Corrosion Resistant Alloy Developments and Selection Criteria

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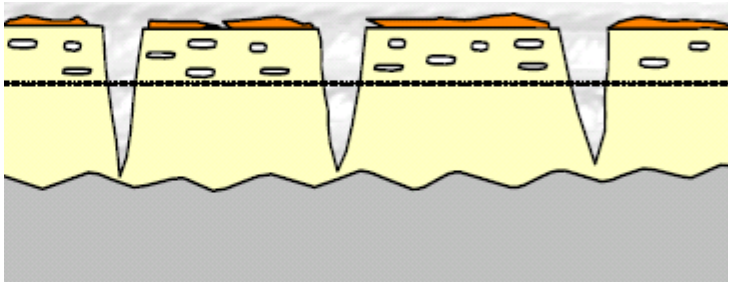
TMR Stainless

Basics of Stainless Steel

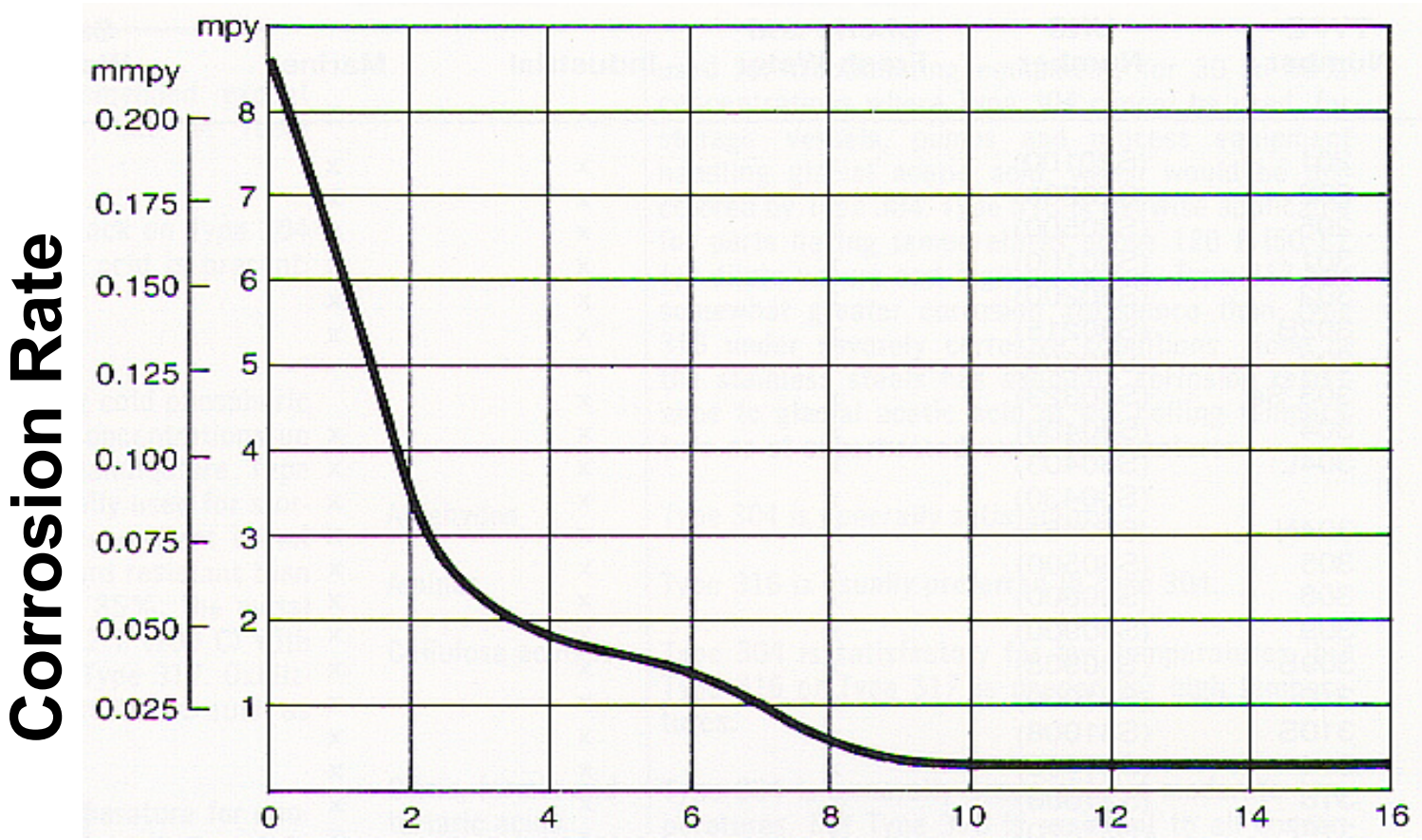
- What is stainless steel?
- Metallurgical categories
- Compositions
- Corrosion resistance
- Mechanical properties

Iron in steel reacts with the surrounding oxygen in air

POROUS NON-PROTECTING Fe2 O3 2H2 O OXIDE LAYER (RUST)



Chromium Increases Corrosion Resistance



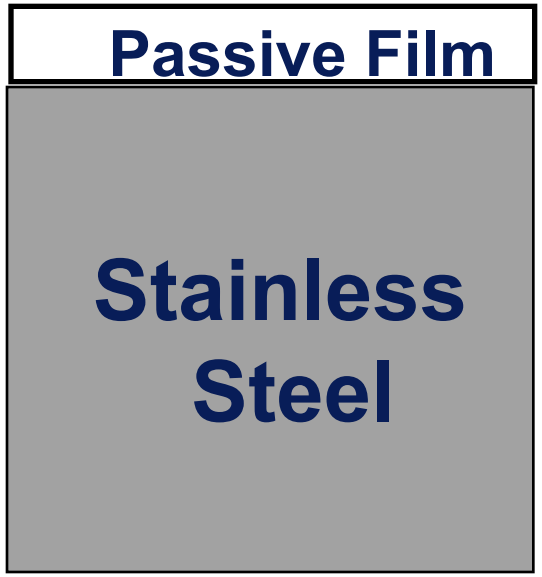
Chromium, Wt. %

How a Stainless Steel Works

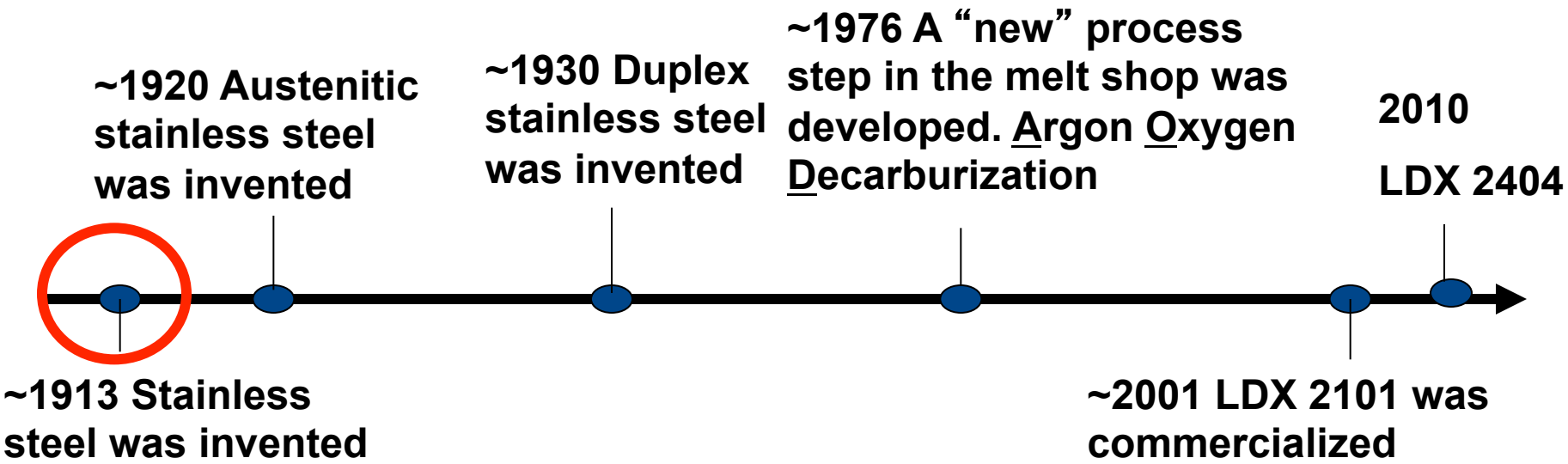
Iron +

< 11% Chromium

> 11% Chromium



Timeline – Stainless Steel Development



Metallurgical Stainless Steel Categories

- Austenitic
- Ferritic
- Duplex
- Martensitic
- Precipitation Hardening

Ferritic stainless steel

	Steel designations		Outokumpu steel names	Typical chemical composition, %					
	EN	ASTM/UNS		C	N	Cr	Ni	Mo	Others
Ferritic	1.4003	S40977	4003	0.02	–	11.5	0.5	–	–
	1.4000	410S	4000	0.03	0.01	12.5	–	–	–
	1.4016	430	4016	0.04	–	16,5	–	–	–
	1.4509	S43932	4509	0.02	–	18	–	–	Nb, Ti
	1.4521	444	4521	0.02	0.01	17.8	–	2.1	Ti

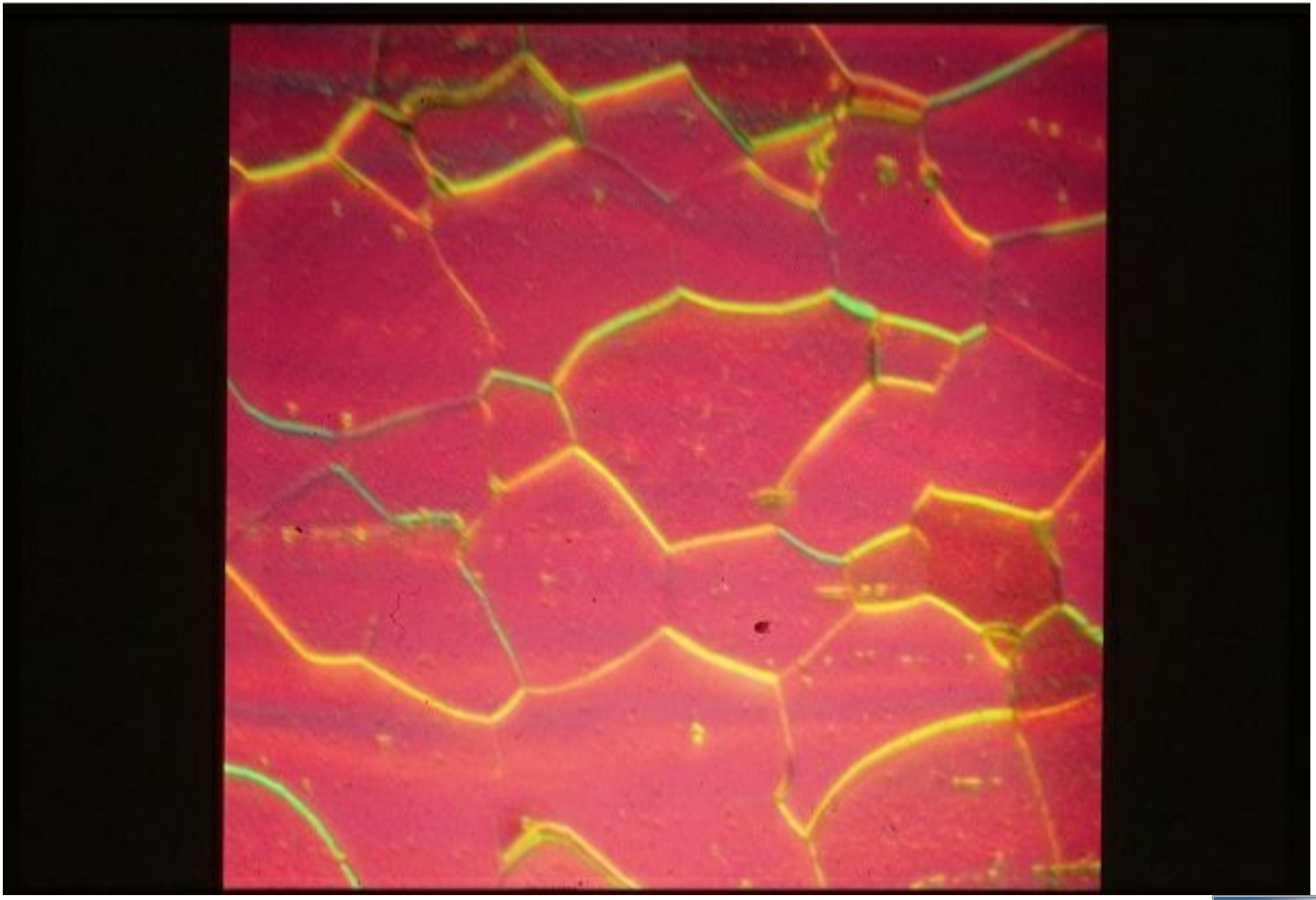
Applications for ferritic grades

Main advantages

- Ferritics are low cost (no nickel)
- Is mainly used indoor where the esthetic properties are more important than other properties such as corrosion resistance mechanical strength

Ex.

