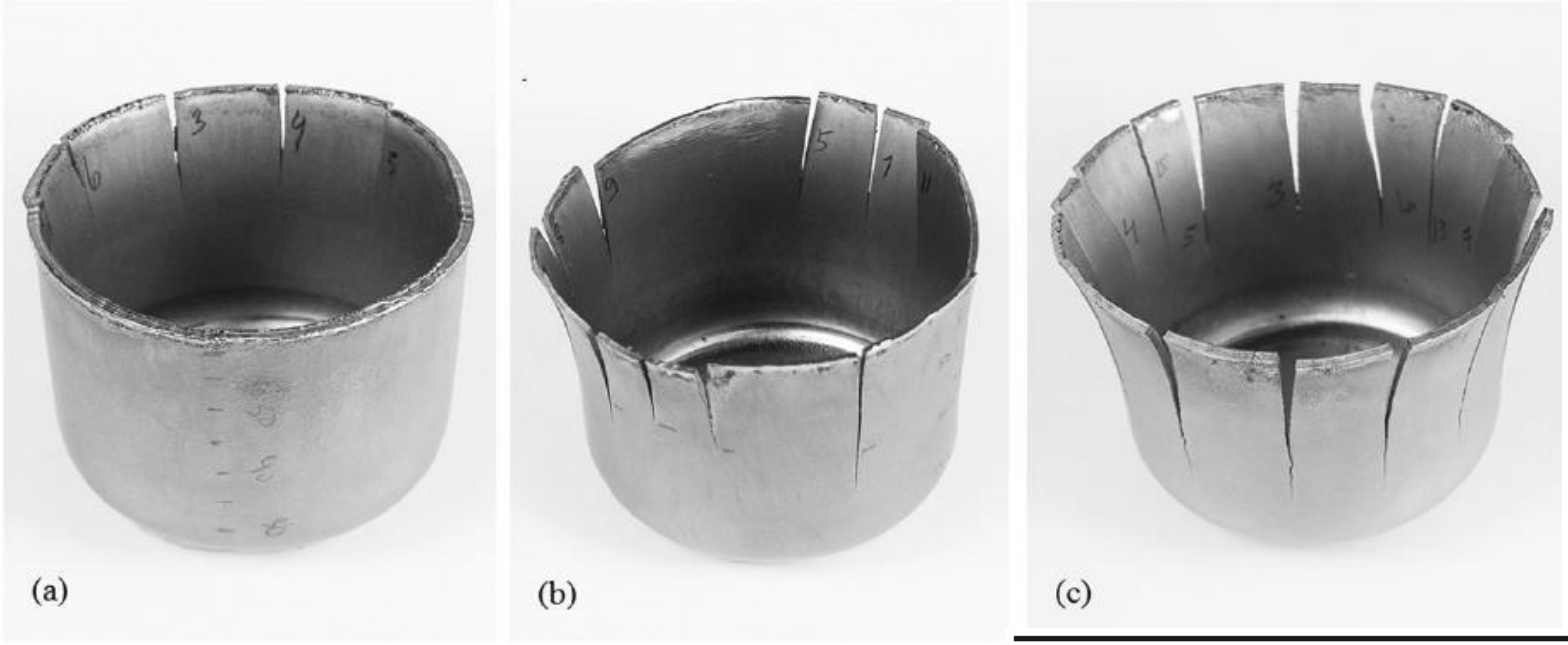
Metastability of austenitic stainless steels → delayed cracking

Delayed cracking: failure that may occur in certain materials after forming operations, e.g. deep drawing. Incubation time before fracture can be hours or days or even several weeks.

Phenomenon related to coexistence of internal hydrogen, strain-induced α'-martensite and tensile residual stresses.

The strain-induced martensitic phase makes the material more prone to delayed cracking, because it is harder and more brittle than austenite and because of high hydrogen diffusivity in bcc lattice



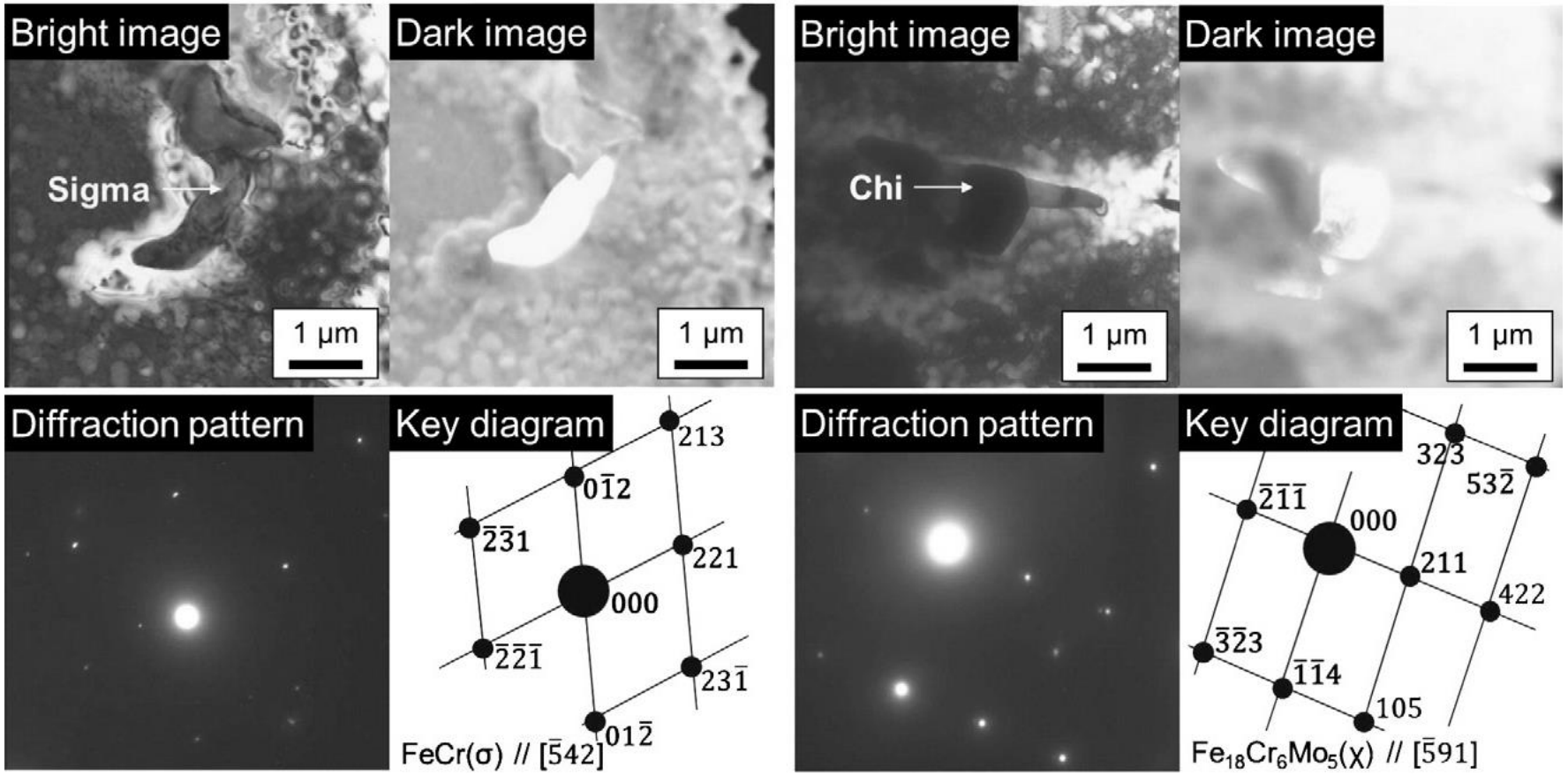
Deep drawn cups: (a) 301-2.0-S, (b) 201-2.0-S and (c) 204Cu-2.0-S. Inner diameter of the cups is 50 mm. (Ortega et al, FFEMS 2014)

Grade	C	Ni	Mn	Cr	Si	Cu	N
301	0.09	6.40	1.22	16.70	1.12	0.25	0.074
201	0.05	3.70	7.16	17.00	0.29	0.21	0.217
204Cu	0.08	1.10	9.00	15.20	0.40	1.68	0.115

Secondary Phases of Concern in Stainless Steels (and Nickel Alloys)

Phase	Composition	Temperature Range	Structure
Carbides	$(Cr,Fe,Mo)_{23}C_6$	600 – 950° C	Cubic
	$(Cr,Fe,Mo,Cb)_6C$	600 – 950° C	Cubic
	$(Cr,Fe,Mo)_7C_6$	950 - 1050° C	Orthorhombic
Nitrides	$(Cr,Fe)_2N$	650 – 950° C	Hexagonal
Sigma σ	(Cr,Fe,Mo,Ni)	550 – 1050° C	Tetragonal
Laves η	$(FeCr)_2(Mo,Nb,Ti,Si)$	550 – 900° C	Hexagonal
Chi χ	$Fe_{36}Cr_{12}Mo_{10}$	600 – 900° C	Cubic

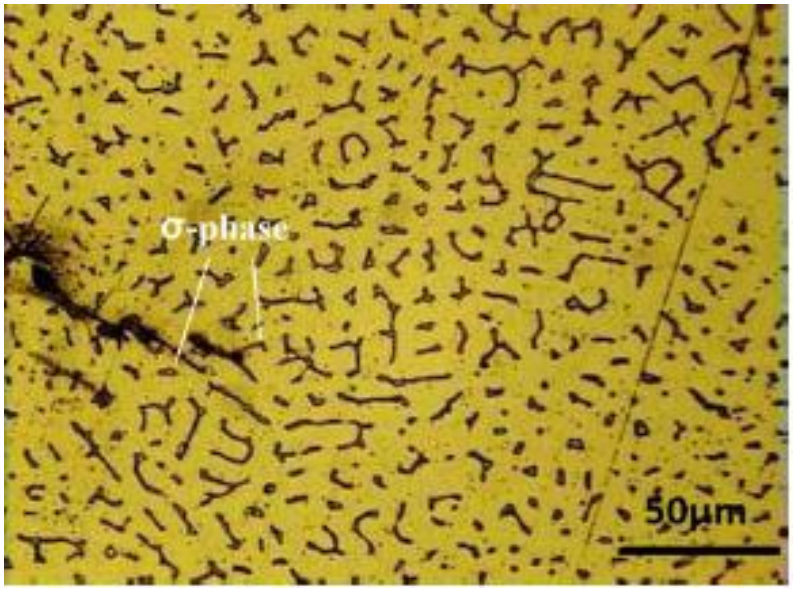
TEM micrographs and diffraction patterns of intermetallic phases (σ and χ phases).

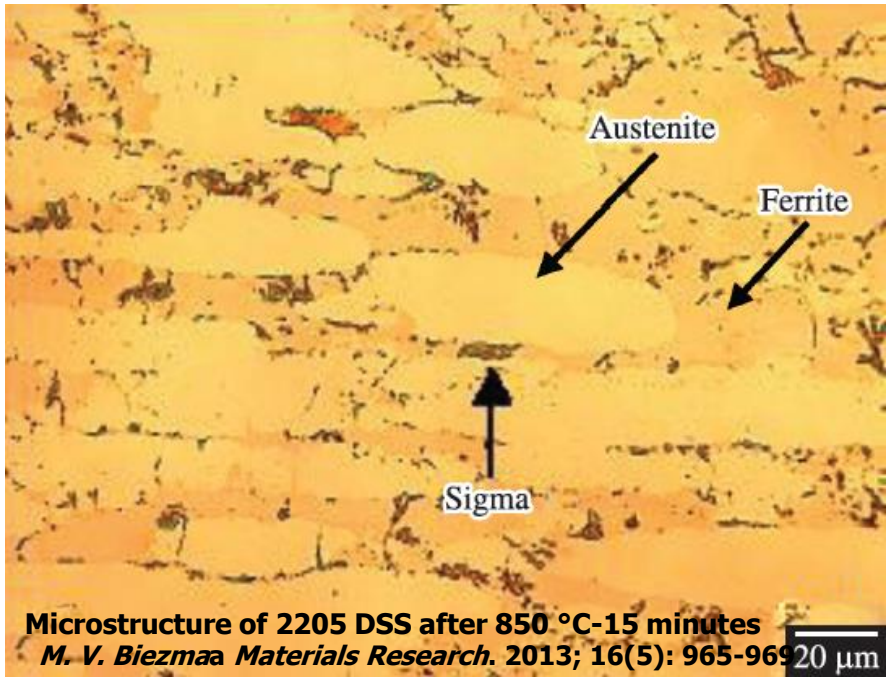


Eun Joon Chuna et al M A T E R I A L S C H A R A C T E R I Z A T I O N 8 6 (2 0 1 3) 1 5 2 – 1 6 6

σ phase:

- often observed in various series of stainless steels and also in Ni alloys
- deterioration of stainless steels properties: mechanical property, corrosion resistance, and weldability
- can be precipitated under an elevated temperature environment 600°C <T<1 000°C
  e.g. casting, rolling, welding, forging, and aging precipitation





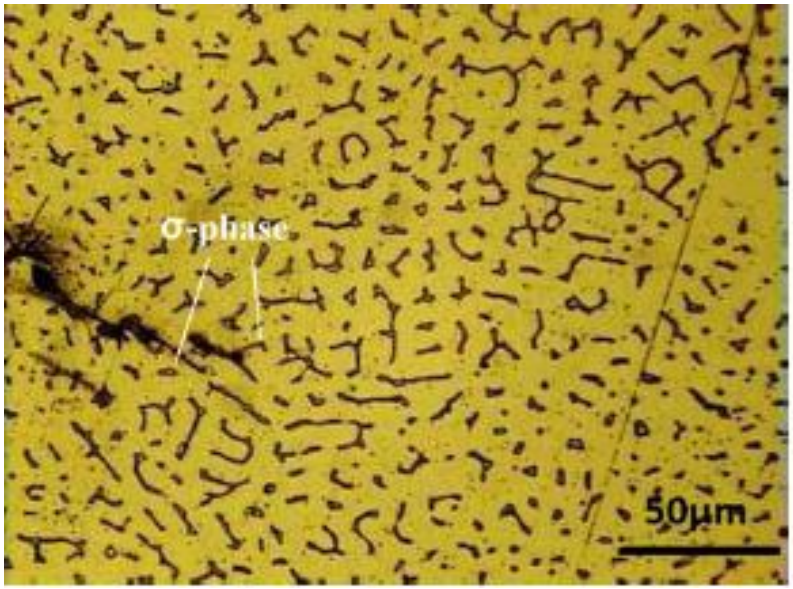
Microstructure of 2205 DSS after 850 °C-15 minutes
M. V. Biezmaa Materials Research. 2013; 16(5): 965-969

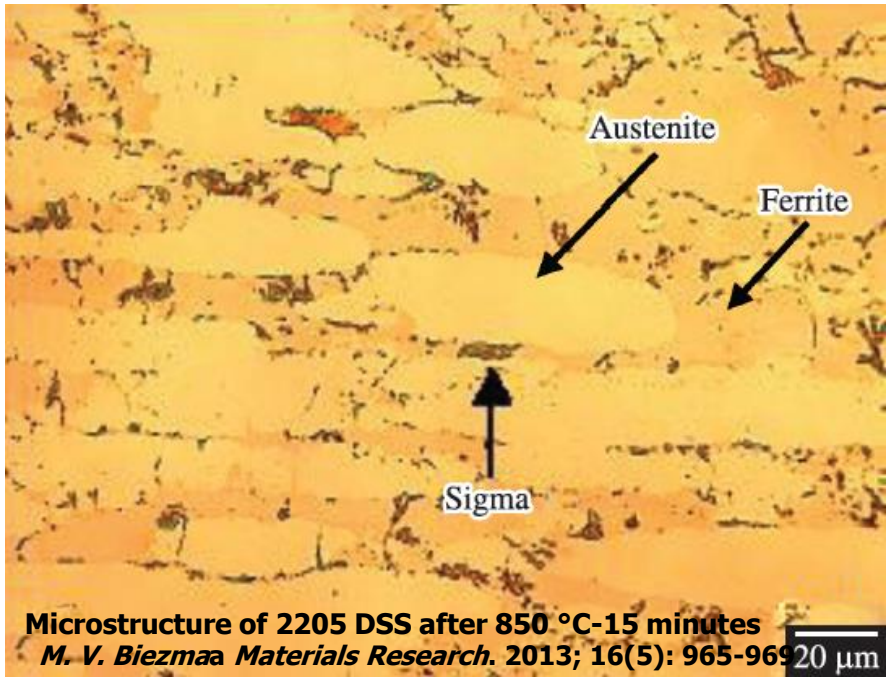
σ phase:

- The σ phase issues from the phase transformation of δ-ferrite to σ phase. When $\delta \rightarrow \sigma$, the σ phase will precipitate in the high Cr-concentrated region of δ-ferrite and is formed directly in δ-ferrite particles

- Cr < 20% → no σ phase precipitation in austenitic stainless steels. However, σ phase can be formed quickly when Cr > 25%~30% → Difficult to prevent when Cr > 20% in stainless steels

- Furthermore, σ phase can also precipitate from γ-austenite <u>when there is no δ-ferrite</u> in the stainless steels





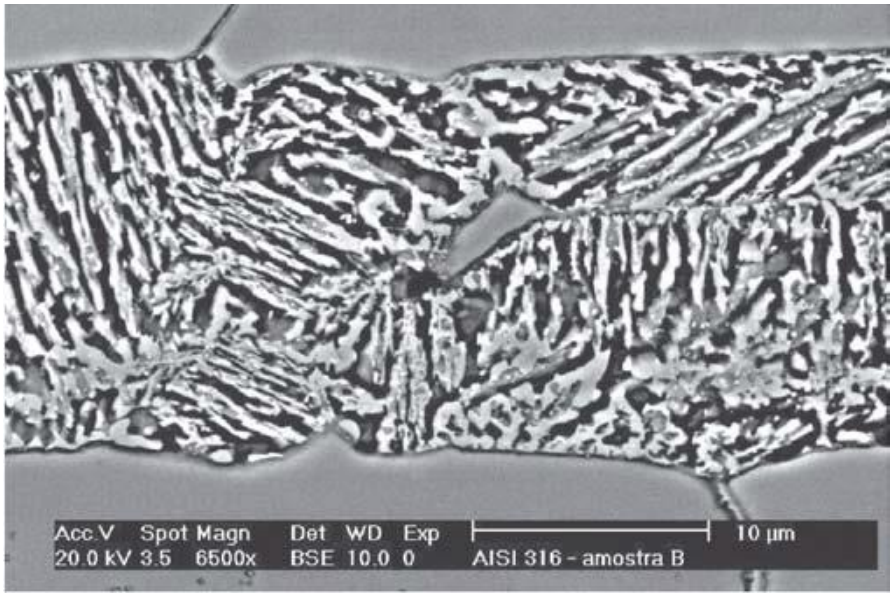
Microstructure of 2205 DSS after 850 °C-15 minutes
M. V. Biezmaa Materials Research. 2013; 16(5): 965-969

σ phase: can also precipitate from γ-austenite when there is no δ-ferrite in the stainless steels

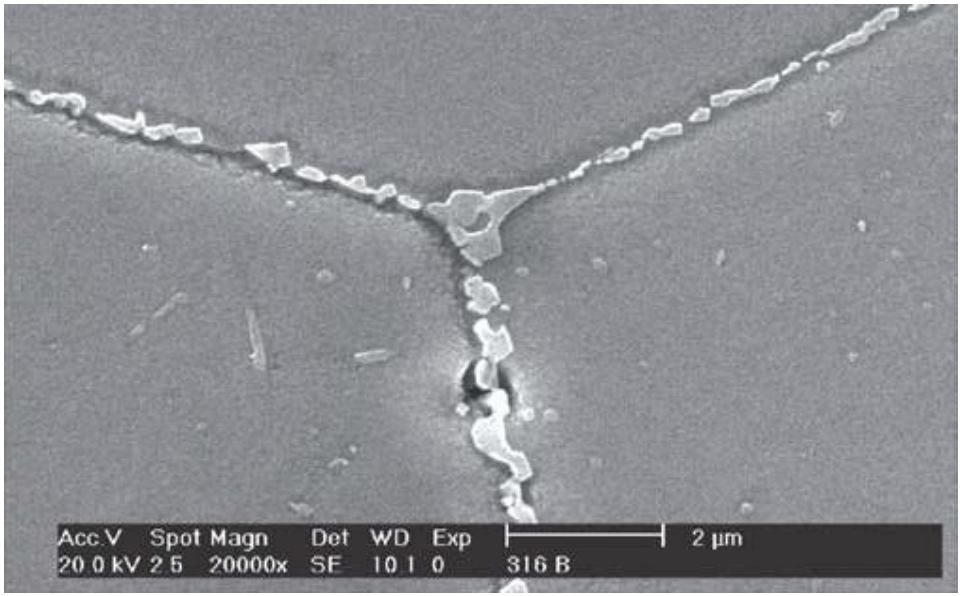
Micrographs of the gauge portion of the tested sample (550 °C /150 MPa/85000 h), showing precipitation of sigma phase in AISI 316L(N),

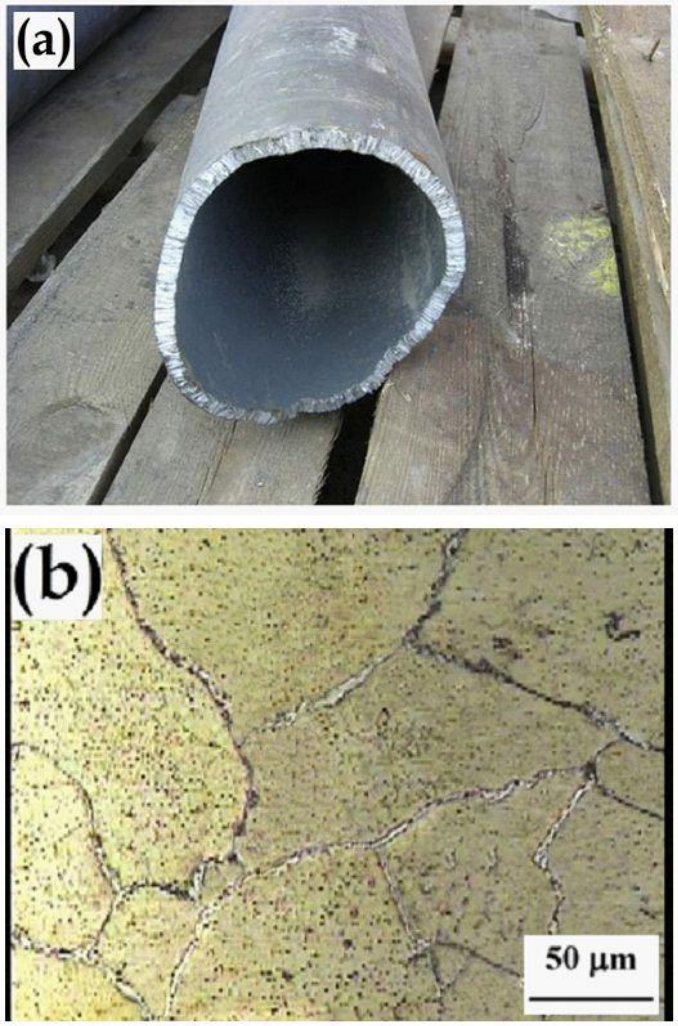
Ronald Lesley Plauta et al , Materials Research, Vol. 10, No. 4, 453-460, 2007

from delta ferrite islands



at austenite grain boundary and triple points



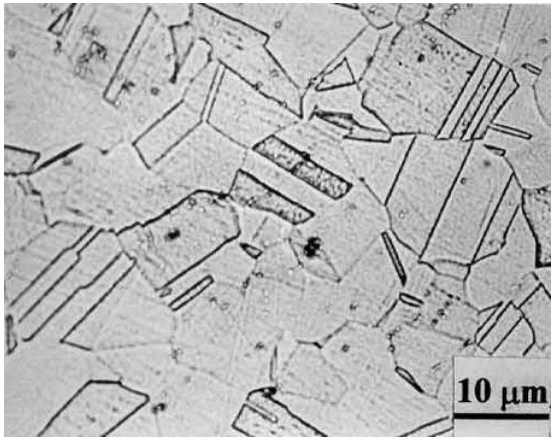


Failed rollerfor metal strip transfer in continuous annealing furnaces. An austenitic matrix and a network of sigma phase precipitates on austenitic grain boundaries in the failed roller.