- Catering appliances
- Kitchen utilities
- White goods
- Wall cladding (indoor)



Ferritic Microstructure

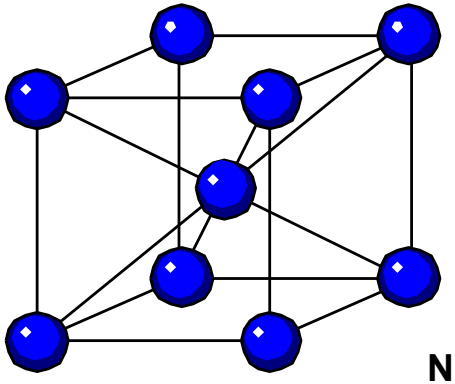
Ferritic Stainless Steels

	Cr	Mo	N (max)	C (max)	Other
409	11	-	0.03	0.03	Ti 6(C+N)
430	16	-	-	0.12	
439	17	-	0.04	0.12	Ti 0.2+4(C+N)
436	16	1.0	-	0.12	Nb 5xC
444	18	2.0	0.035	0.025	Ti+Nb= 0.2+4(C+N)

Ferritics - no success originally!

The ferritics were too brittle because of poor melting technology - the carbon contents were too high originally!

BCC - Body Cubic Centered Ferrite

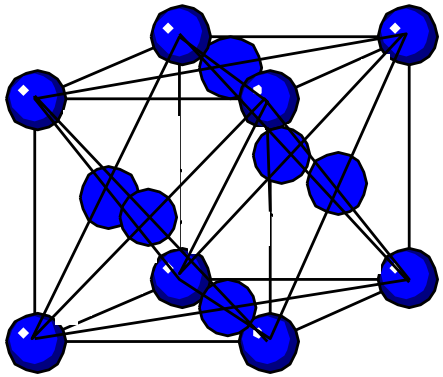


Ferrite

+Ni

Nickel changed the crystal structure

FCC - Face Cubic Centered Austenite



Austenite

Austenitic Stainless Steels

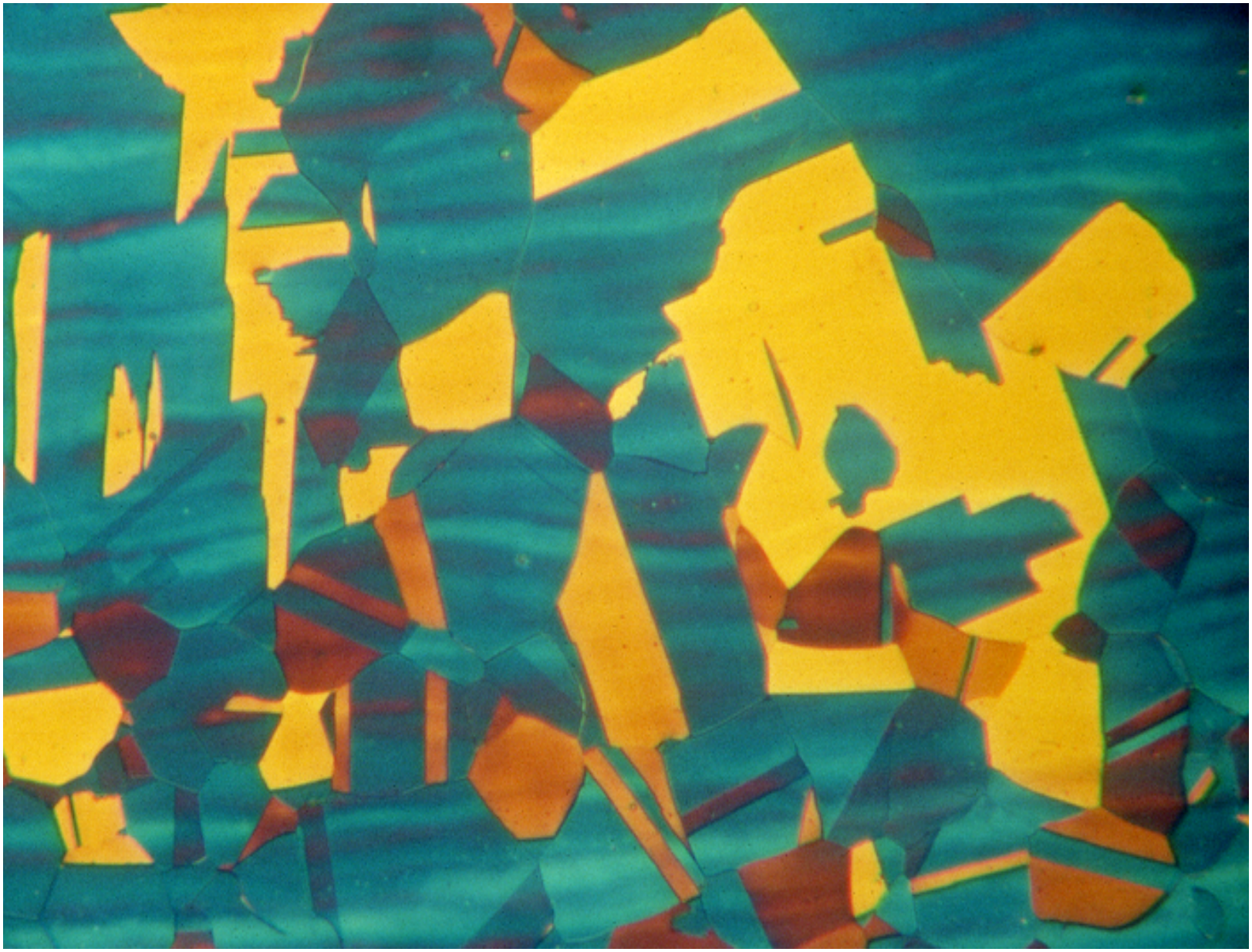
"Basic Grade"

Type 304 (18Cr-8Ni)

- Versatile, good for many situations
- Limited corrosion resistance
- Limited strength

Austenitic stainless steel

	Steel designations		Outokumpu steel names	Typical chemical composition, %					
	EN	ASTM/UNS		C	N	Cr	Ni	Mo	Others
Austenitic	1.4310	301	4310	0.10	–	17	7	–	–
	1.4318	301LN	4318	0.02	0.14	17.7	6.5	–	–
	1.4372	201	4372	0.05	0.20	17	4	–	7Mn
	1.4568	631	4568	0.08	0.02	16.6	7.6	–	Al
	1.4301	304	4301	0.04	–	18.1	8.1	–	–
	1.4307	304L	4307	0.02	–	18.1	8.1	–	–
	1.4311	304LN	4311	0.02	0.14	18.5	9.2	–	–
	1.4541	321	4541	0.04	–	17.3	9.1	–	Ti
	1.4550	347	4550	0.05	0.04	17.5	9.5	–	Nb
	1.4305	303	4305	0.05	–	17.3	8.2	–	S
	1.4303	305	4303	0.04	–	17.7	12.5	–	–
	1.4306	304L	4306	0.02	–	18.2	10.1	–	–
	1.4567	S30430	4567	0.01	–	17.7	9.7	–	3Cu
	1.4401	316	4401	0.04	–	17.2	10.1	2.1	–
	1.4404	316L	4404	0.02	–	17.2	10.1	2.1	–
	1.4427[1]	–	4427	0.02	0.05	16.9	10.7	2.6	S
	1.4436	316	4436	0.04	–	16.9	10.7	2.6	–
	1.4432	316L	4432	0.02	–	16.9	10.7	2.6	–
	1.4406	316LN	4406	0.02	0.14	17.2	10.3	2.1	–
	1.4429	S31653	4429	0.02	0.14	17.3	12.5	2.6	–
	1.4571	316Ti	4571	0.04	–	16.8	10.9	2.1	Ti
	1.4435	316L	4435	0.02	–	17.3	12.6	2.6	–
	1.3952[1]	–	3952	0.02	0.18	16.9	13.2	2.7	–



Austenitic Microstructure

Chemical Composition

	Cr	Ni	Mo	N	C (max)
304	18	8	–	0.06	0.08
304L	18	8	–	0.06	0.03
316	17	11	2	0.06	0.08
316L	17	11	2	0.06	0.03
317L	18	12	3.0	0.06	0.03
317LMN	18	14	4.3	0.16	0.02
904L	20	25	4.5	0.06	0.02
254 SMO	19	18-24	6.2	0.20	0.02

Applications for austenitic grades

Main advantages

- Very good formability
- Very good corrosion resistance (4565)
- Very good weldability
- Tough at low temperatures
- Good high temperature strength
- Not magnetic (austenite)

Ex.