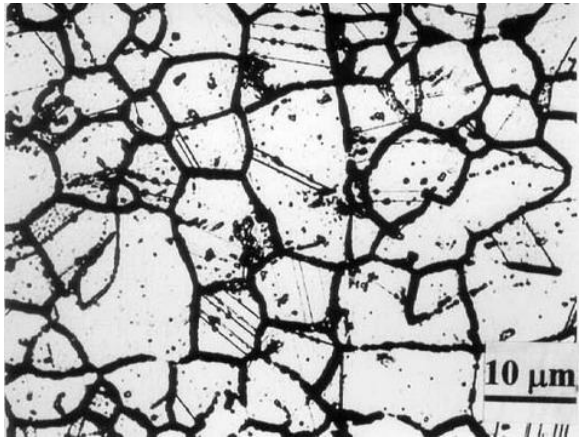
Materials Science » Metals and Nonmetals » "Metallurgy - Advances in Materials and Processes", book edited by Yogiraj Pardhi, ISBN 978-953-51-0736-1, 2012 **Chapter 5 Homogenization Heat Treatment to Reduce the Failure of Heat Resistant Steel Castings** By Mohammad Hosein Bina DOI: 10.5772/50312

Sensitization of Stainless Steel

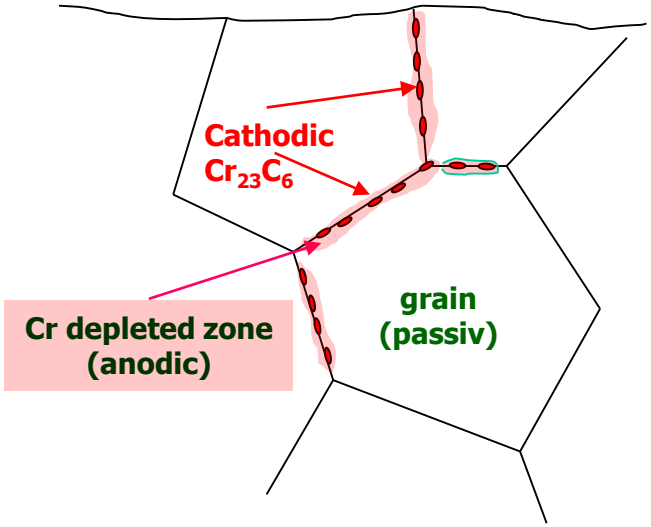
- Sensitization happens when SS held at an intermediate temperature (425°C – 815°C) → Cr carbides precipitate at grain boundaries
- For the carbide to precipitate: must get Cr from the surrounding metal → Cr depleted zone around the grain boundaries which will be less corrosion resistant, specifically to intergranular corrosion
- Sensitization particularly important in metals that are welded



unsensitized 304 stainless steell



sensitized 304



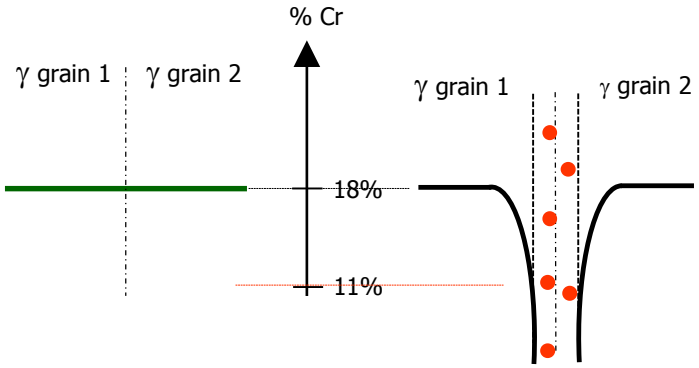
STAINLESS STEELS FOR VERY SEVERE ENVIRONMENTS

Benefit of austeno-ferritic grades for intergranular corrosion resistance

AUSTENITIC

- In ASS, Cr is homogeneously distributed in all γ grains and is above 18%Cr

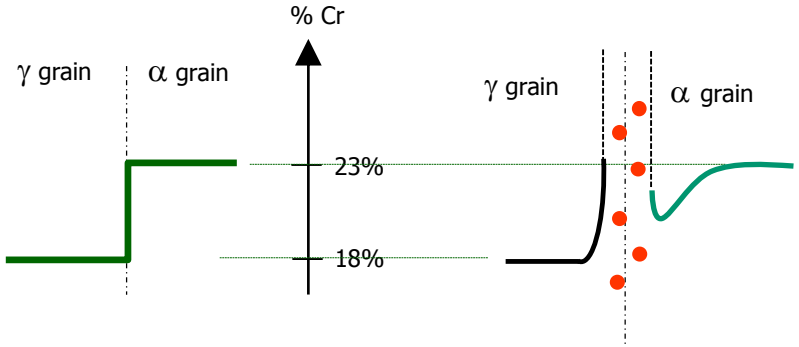
- If $Cr_{23}C_6$ at grain boundary,
  → a Cr depleted zone occurs
  → %Cr falls below 11%
  → depleted zone is no more corrosion resistant
  → intergranular corrosion



DUPLEX

- In a DSS, Cr is more abundant in ferrite than in austenite
- Cr diffuses more rapidly in α phase than in γ phase

→ To precipitate $Cr_{23}C_6$ at grain boundary, Cr is sucked from α
→%Cr does not vary in γ and therefore does not fall below 11%
•no Cr depleted zone = no corrosion problem



STAINLESS STEELS FOR HOSTILE ENVIRONNEMENTS

Stabilize as much as possible the protective oxide layer → add Mo, W, N

Avoid precipitation of $Cr_{23}C_6$,

Maintain Cr in solid solution or precipitate TiC or NbC → Add Ti and Nb

Avoid segregation S, P

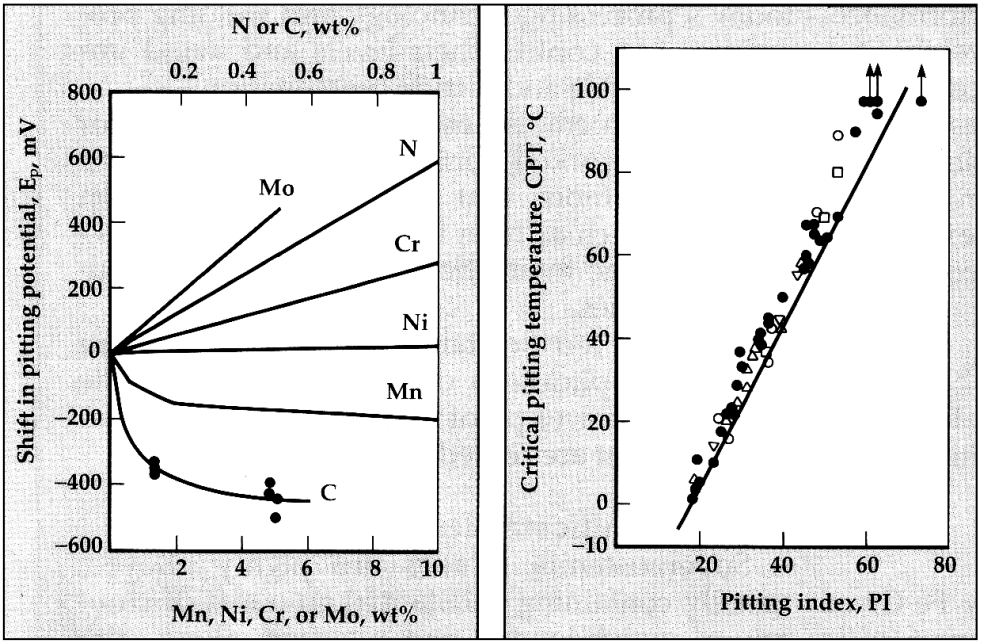
Avoid introduction of inclusions

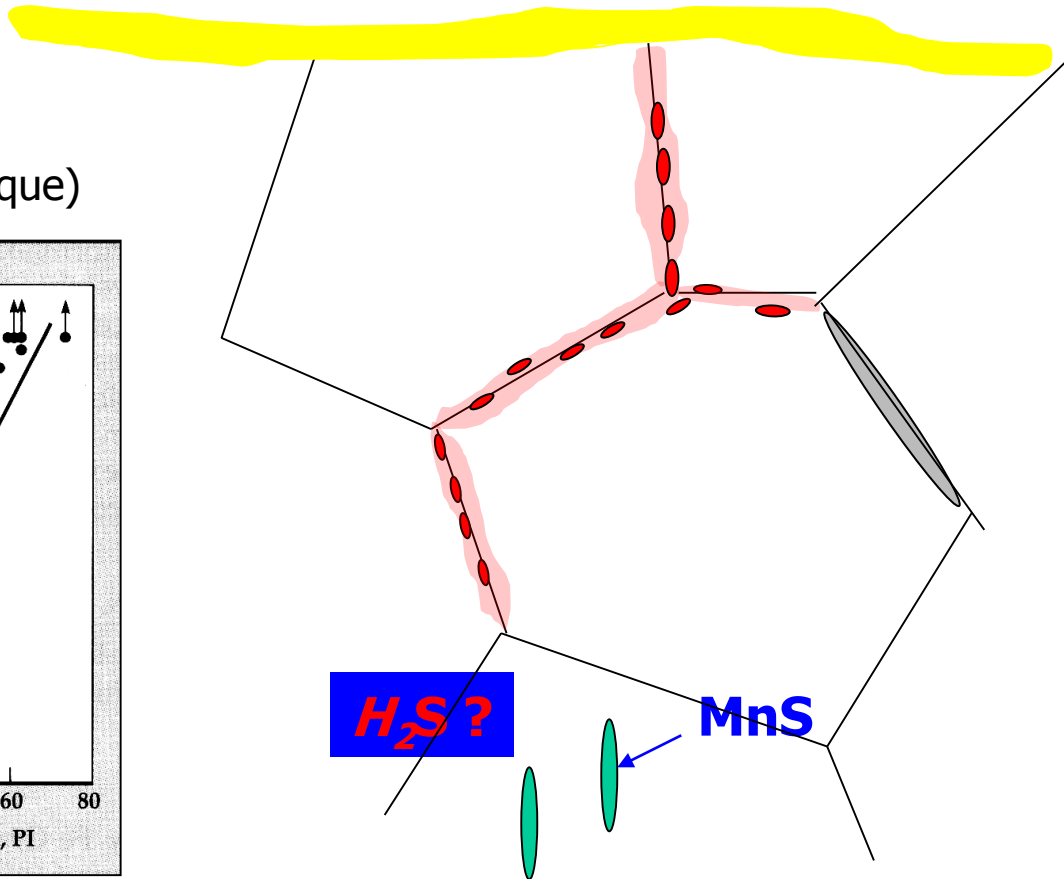
→ AOD and VOD

PI = %Cr + 3.3%Mo + X%N

pitting index

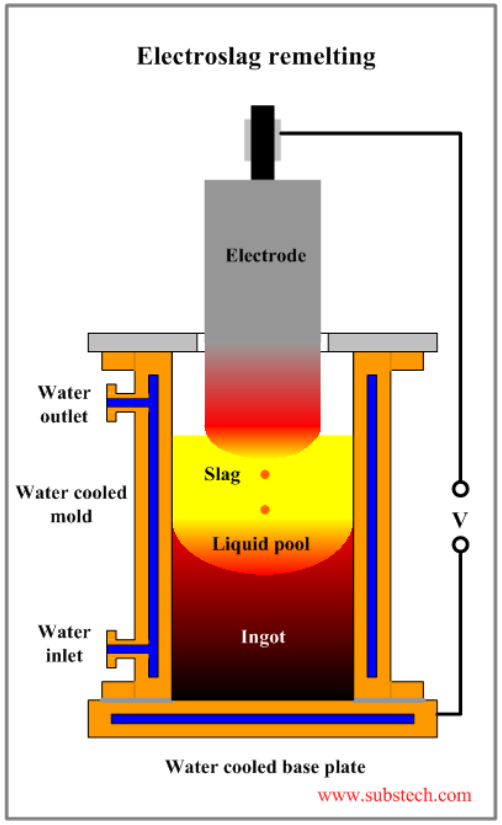
X = 0 (ferritique), 16 (duplex), 30 (austénitique)





ESR: Electro Slag Remelting process

- consumable electrod: cast or forged cylindrical parts made of an alloy to be remelt
- ESR starts when the lower tip of a consumable electrode is immersed into a pool of molten slag
- The premelted slag possessing electrical conductivity is located on the water-cooled mold base connected to a power supply.
- The electric current (commonly AC) passing through the slag keeps it at high temperature, which is about 360ºF (200ºC) higher than the melting point of the remelted metal.
- The electrode tip is heated by the hot slag and starts to melt forming droplets of liquid metal, which disconnect from the electrode and sink through the slag layer.
  The slag composition is based on calcium fluoride (CaF_2), lime (CaO) and alumina (Al_2O_3).



The slag composition provides the following properties:

•Melting point lower than that of the remelted alloy;
•Required level of viscosity;
•Required level of electrical conductivity;
•High solubility of sulfur;
•Capability to adsorb non-metallic inclusions.

The molten steel in form of both liquid film on the electrode tip and descending droplets contacts with the slag get refined due to desulfurization and removal of non-metallic inclusions (sulfides and oxides).

The droplets enters the molten steel pool, bottom of which is progressively solidifying. The water-cooled copper mold provides relatively high gradient of temperature resulting in high solidification rate. Solidification front is moving upwards (unidirectional solidification) forming sound homogeneous metal structure.

The ingot has a good surface quality due to a thin slag film covering it.

Advantages of Electroslag Remelting

•Deep desulfurization;
•Refining non-metallic inclusions;
•Homogeneous Distribution of non-metallic inclusions
•Fine Grain structure;
•No Shrinkage defects;
•Low macro segregation;
•Good surface quality;
•Controllable process.