- Chemical and pharmaceutical
- Oil and gas
- Architectural, Building and construction

Austenite

- High toughness
- Good weldability
- Good formability
- Higher thermal expansion
- Non-magnetic

Ferrite

- Low toughness
- Limited weldability
- SCC resistant
- Higher thermal conductivity
- Magnetic

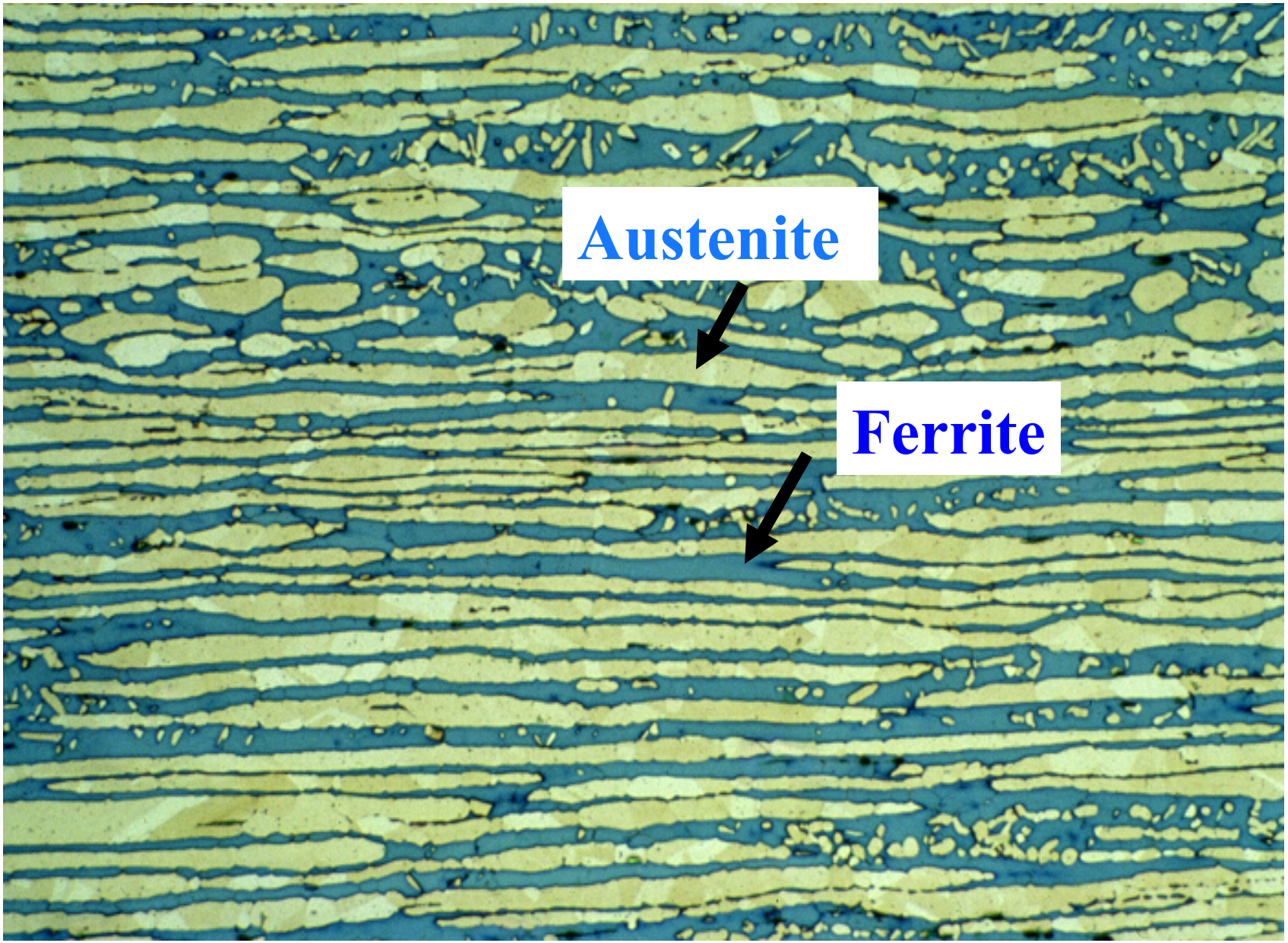
Duplex Stainless Steels combine Austenite <u>and</u> Ferrite

- Low nickel
- High chromium
- Medium molybdenum
- High nitrogen

Duplex

- Duplex had twice the strength of austenitics, the melting process was not tightly controlled, which resulted in poor fabrication
- By 1930 two duplex grades were commercially available from Avesta Steel Works
  - Grade 453E (26Cr-5Ni) – Heat resistant grade
  - Grade 453S (26Cr-5Ni-1Mo) – Improved wet corrosion resistance

Autoclave for gun powder built in duplex grade 453S in 1933



Duplex Microstructure

Characteristic properties of duplex grades

- Good resistance to pitting and crevice corrosion
- High resistance to SCC (Stress Corrosion Cracking) and corrosion fatigue
- High mechanical strength
- Good fatigue, abrasion and erosion resistance
- High energy absorption
- Low thermal expansion
- Good weldability and machinability

Chemical Composition

Duplex	Cr	Ni	Mo	N	C (max)
2205	22	5	3	0.18	0.03
2507	25	7	4	0.25	0.03
Lean Duplex					
LDX 2101	21	1.5	0.3	0.22	0.03
2304	23	4	0.2	0.10	0.03
LDX 2404	24	4.0	1.6	0.27	0.03

Applications for Duplex

Main advantages

- Twice the strength
- Very good pitting and crevice corrosion resistance
- Price stability

Ex.

- Storage tanks
- Pressure vessels
- Architectural, Building and construction
- Heat exchangers
- Pipes and fittings
- Rebar

Types of Stainless Steels

Austenitic	Type 304
Ferritic	Type 430
Duplex	Type 2205

Chemical Composition

Type	%Cr	%Ni	%Mo
304	18	8	
430	16		
2205	22	5	3

Alloying Elements

- Chromium – corrosion resistance
- Molybdenum – chloride pitting resistance
- Nickel – ductility, toughness, weldability
- Nitrogen – strength, pitting resistance

Compositions for Increased Corrosion Resistance

- Increase chromium (Cr)
- Increase molybdenum (Mo)
- Increase nitrogen (N)

Corrosion Resistance

- Higher numerical alloy designations do not imply better corrosion resistance - Type 430 is not better than Type 316

- Relative alloy corrosion resistance in chloride-bearing environments can be calculated using the Pitting Resistance Equivalent Number (PREN)

Corrosion Resistance

PREN = %Cr + 3.3(%Mo) + 16(%N)

T430 PREN = 16 + 3.3 (0) + 16 (0)

= 16

T316 PREN = 16 + 3.3 (2) + 16 (0)

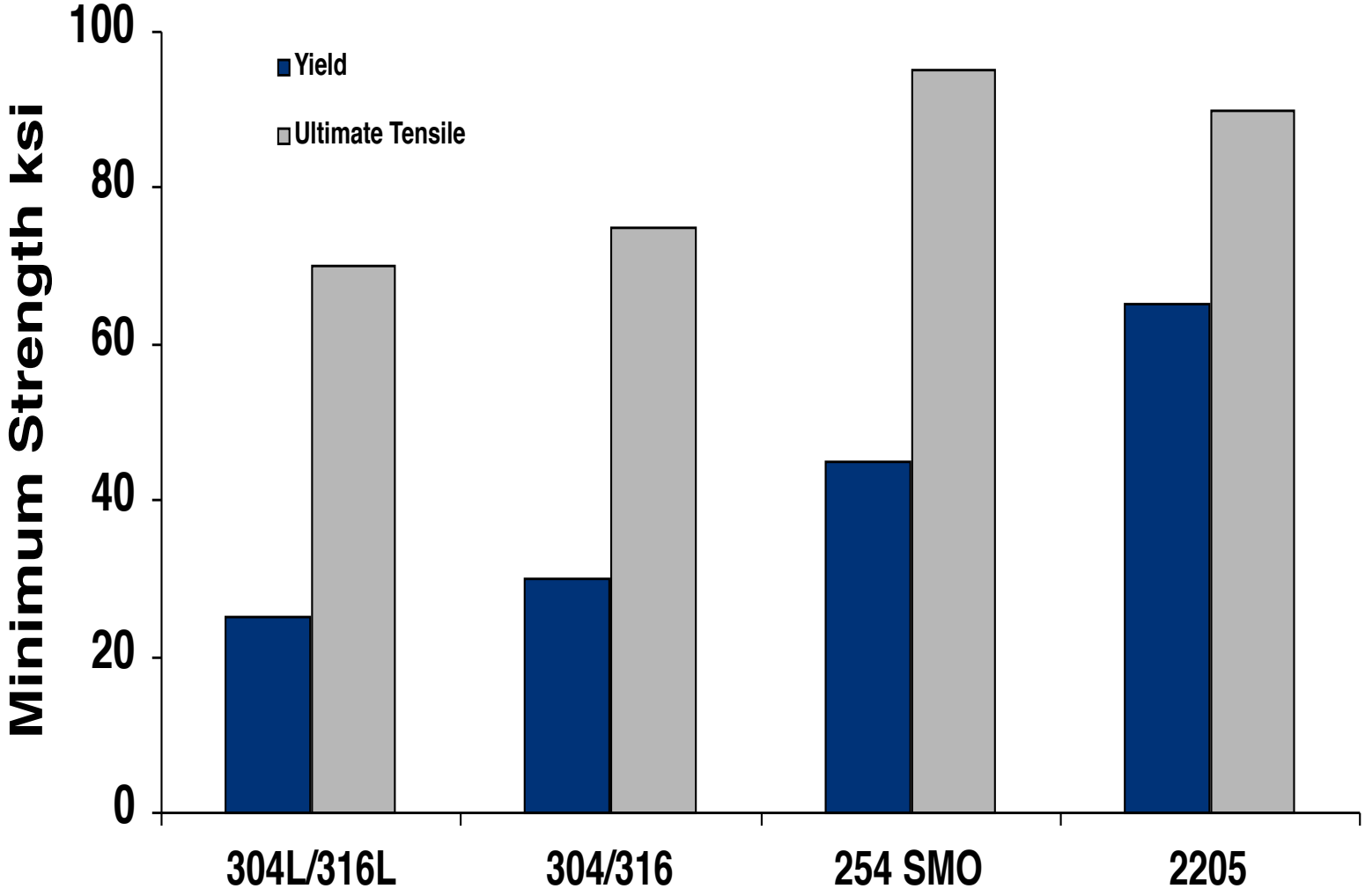
= 22.6

T316 is more pitting resistant than T430

PREN=%Cr+3.3(%Mo)+16%N

	Cr	Mo	N	PREN
304L	18			18
316L	16	2		23
317LMN	18	4.3	0.14	35
904L	20	4.5		35
254SMO	20	6	0.2	43
654SMO	24	7.3	0.5	56
2205	22	3	0.18	35

Strength by Grade



Summary

- Five different stainless steel families
- Austenitic, Ferritic, Duplex – three most common families
- Select stainless steel based on corrosion resistance, strength and cost