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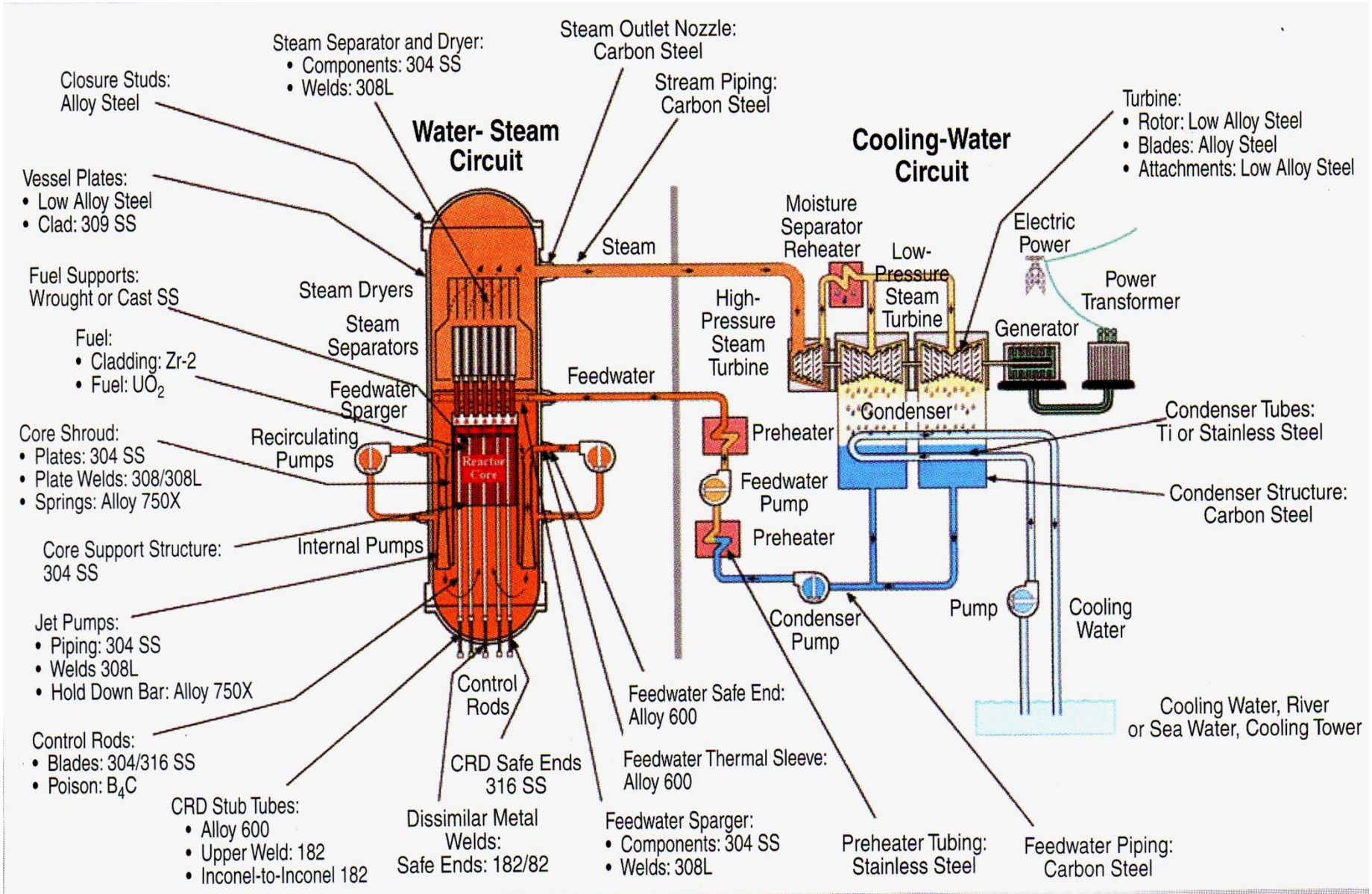
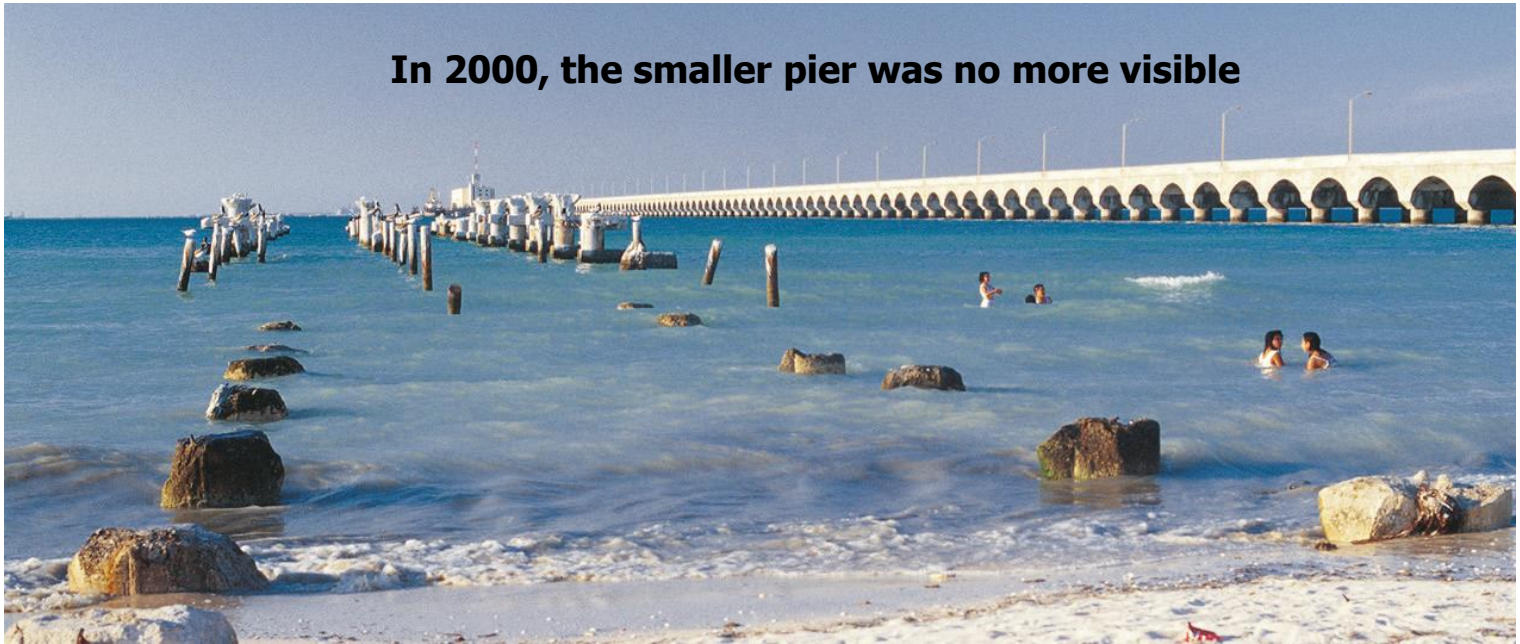


Figure 2. An outline of BWR components and materials. (Image courtesy of R. Staehle.)

In 1969 a much smaller pier (left) was built using carbon steel rebar alongside the 1941 Progreso Pier (right).



Hong Kong- Zhuhai- Macau Bridge[9]
(construction began in 2009, to be completed in 2015)

The prestigious Hong Kong- Zhuhai- Macau causeway project is one of the largest bridge projects in the world. The life time requirement is 120 years without maintenance. Therefore stainless steel reinforcement has been specified in the critical areas of the structure, mainly in splash zones. Eventually 15000MT of stainless will be used.

中国的巨型大桥

*香港新建的单跨斜拉桥寿命也许不像长城那样长，但其设计寿命也已长达**120**年。*

Hong Kong stonecutter viaduc

The world's second longest spanning cable-stayed bridge, with a main span of 1,018m

The towers are 298m tall with 1,600 tonnes of structural stainless steel in the cable-stay anchorage zone and 2800 tonnes of stainless rebar in the reinforced concrete lower part of the towers.

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Improvement of mechanical properties
Research performed at UMET

Fatigue Behaviour of High Nitrogen Austenitic and Duplex Stainless Steels

Work supported by USINOR (now ARCELOR), European Community, VSG

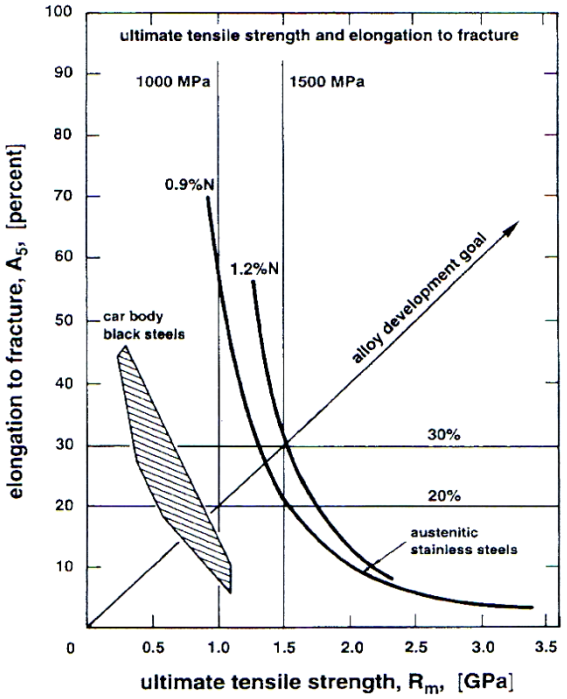
Why Nitrogen in austenitic stainless steels ?

→ Small atoms : interstitials

→ Produces the most strongest solid solution hardening

→ Large number of sites in FCC : large variation in content

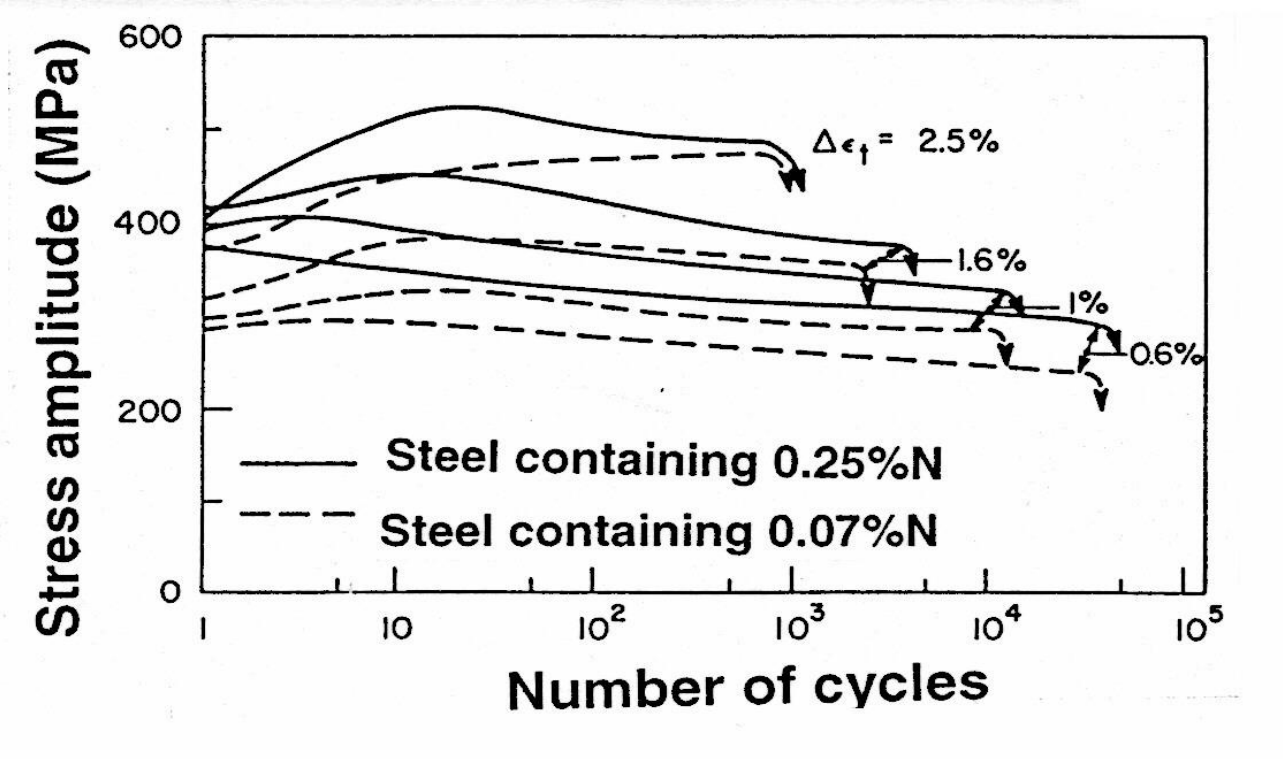
→ FREE !