Passivity

Uniform corrosion

Pitting & Crevice corrosion

Stress Corrosion Cracking

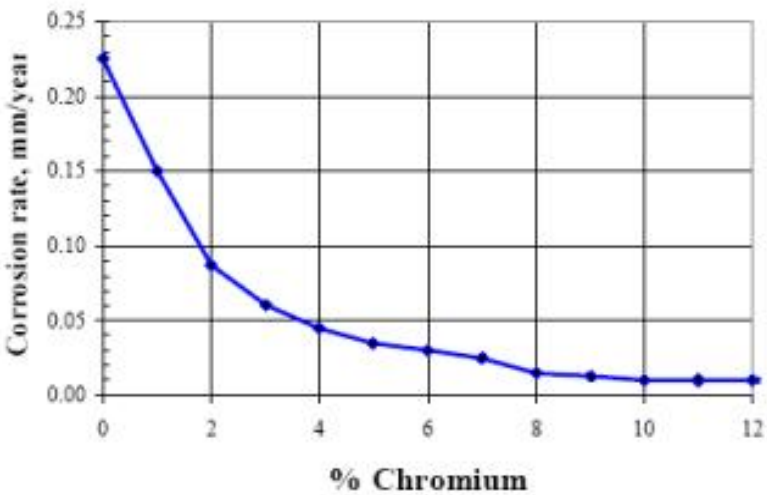
Stainless Steel

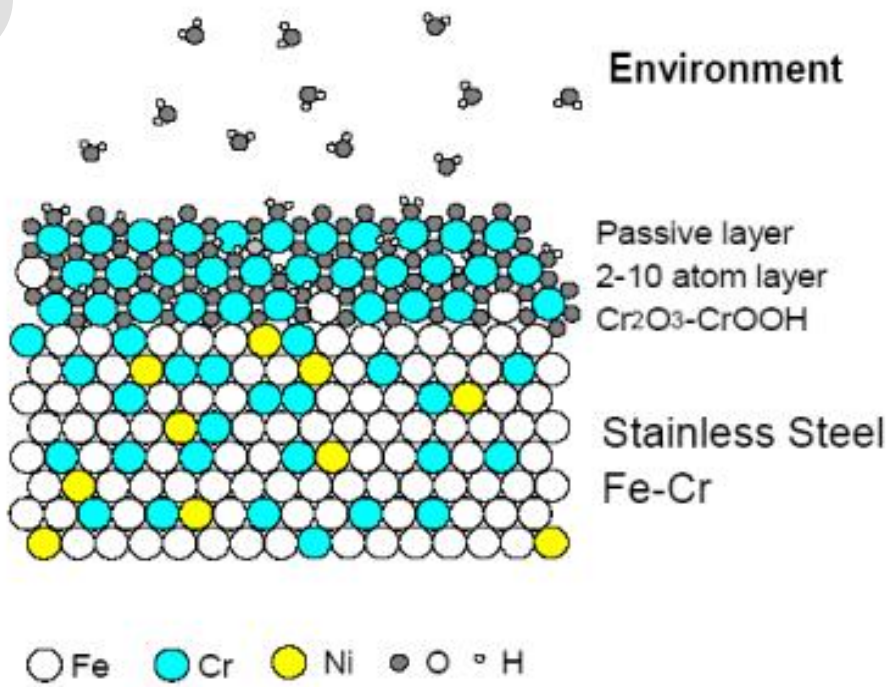
>12 % Cr

- Passive film
- Corrosion rate drops

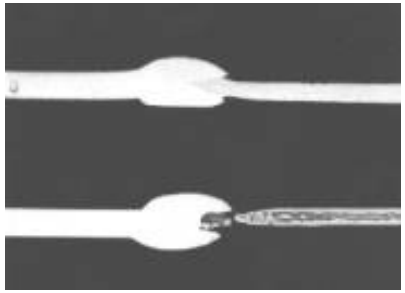
Passive layer
Metal

Passive film 10-30 Å





Different types of corrosion in stainless steel



- Uniform Corrosion
- Pitting Corrosion
- Crevice Corrosion
- Stress Corrosion Cracking
- Corrosion fatigue
- Intergranular Corrosion
- Galvanic Corrosion
- Atmospheric Corrosion
- MIC – Microbiological Corrosion

Uniform Corrosion

- Uniform removal of metal over the entire

  exposed surface

- The alloy thins with time

- Uniform corrosion is usually caused by exposure to an inappropriate acid environment

Pitting Corrosion

Pitting most frequently takes place in neutral environments containing chlorides.

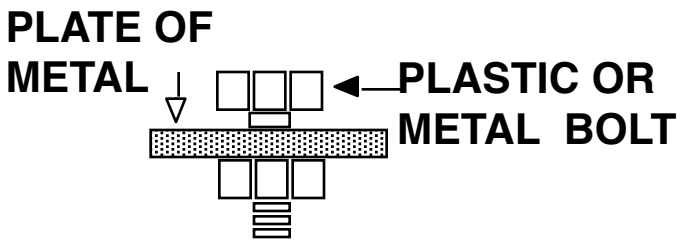
Small and deep pits growths with increased rate
↳rapid penetration of the metal

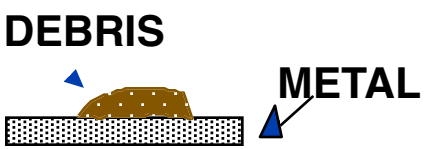
Resistance to pitting corrosion increases with increases amount of Cr, Mo and N.

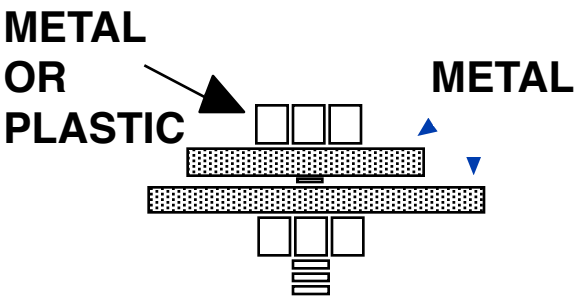
Crevice Corrosion

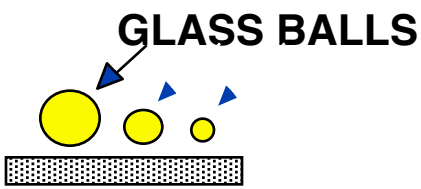
- A form of localized corrosion that occurs within crevices and shielded areas
- Occurs more easily than pitting
- Crevice corrosion of stainless steel is usually associated with halides
- Crevice geometry is important (deep and tight crevices are more detrimental)

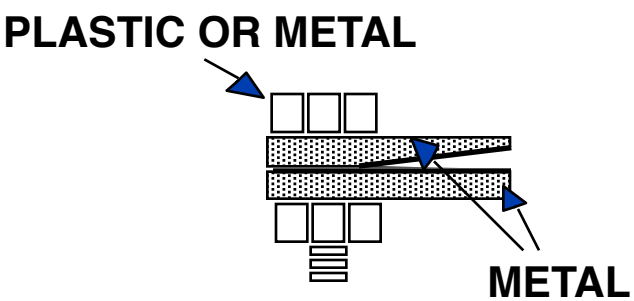
Sites for Crevice Corrosion

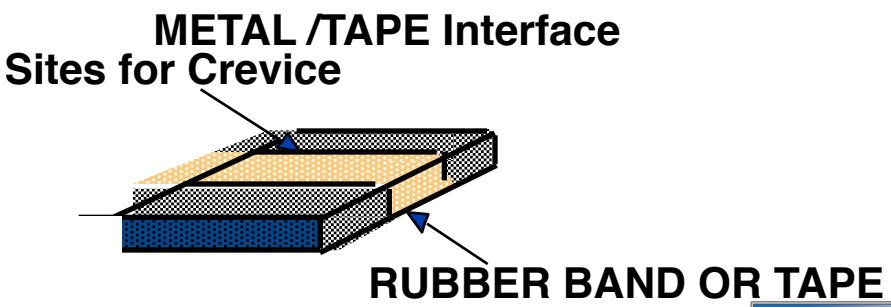












Corrosion resistance - What is chloride (Cl^-)?

A very common ion found in water and in many salts

- Tap water < 250 ppm
- Salty taste > 250 ppm
- Brackish water ~ 3000 ppm
- Seawater 20000 – 30000 ppm

Environmental Factors
- pitting & crevice corrosion

The following promote pitting and crevice corrosion

- Increased chloride concentration
- Lower pH
- Higher temperatures

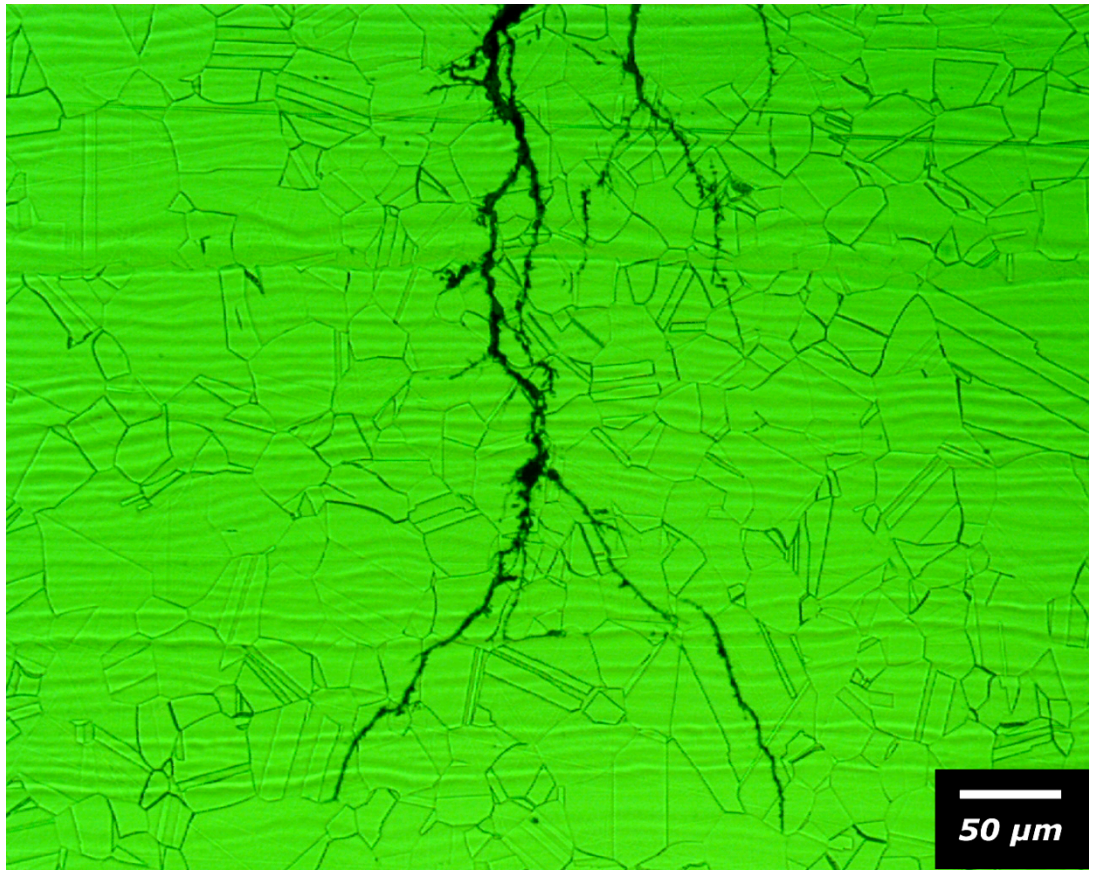
- Liquid/vapor interfaces
- More oxidizing conditions

Environmental Effects - SCC

- The following promote the chloride SCC of stainless steel
  - Increased concentration of chlorides
  - Lower pH
  - Oxygen content
  - Higher temperatures ⇨
  - Wet/dry interfaces
  - Tensile stress

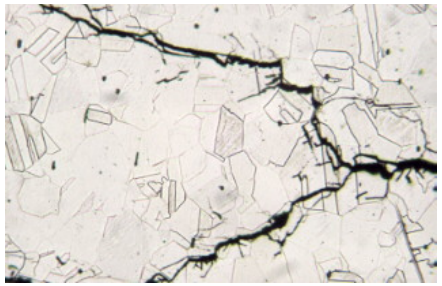
Chloride SCC unlikely at temperatures < 150 °F