Mechanisms of cyclic plasticity of stainless steels

Role of nitrogen content in Stainless Steels

TYPE 316L : 0.03%N to 0.25%N



Tests at R.T

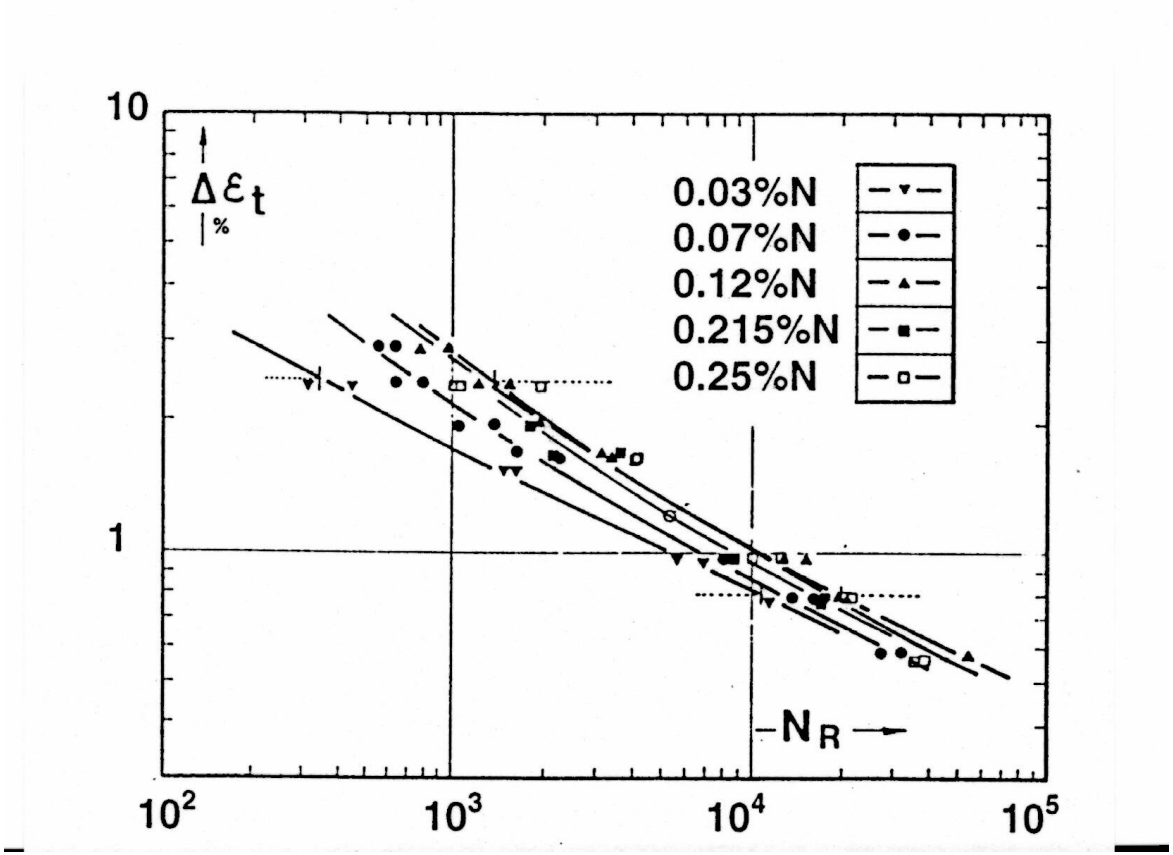
Nitrogen favours cyclic softening

Nitrogen increases cyclic stresses

Mechanisms of cyclic plasticity of stainless steels

Role of nitrogen content in Stainless Steels

TYPE 316L : 0.03%N to 0.25%N



Tests at R.T

Nitrogen increases fatigue lives

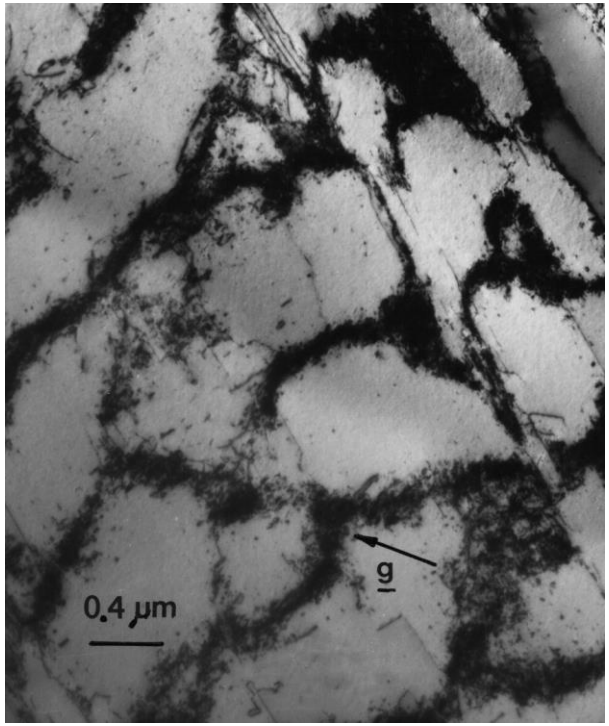
Mechanisms of cyclic plasticity of stainless steels

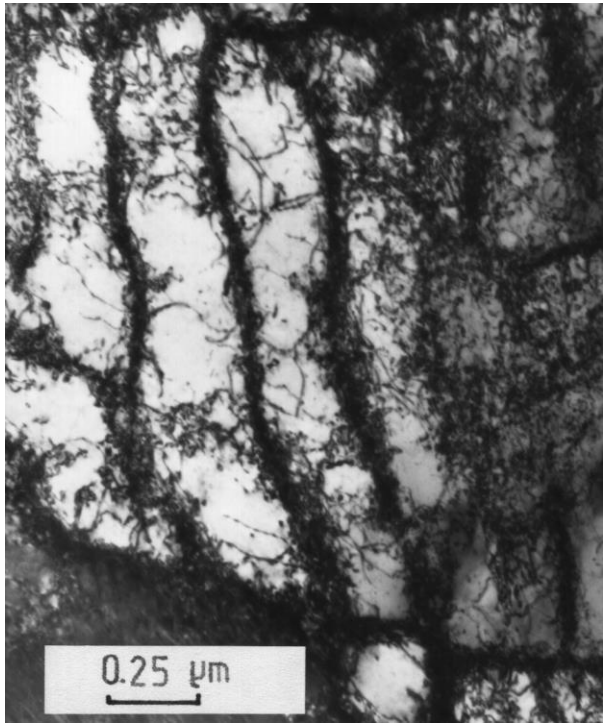
Role of nitrogen content in Stainless Steels

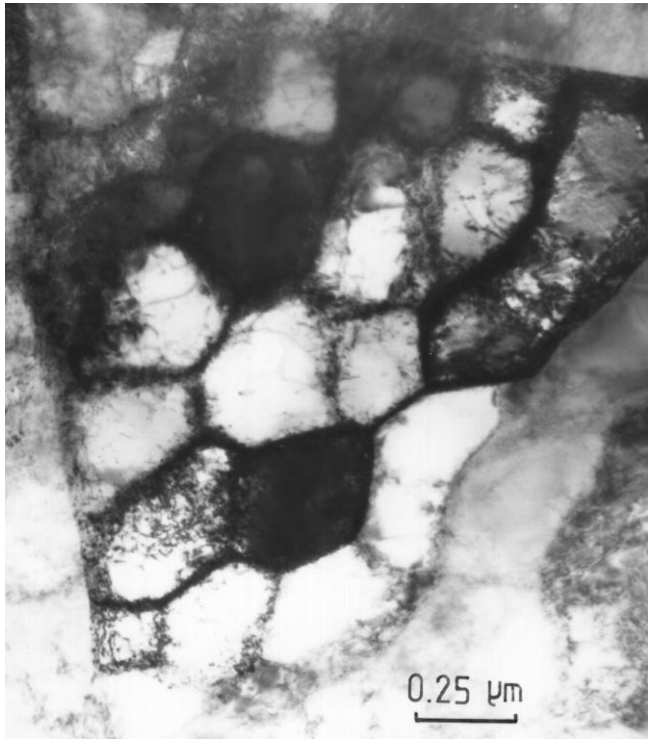
316L 0.03%N

Wavy Slip (R.T.)

Increasing strain amplitude ➔







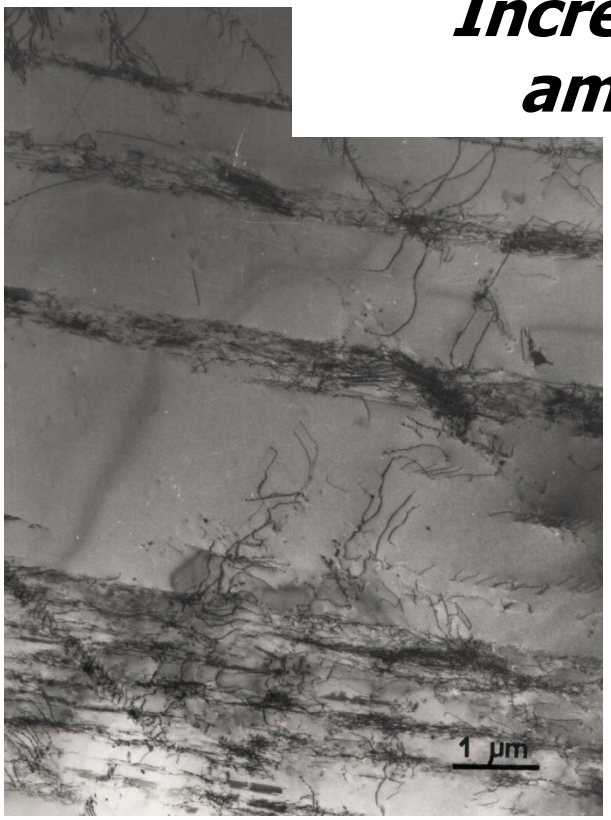
Mechanisms of cyclic plasticity of stainless steels

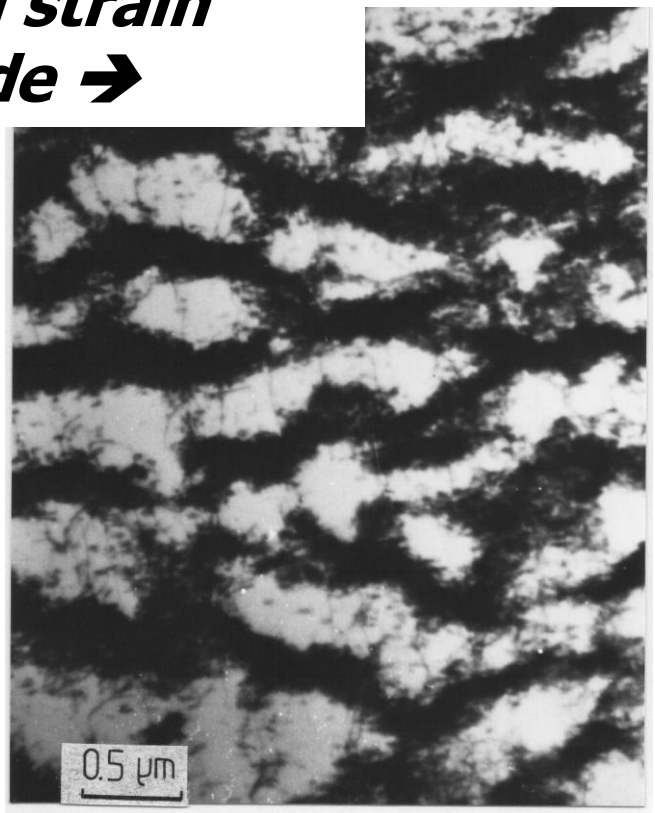
Role of nitrogen content in Stainless Steels

316L 0.25%N

Planar Slip (R.T.)

Increasing strain amplitude ➔





NITROGEN promotes planar glide and cyclic softening

Mechanisms of cyclic plasticity of stainless steels

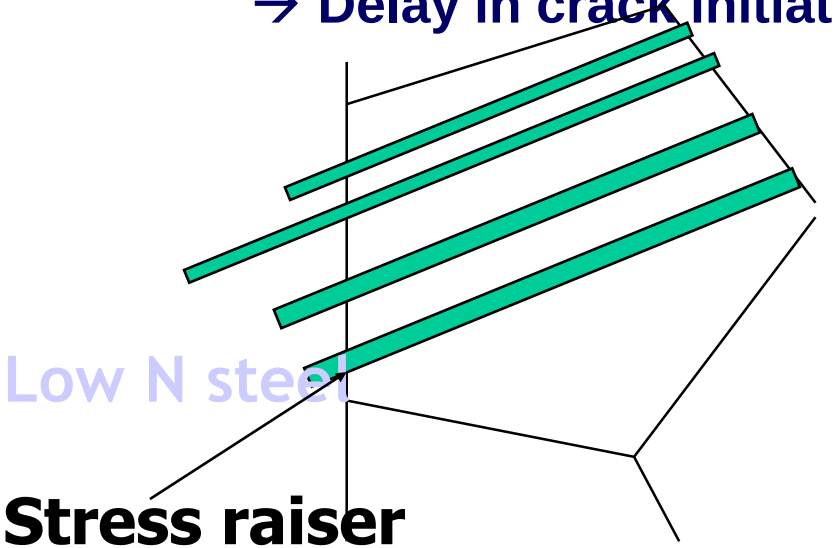
CONCLUSIONS

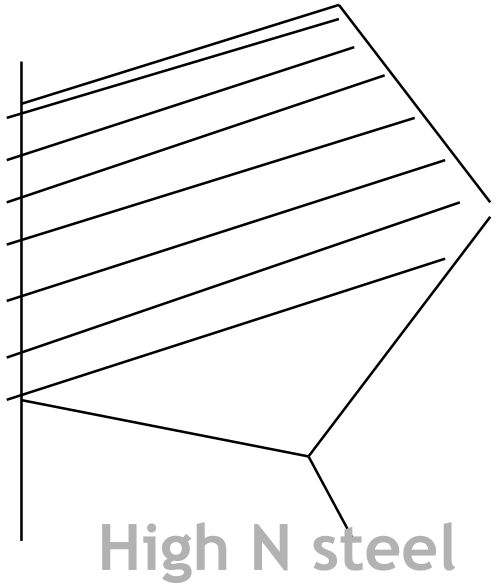
Role of nitrogen content in Stainless Steels:

-Solid solution hardening

-Promotes planar slip → INCREASES FATIGUE RESISTANCE

→ Better distribution of plastic deformation
→ Reduction of strain localisation
→ Delay in crack initiation





Improvement of mechanical properties
Research performed at UMET

Fatigue Behaviour of Fine Grained Austenitic Stainless Steels

Fatigue behaviour of Ultra Fine Grained austenitic stainless steels

Work supported by ARCELOR and ADEME (agency for energy mastership)
In the frame of Stéphanie BROCHET PhD work

UGINE & ALZ
Groupe Arcelor

ADEME

Motivation :

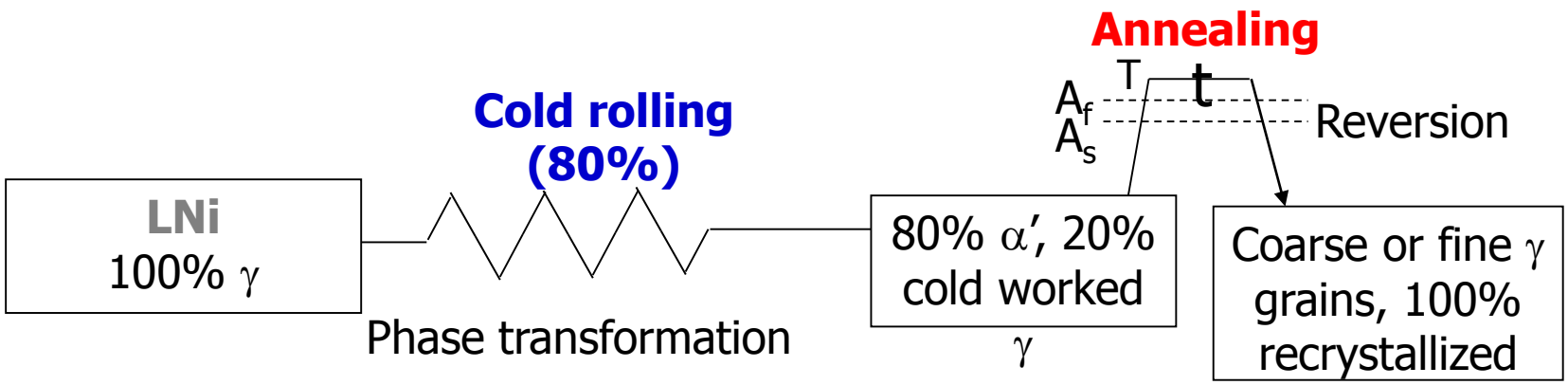
- Increase mechanical properties
- Reduce structure weight
- Decrease of material/production costs