Stress Corrosion Cracking



Stress corrosion

Chloride induced stress corrosion



304L

316L

~~Ni~~

430

Ferritic SS

-Ni

LDX 2101
2304
2205 Code+2
2507

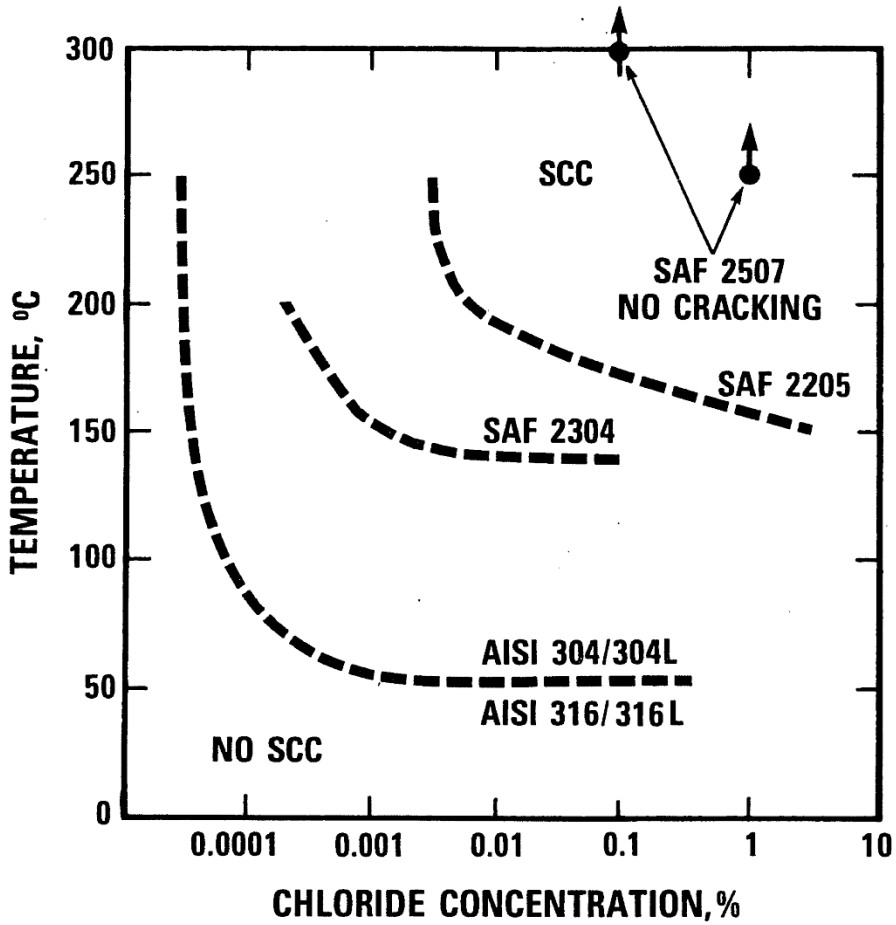
Duplex SS

+Ni

904L
254 SMO
4565
654 SMO

Superaustenitic SS

Chloride SCC of Duplex SST



Reference - Sandvik, *A High Performance Duplex Stainless Steel*

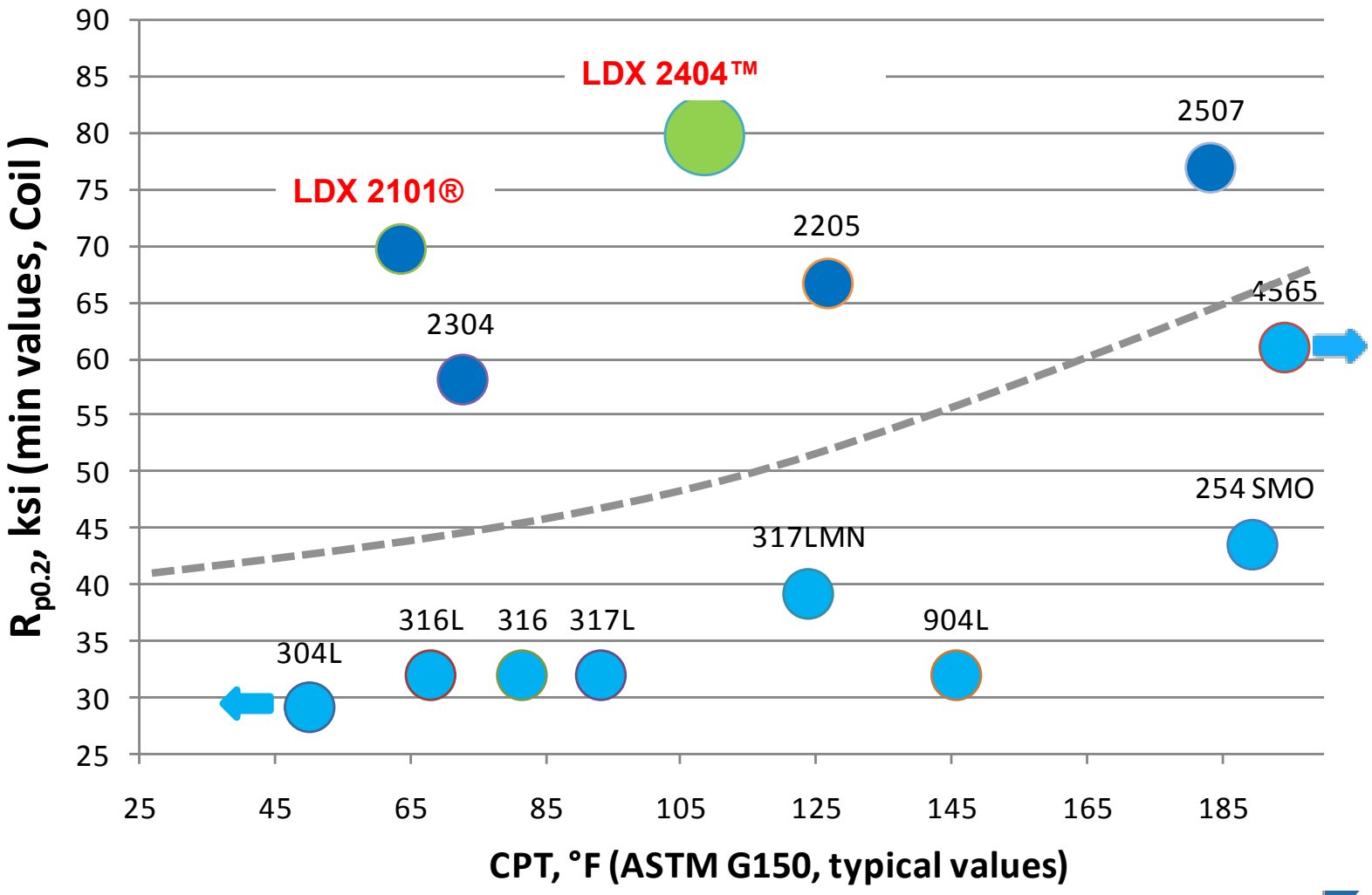
New Developments: spotlight on LDX Family

LDX family

Typical chemical composition weight %									
Outokumpu	ASTM	Cr	Ni	Mo	N	Other	PRE*	YS**	TS
LDX 2101®	**S32101**	**21.5**	**1.5**	**0.3**	**0.22**	**Mn**	**26**	**77**	**87**
2304	S32304	23	4.8	0.3	0.10		26	58	79
LDX 2404™	**S82441**	**24**	**3.6**	**1.6**	**0.27**	**Mn**	**33**	**79**	**108**
2205 code +2	S32205	22	5.7	3.1	0.18		35	65	92
2507	S32750	25	7	4	0.27	Mn	42	80	116
4307	304L	18.1	8.1	-	-		18	30	75
4404	316L	17.2	10.1	2.1	-		24	25	70
4432	316L	16.9	10.7	2.6	-		25	25	70
904L	N08904	20	25	4.3	-	Cu	34	31	71
254 SMO®	S31254	20	18	6.1	0.20	Cu	43	45	95

•PRE = %Cr + 3.3x%Mo + 16x%N
•** min values may vary depending on product form and standard used

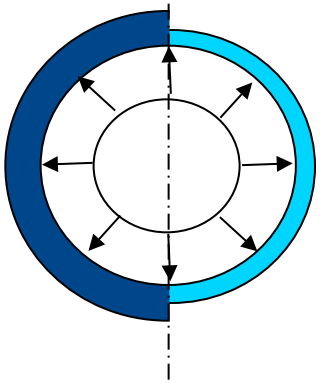
Positioning of Duplex vs Austenitic



Duplex strength adds superior value:

Tension 'Pressurized pipe'

Std austenitic | Duplex



Tension 'Pressurized vessel or pipe'

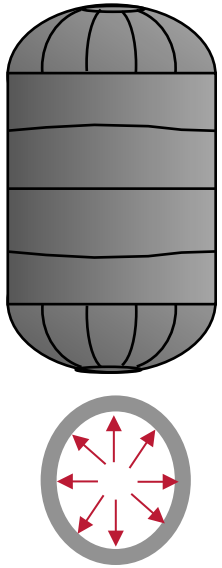
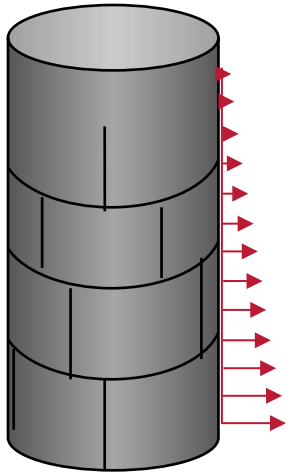
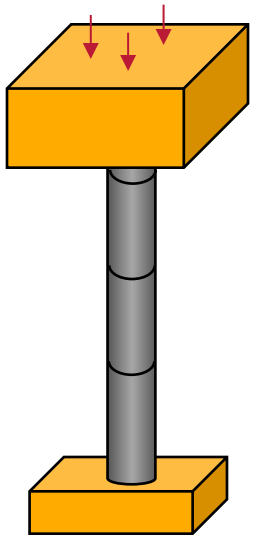


Plate bending 'Storage tank'

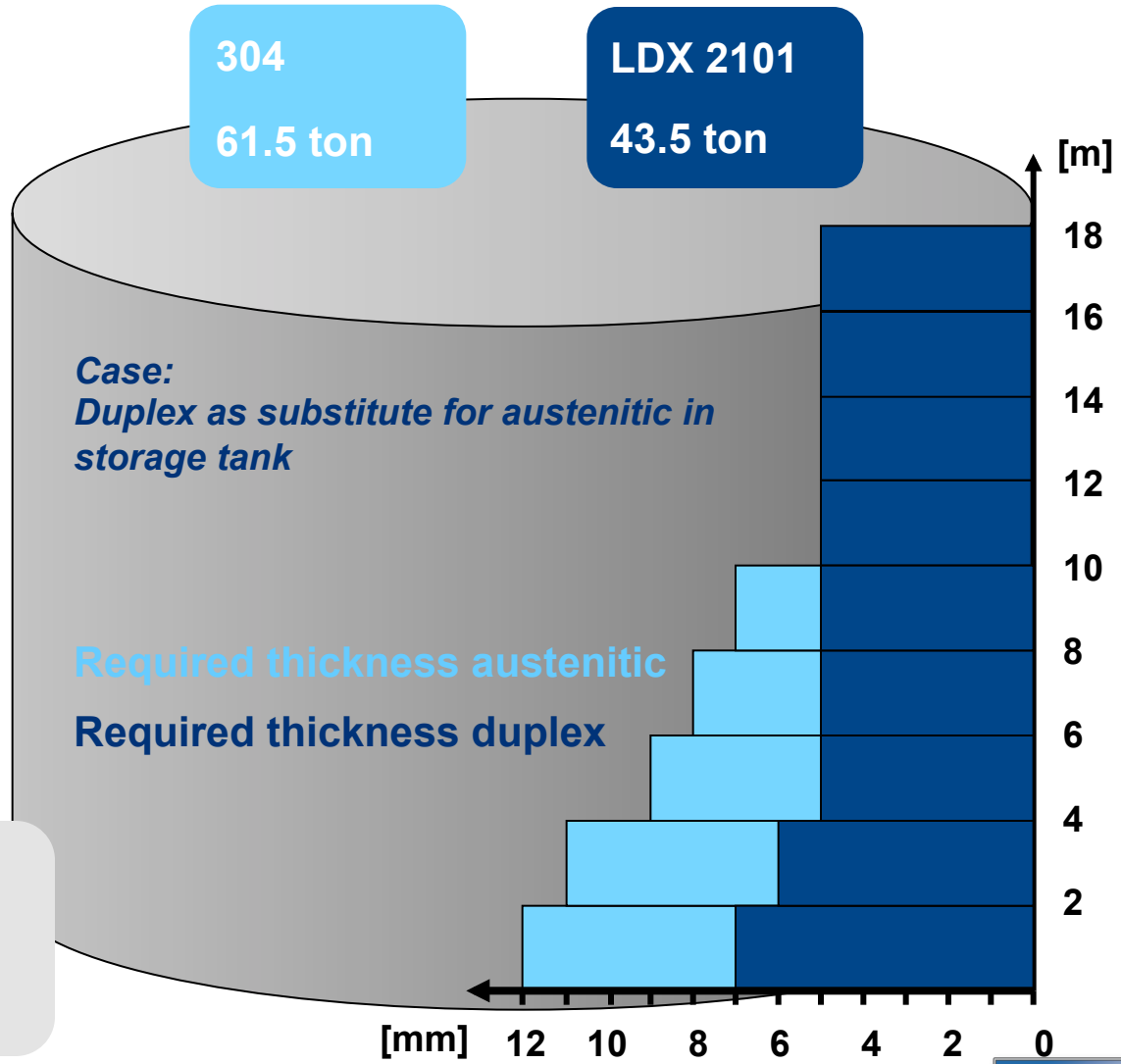


Buckling 'Column'