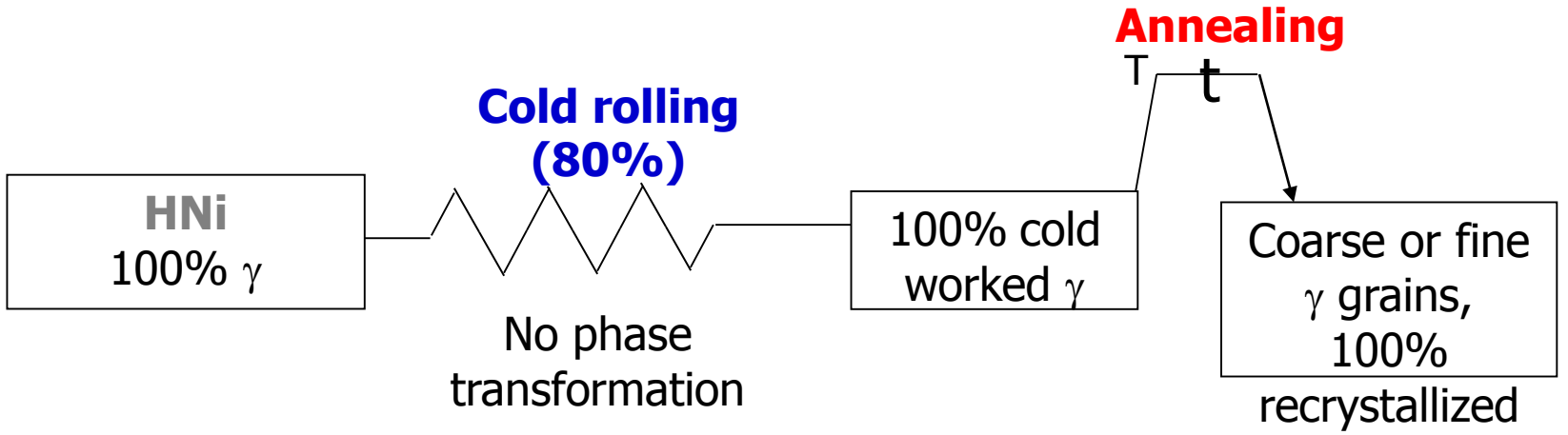
Materials

Element	C	Mn	Si	Cr	Cu	Mo	N
% (wt)	0,02	1,5	0,4	15,4	0,2	3,1	0,02

11%Ni: HNi steel

9%Ni: LNi steel

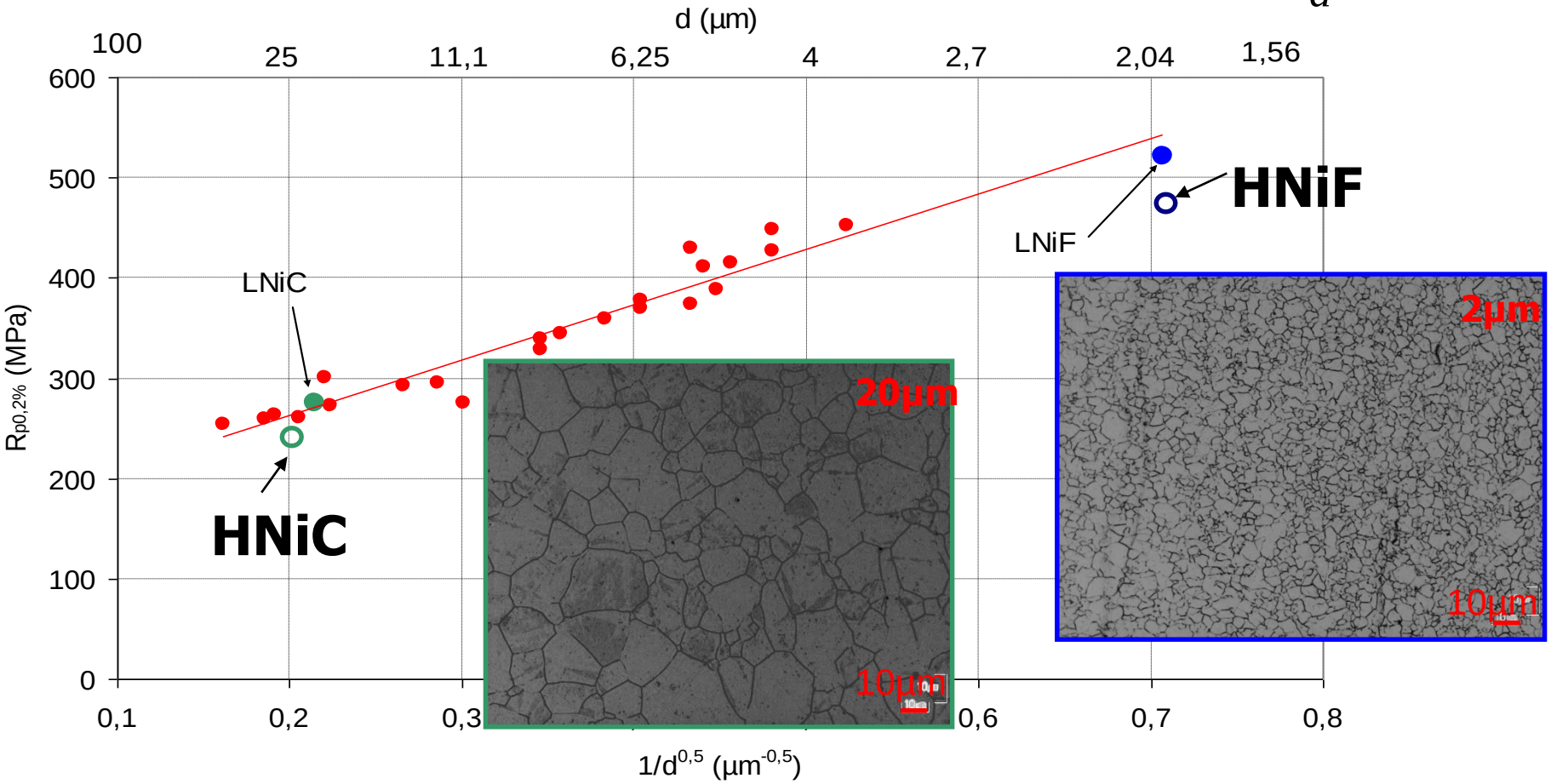




Optimization of experimental parameters (T, t) to obtain fine grains

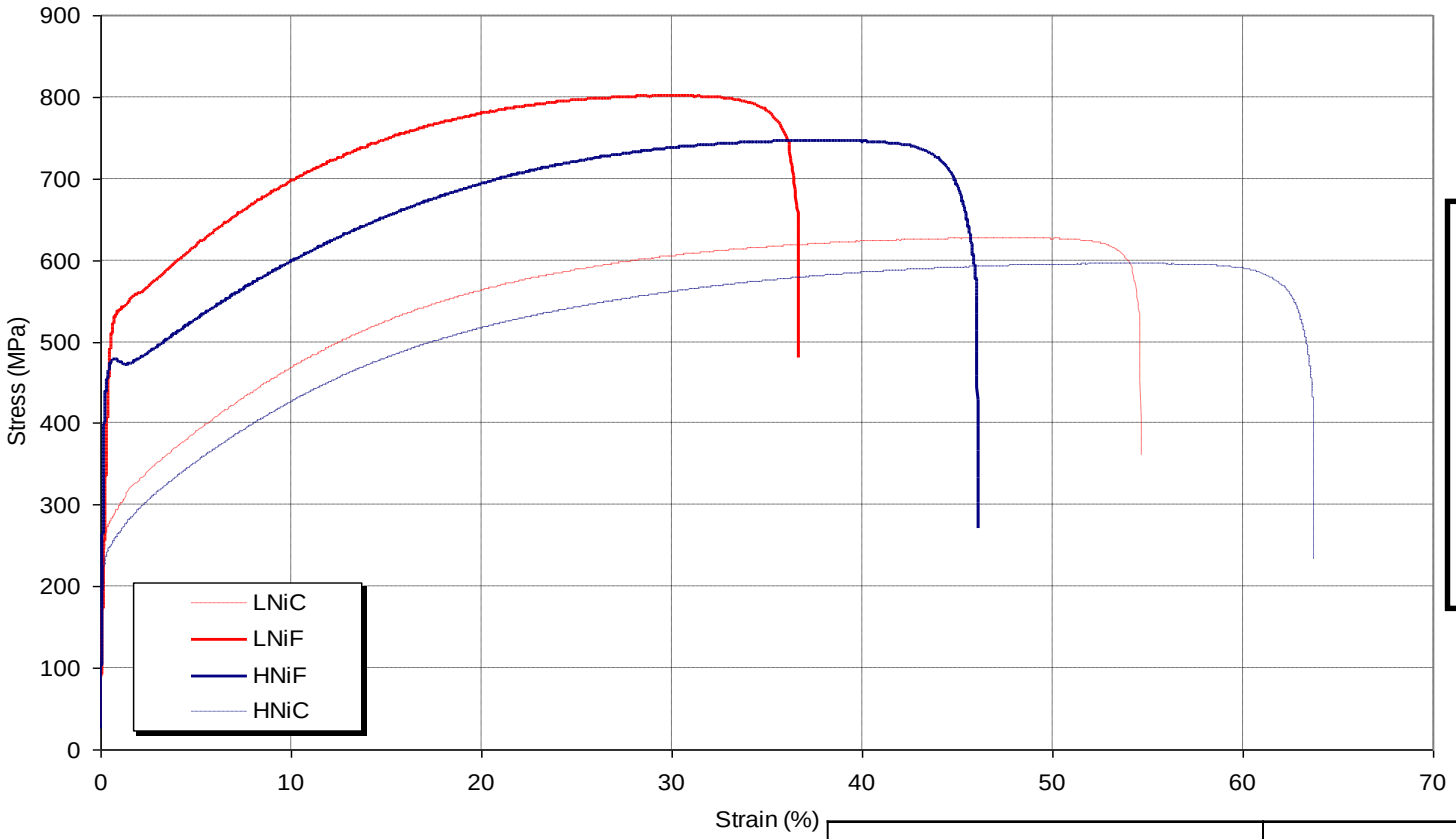
Materials

$$R_{p0,2\%} = 153.52 + \frac{550.53}{d^2}$$



Choice of microstructures for fatigue tests : 2µm and 20µm

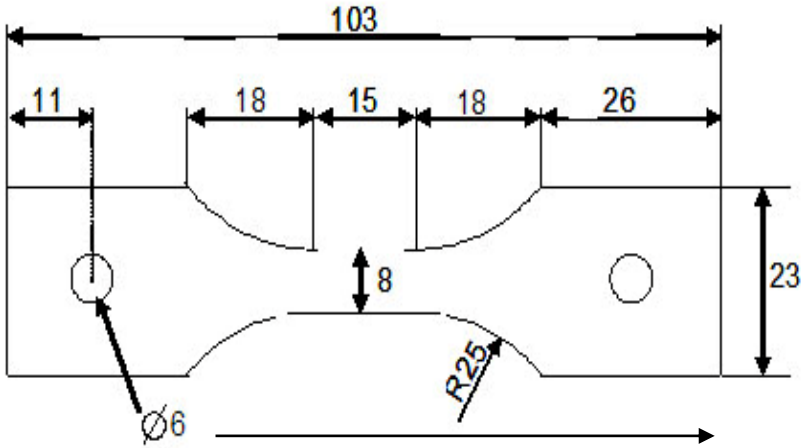
Tensile behaviour of Fine and Coarse grained Materials



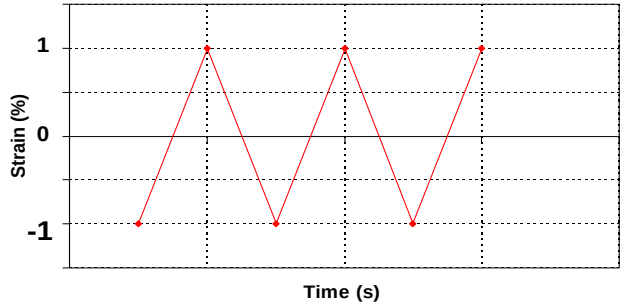
→ Synergic effect between grain size and chemical composition

	HNi Steels		LNi Steels	
	HNiF	HNiC	**LNiF**	LNiC
Yield stress (MPa)	**468**	240	**526**	276
Ultimate tensile strength (MPa)	**746**	597	**790**	625
Elongation to fracture (%)	**46**	63	**36**	54

Fatigue testing : experimental



Rolling direction



- Total strain controlled (R_ε= -1)
- Strain rate $4.10^{-3}s^{-1}$

Sample thickness : 1 mm → Aluminium stiffener

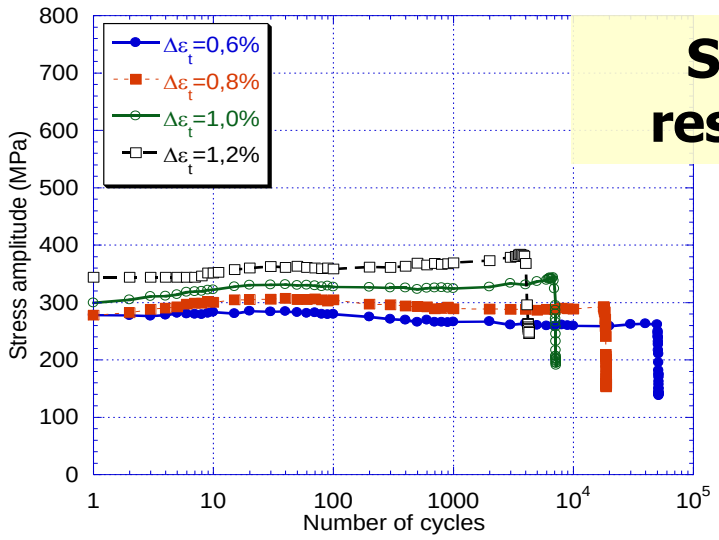
Fatigue behaviour of Fine and Coarse grained Materials: cyclic accommodation