Duplex thickness : 50% reduction	50%	30%	15%

Duplex strength adds superior value:



Duplex potential weight saving: ~30%

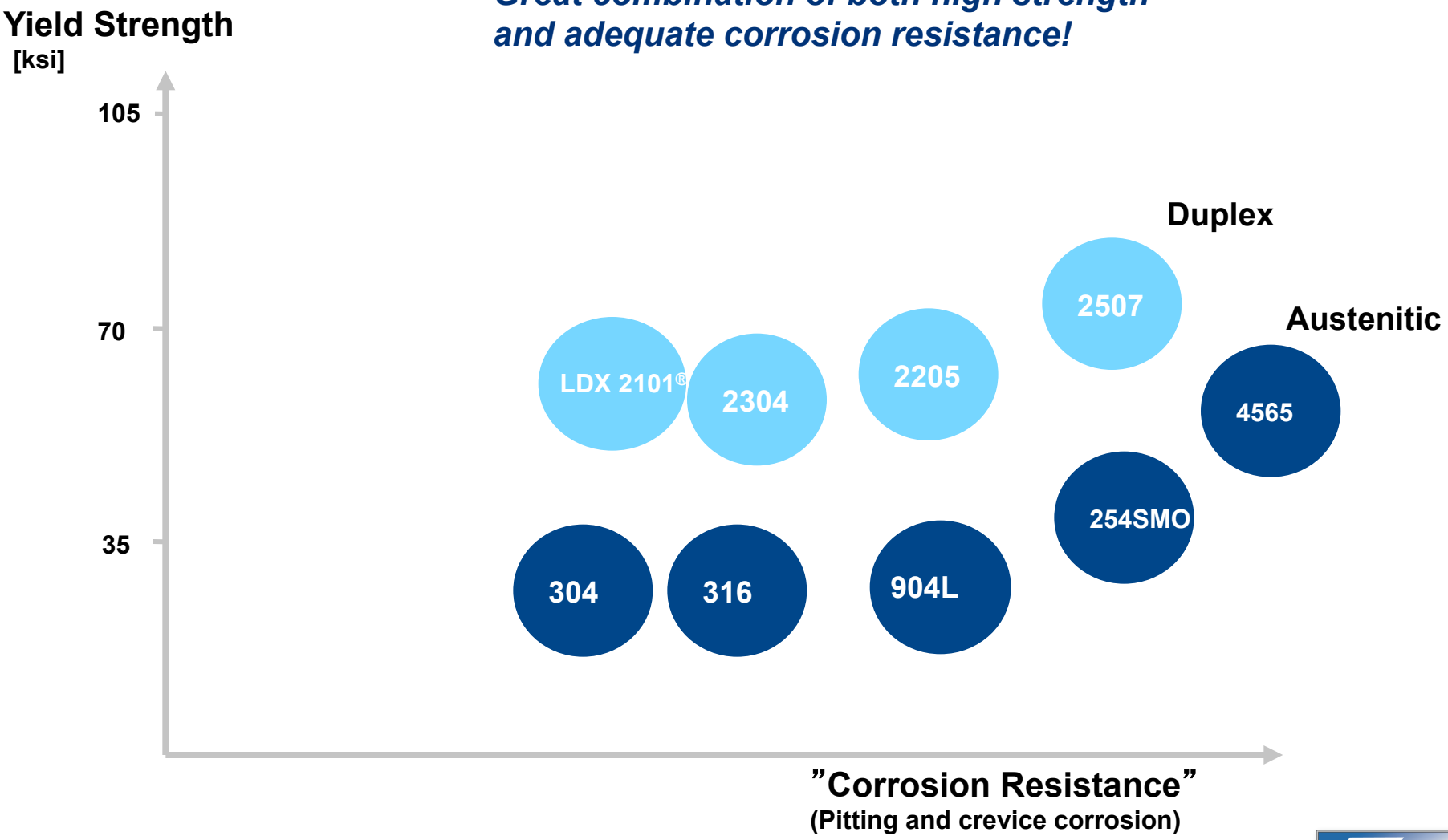
Filler material saving potential LDX 2101® : 39%

Duplex benefits

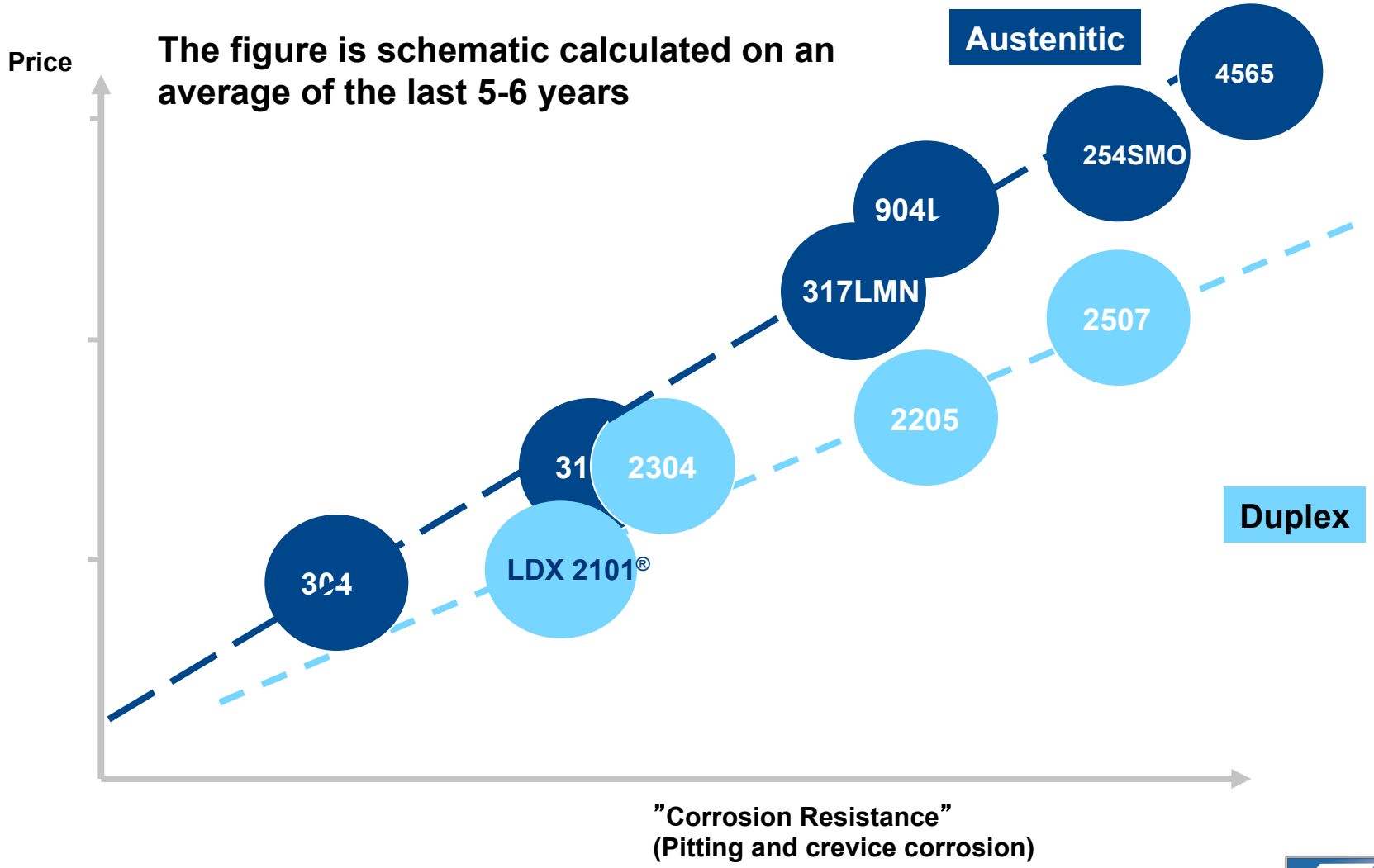
- Thinner gauges
  - cost advantage!
- Minimal maintenance, long lifespan
  - life-cycle cost advantage!
- Low nickel content
  - cost stability!

Positioning of Duplex grades

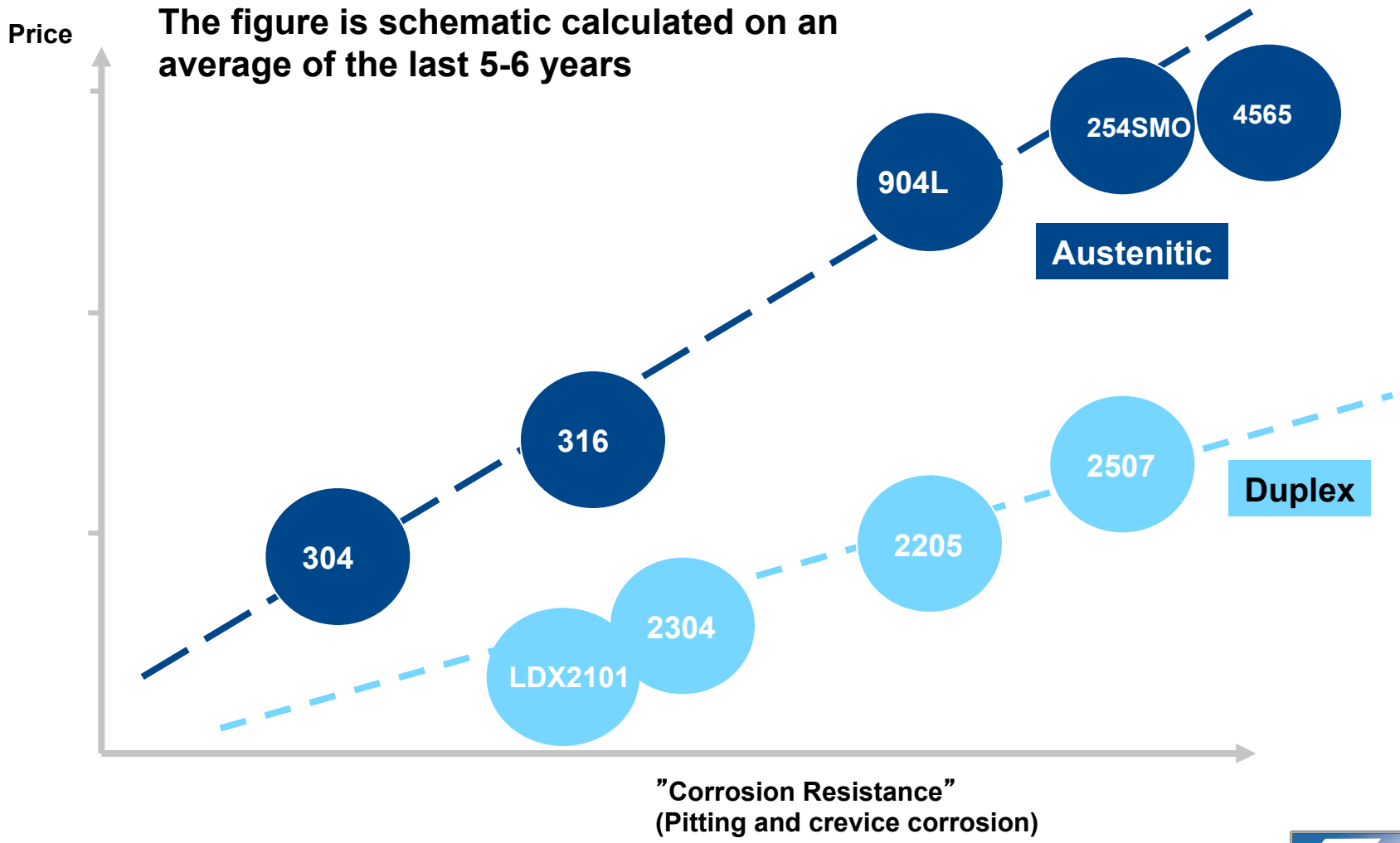
Great combination of both high strength and adequate corrosion resistance!



Price per PRE (corrosion resistance)



Price per PRE (corrosion resistance) considering a thickness reduction due to strength



Why is duplex stainless steel so popular?

- Better resistance to pitting and crevice corrosion at a lower cost
- Twice the strength
- Good fatigue, abrasion and erosion resistance
- High resistance to SCC (Stress Corrosion Cracking) and corrosion fatigue
- High energy absorption
- Low thermal expansion
- Good weldability and machinability

Similarities: Austenitic vs. Duplex Welding

- **Same pre-weld joint cleaning**
  - Remove all debris, dirt, paint and oil
  - Remove water or moisture

- **Same joint preparation**
  - Remove heavy oxides
  - Remove rough grinding burrs
  - Ascertain accurate edge geometry
  - Machine or grind edge profile

- **Similar joint design**
  - Provide backing gas shielding
  - Ensure full penetration weld

Differences: Austenitic vs. Duplex

- Excessive ferrite
- Sigma phase

Differences Austenitic vs. Duplex

- Qualification extremely important
  - Appearance of weld gives no indication of quality
  - Written procedures and trial welds necessary to prevent precipitation of detrimental second phases and assure quality

Differences Austenitic vs. Duplex

- Less thermal expansion - less distortion
- Less hot cracking
- Sensitive to H_2-cracking
  - Remove moisture from joint
  - Store electrodes at elevated temperature
  - Avoid hydrogen in backing or shielding gas

Welding Processes for Duplex Stainless Steel

- Shielded Metal Arc Welding:
  SMAW, covered electrodes, “stick”
- Gas Tungsten Arc Welding:
  GTAW, “TIG”
- Gas Metal Arc Welding:
  GMAW, “MIG”
- Flux Core Arc Welding: “FCAW”
- Submerged Arc Welding: “SAW”

2205 Welding

- Always use filler metal, even for repair
- Use 2209 (7 - 9% nickel)
- Preheating is not necessary unless condensation
- Heat input 15 - 40 kJ/inch
- Interpass temperature below 250°F
- Post-weld heat treatment is not normally necessary. Above 600°F alpha prime precipitation is a concern (885 embrittlement)

Dissimilar Metal Welds

- Duplex can be welded to austenitic stainless steels and carbon steels
- E309LMo/ER309LMo or E2209/ER2209 filler used when welding to austenitic stainless steel
- E309L/ER309L or E309LMo/ER309LMo filler used when welding to carbon steels

Post-fabrication cleaning treatments

Grinding (abrasive discs or flapper wheels)

Do not smear (eg. wire brushes) or overheat the surface (eg. worn abrasives or excessive pressure)

Blasting (eg. Fine mesh glass beads)

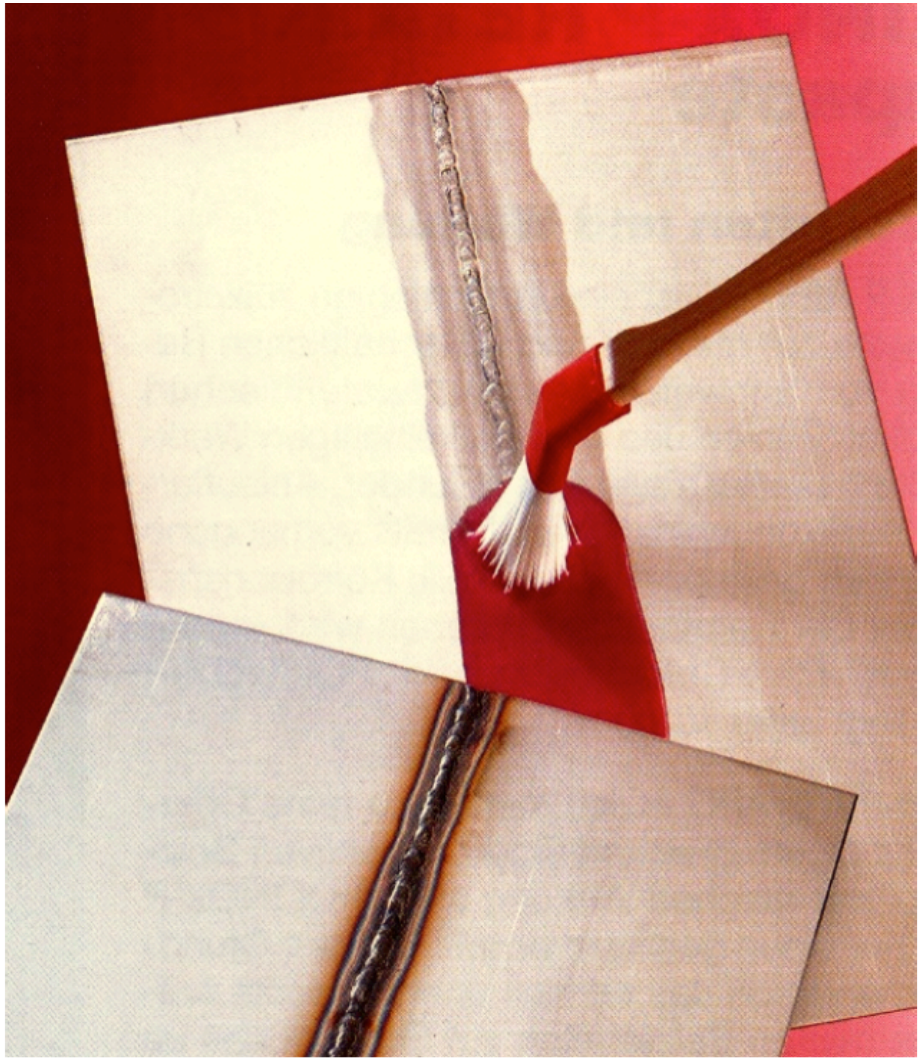
Local or large area cleaning results in smooth surface finish

Pickling (mixed nitric-hydrofluoric acids)

Immersion, spray or paste

Electropolishing Site or shop treatment

Better result



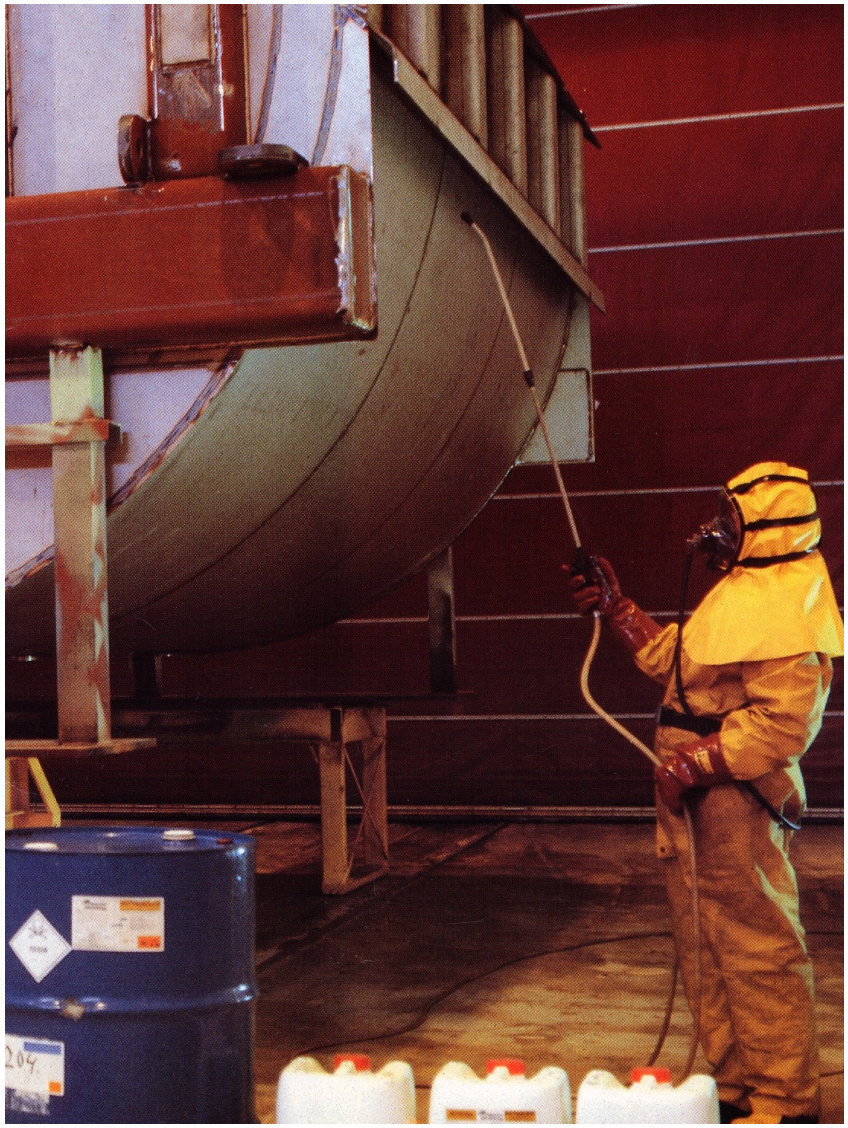
Pickling with paste

Pickling

Chemical treatment to remove heat tint, and the underlying chromium-depleted layer and surface contamination

Covered by:
ASTM A 380

Spray Pickling



Chemical Composition and Properties

Typical chemical composition weight %

Outokumpu	EN	ASTM	Cr	Ni	Mo	N	PRE*	$R_{p0.2}$**	
LDX 2101®	1.4162	S32101	21.5	1.5	0.3	0.22	26	450***	Lean Duplex
2304	1.4362	S32304	23	4.8	0.3	0.10	26	400	Duplex
2205	1.4462	S32205	22	5.7	3.1	0.18	35	460	Duplex
2507	1.4410	S32750	25	7	4	0.27	43	530	Super Duplex
4307	1.4307	304L	18.1	8.1	-	-	18	200	Austenitic
4404	1.4404	316L	17.2	10.1	2.1	-	24	220	Austenitic
4432	1.4432	316L	16.9	10.7	2.6	-	25	220	Austenitic
904L	1.4539	N08904	20	25	4.3	-	34	220	Austenitic
254 SMO®	1.4547	S31254	20	18	6.1	0.20	43	300	Super Austenitic
4565	1.4565	S34565	24.5	17.5	4.5	0.50	47.5	420	Super Austenitic

*** PRE = %Cr + 3.3x%Mo + 16x%N**
**** [MPa] Hot rolled plate, min values at 20°C according to EN 10088**
*****Not yet in EN 10088, Rp0.2 according to ASTM A240**