Coarse grained steel

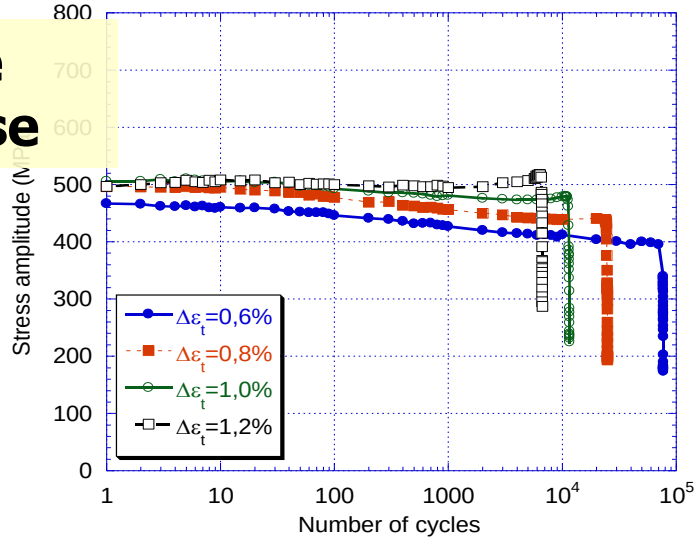
Fine grained steel

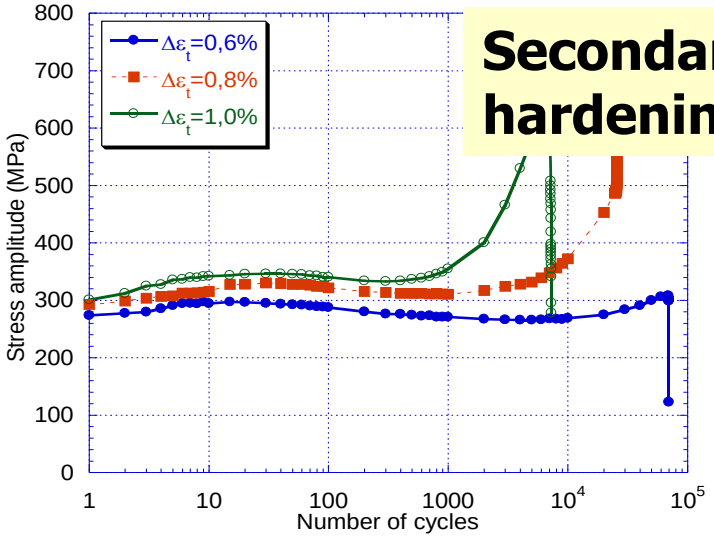
HNi

LNi

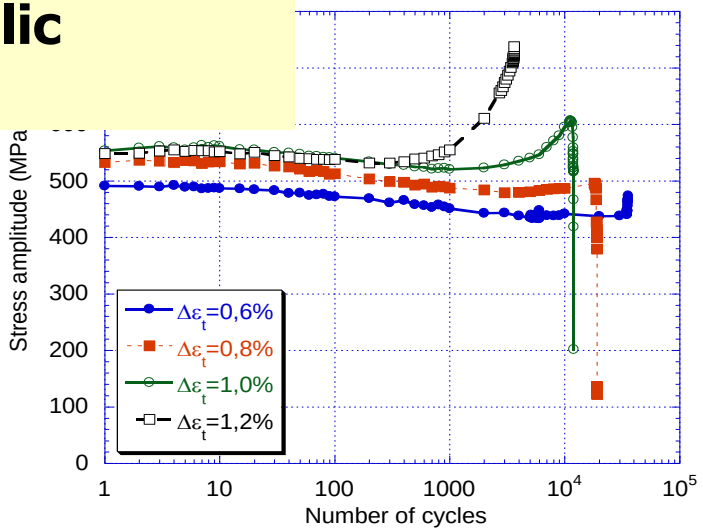


Stable response

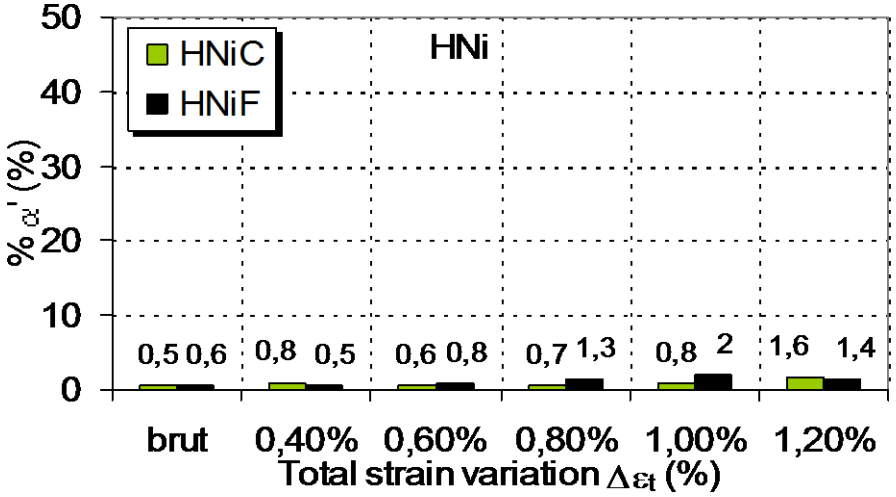


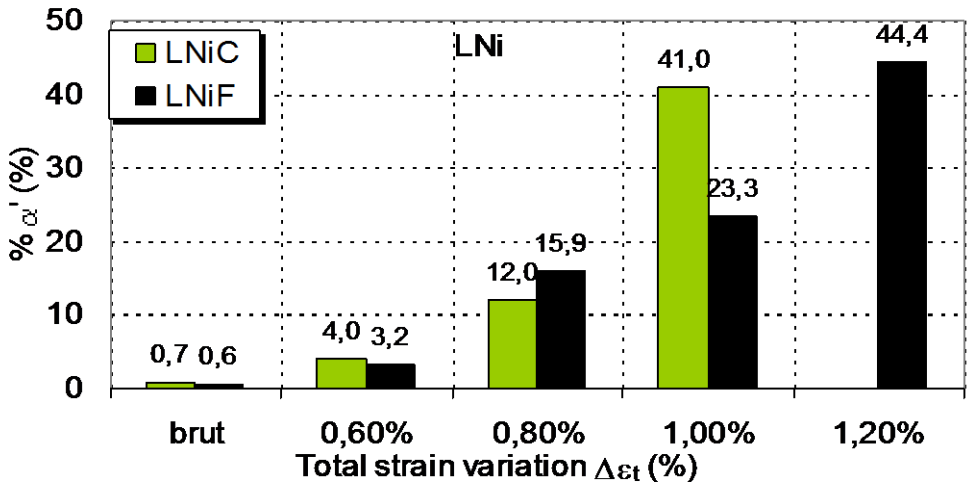


Secondary cyclic hardening

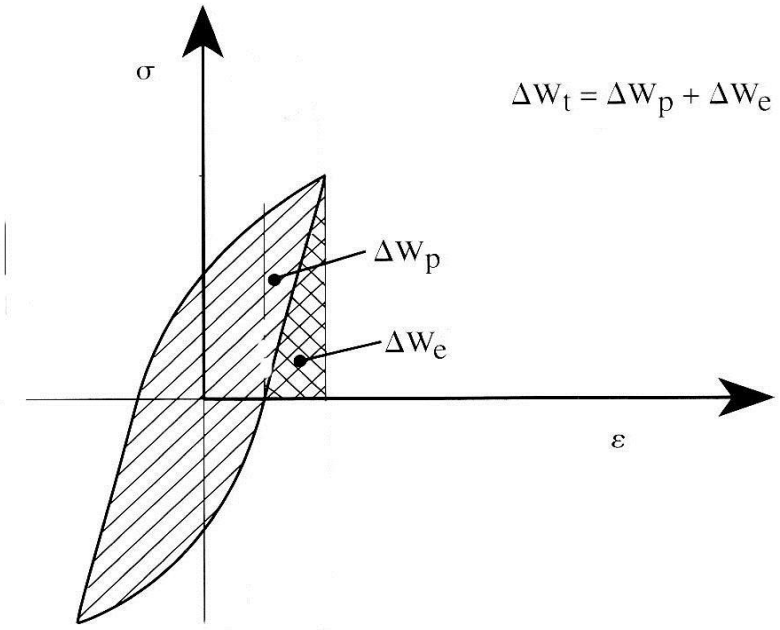


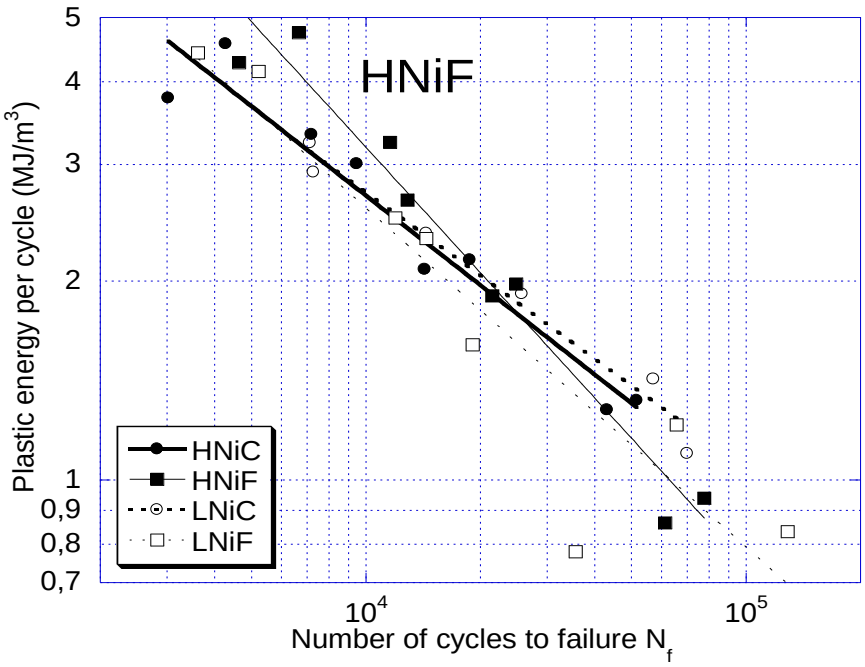
Origin of the secondary hardening : Martensitic transformation → quantification of α'



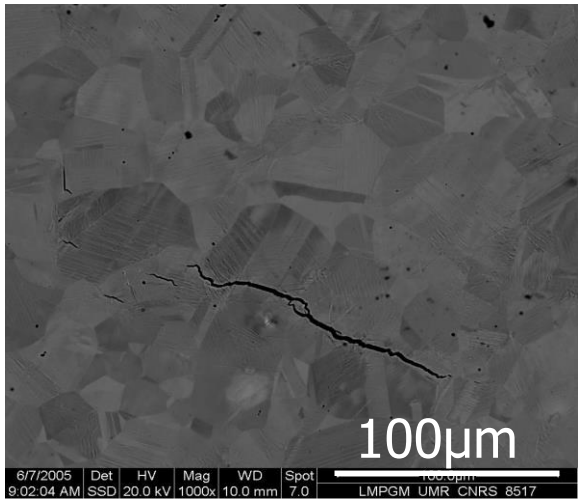
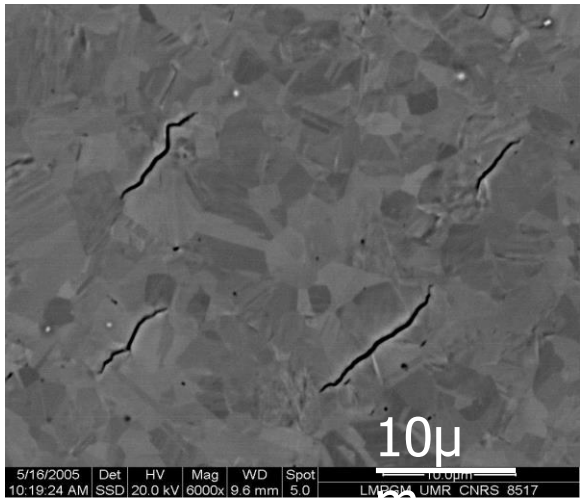
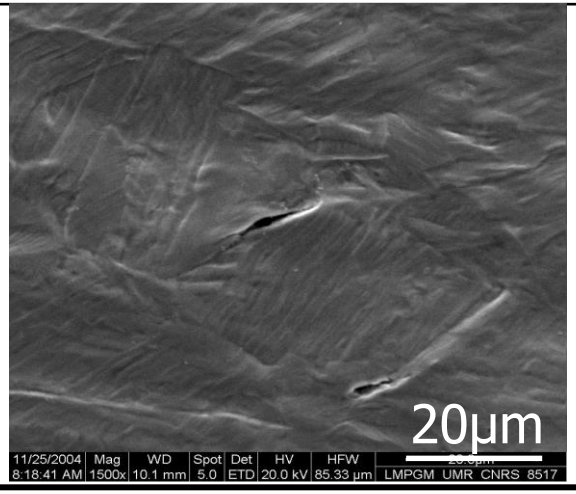
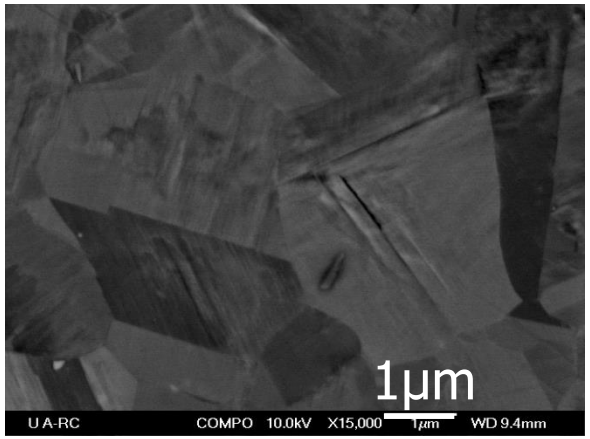


Energy criteria: Taking into account stress, total and plastic strain → good way to compare the effect of microstructures on fatigue resistance





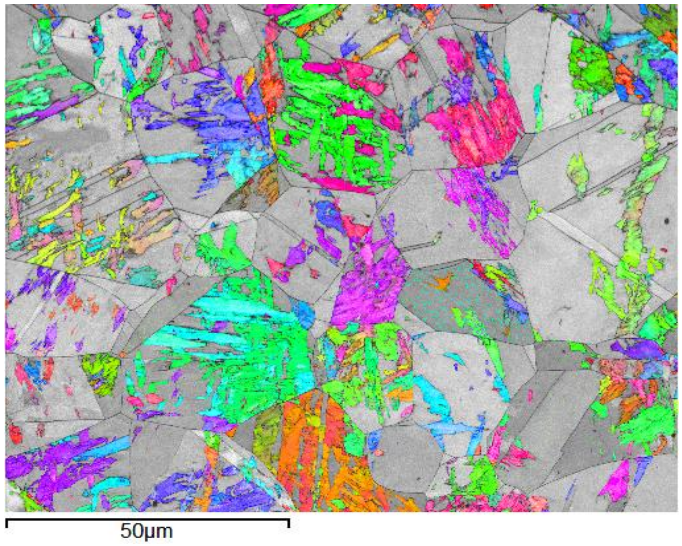
Fatigue behaviour of Fine and Coarse grained Materials: short cracks

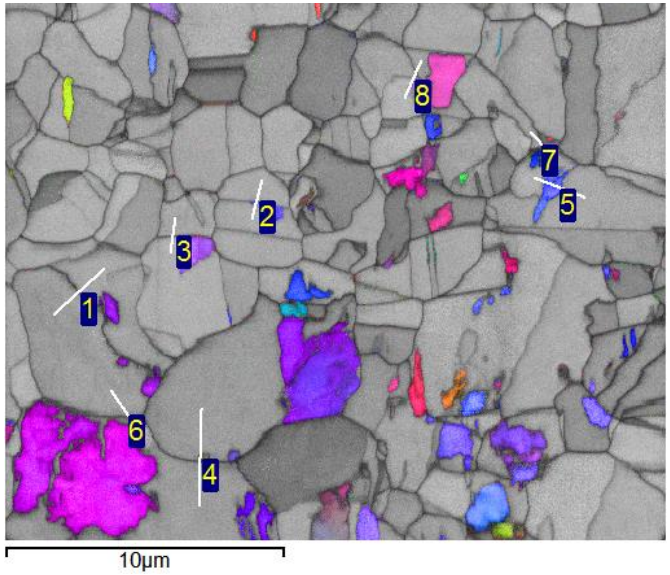
	Coarse grain	Fine grain	
HNi			• Numerous short cracks 1grain<size<10grains • Typical mechanism of fatigue cracking in austenitic stainless steel: nucleation, coalescence, propagation, failure
LNi			• Scarce cracks • Localization One crack=failure

→ **Composition effect**

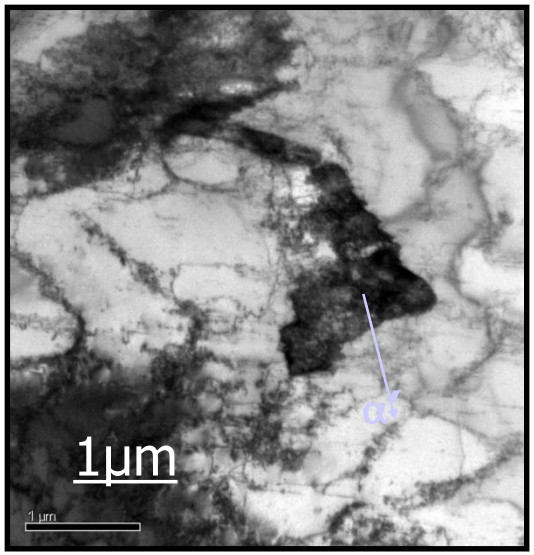
Fatigue induced martensite in LNi γ grains after LCF

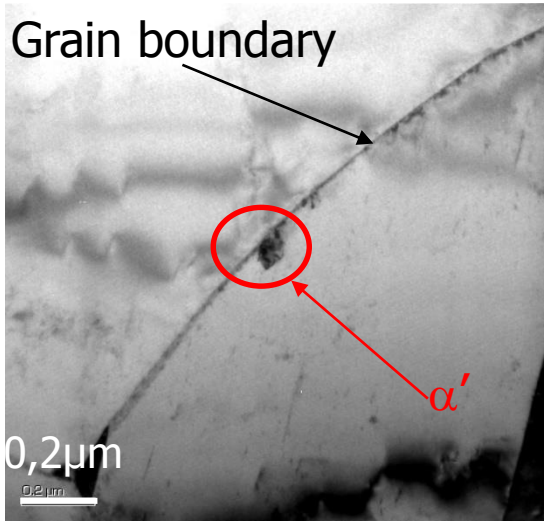
EBSD





TEM





Coarse grained steel

-Direct transformation γ → α′

-Nucleation: interior of grains

-Morphology: laths

-Observation of different α′ orientations inside a same γ grain

Fine grained steel

-Direct transformation γ → α′

-Nucleation: high disoriented boundaries (grain boundaries, twins)

-Morphology: grain type

-1 γ grain= 1 α′ orientation

Conclusions

- **Fine grained microstructures obtained with the control of thermo-mechanical process, tensile properties improved in a Low and High nickel austenitic stainless steels**

- In fatigue,
  - **Decreasing Ni content**
    - **Promote cyclic strain induced martensite**
    - No noticeable effect on fatigue life
    - Does not modify fatigue dislocation structure type of g grains
    - Multi cracking → single cracking

  - **Decreasing of the grain size**
    - **Higher stress ranges reached with good fatigue resistance**
    - Affects mechanism of phase transformation

  - Mechanisms of martensitic transformation **: new mechanism**
    - LNiC: cells boundaries, walls…
    - LNiF: vicinity of grain boundary + cells boundaries, walls…

Final conclusion

With strong research activities in metallurgy, stainless steels can be produced conbining high mechanical and high fatigue resistance with a reduced cost

Дякуємо Вам за увагу