Nominal Composition of Higher Alloyed Grades

Alloy	UNS Number	Cr	Ni	Mo	Cu	N	Other
Austenitic Stainless Steels							
317LMN	S31726	18	14	4.1	-	0.15	-
904L	N08904	20	25	4.5	1.5	-	-
254 SMO	S31254	20	18	6.1	0.75	0.2	-
4565	S34565	24.5	17.5	4.5	-	0.5	6Mn
654 SMO	S32654	24	22	7.3	0.5	0.5	3Mn
Duplex Stainless Steels							
2205	S32205	22.5	5	3.2	-	0.15	-
2507	S32750	25	7	4	-	0.25	-
Nickel-base Alloys							
Alloy 625	N06625	22	62	9	-	-	3Nb
Alloy C-276	N10276	16	67	16	-	-	3W

ASTM Minimum Mechanical Properties of Alloys

Alloy	UNS Number	Yield Strength (ksi)	Tensile Strength (ksi)	Elong. (%)
Austenitic Stainless Steels				
317LMN	S31726	35	80	40
904L	N08904	31	71	35
254 SMO	S31254	45	95	35
4565	S34565	60	115	35
654 SMO	S32654	62	109	40
Duplex Stainless Steels				
2205	S32205	65	95	25
2507	S32750	80	116	15
Nickel-base Alloys				
Alloy 625	N06625	40	100	30
Alloy C-276	N10276	41	100	40

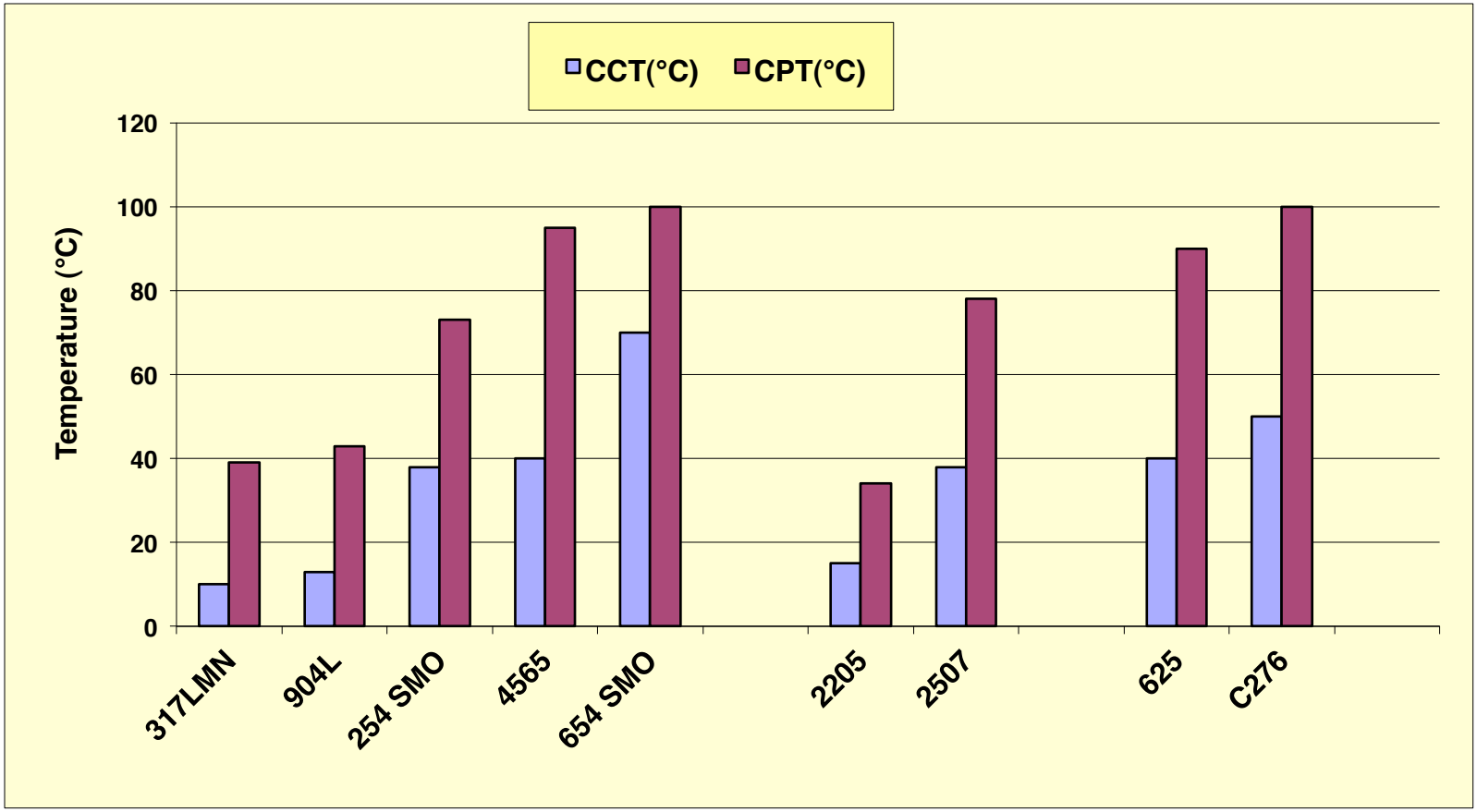
Pitting Corrosion (CPT) and Crevice Corrosion (CCT) Temperature (˚C) ASTM G 48

Alloy	UNS Number	Cr	Mo	N	PRE*	CPT** G48-E	CCT** G48-F
Austenitic Stainless Steels							
317LMN	S31726	18	4.1	0.15	36	-	-
904L	N08904	20	4.5	-	35	40	10
254 SMO	S31254	20	6.1	0.2	46	65	35
4565	S34565	24.5	4.5	0.5	54	95	40
654 SMO	S32654	25	7.3	0.5	56	>bp	70
Duplex Stainless Steels							
2205	S32205	22.5	3.2	0.15	38	30	20
2507	S32750	25	4	0.25	46	65	35
Nickel-base Alloys							
Alloy 625	N06625	22	9	-	52	90	40
Alloy C-276	N10276	16	16	-	69	>bp	50

* PRE = %Cr + 3.3 %Mo + 30 %N

**The CPT/CCT values are typical values. Different products and different surface finishes, e.g. mill finish surfaces, may show values that differ from the values given in this table.

Pitting Corrosion (CPT) and Crevice Corrosion (CCT) Temperature (˚C) ASTM G 48



Superaustenitic or Superduplex?

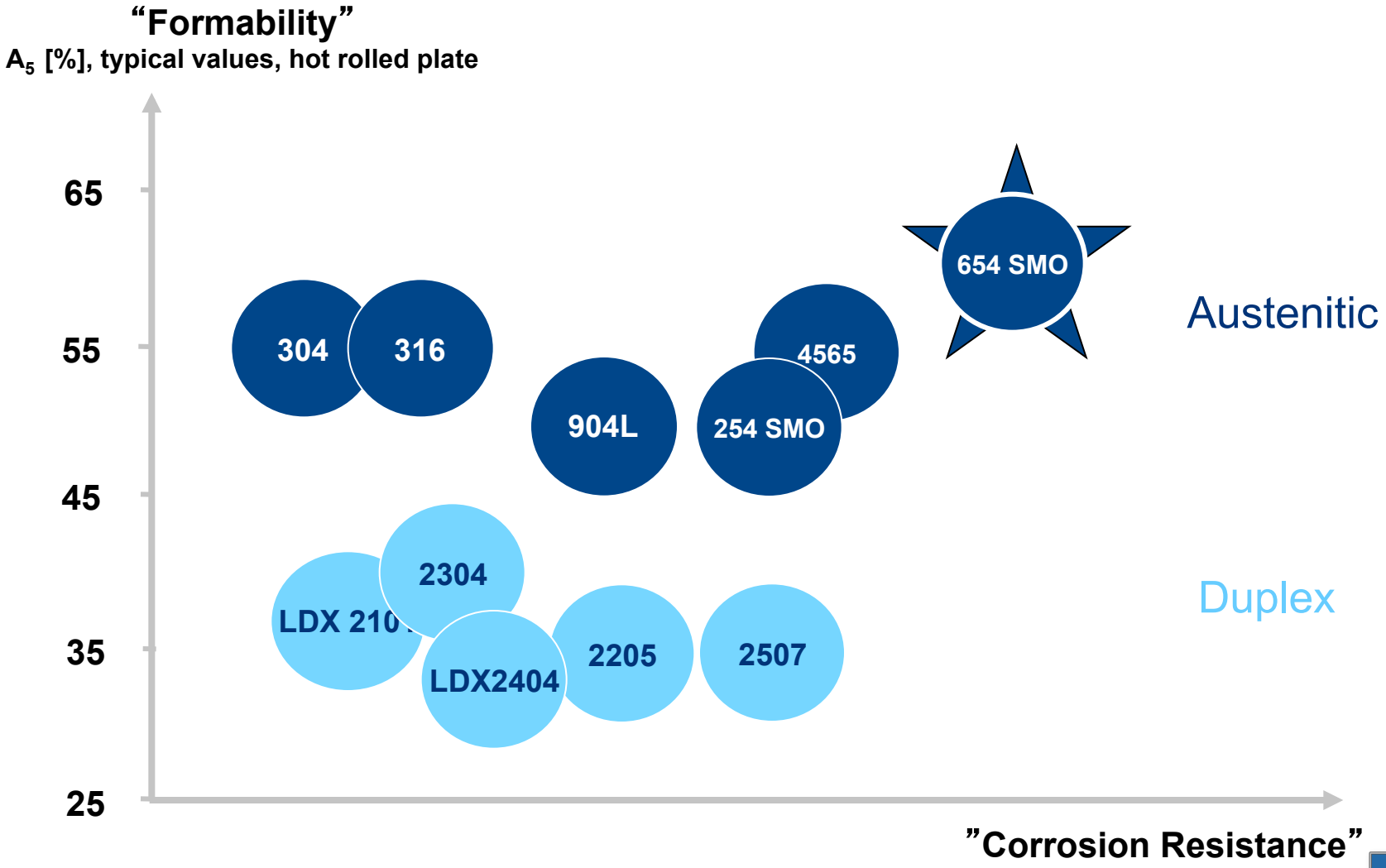
	Superaustenitic	Superduplex
	Slightly better weldability	Lower raw-material cost
Intermetallic phases	Slower precipitation kinetics	More susceptible to intermetallic phases due to fast reactions in the ferritic phase
Strength	High strength due to increased addition of Nitrogen	Higher strength
Temperature range	-196 to 400 °C -321 to 752 °F	-50 to 300 °C -58 to 572 °F
Corrosion properties	Better resistance to uniform corrosion in active conditions	Somewhat better crevice corrosion resistance

Example:
654 SMO® vs. C-276

Property	654 SMO®
Pitting corrosion resistance	Better
Crevice corrosion resistance	Better
Price stability[1]	Better
Mechanical strength	Better
Uniform corrosion resistance[2]	Similar
Fabricability	Similar

[1]due to relatively low Ni & Mo content
[2]strongly dependent on the environment

654 SMO® – Properties



654 SMO® – Suitable applications

- Sea water cooled heat exchangers
  - Plate heat exchangers (PHE's)
  - Tubular heat exchangers
- Condenser tubing
- Various equipment in "aggressive" environments – Process vessels, tanks, linings, pipes, etc

High Alloyed Stainless Steel Grades

Alloy	UNS Number	Cr	Ni	Mo	Cu	N	Other
Austenitic Stainless Steels							
317LMN	S31726	18	14	4.1	-	0.15	-
904L	N08904	20	25	4.5	1.5	-	-
254 SMO	S31254	20	18	6.1	0.75	0.2	-
4565	S34565	24.5	17.5	4.5	-	0.5	6Mn
654 SMO	S32654	24	22	7.3	0.5	0.5	3Mn
Duplex Stainless Steels							
2205	S32205	22.5	5	3.2	-	0.15	-
2507	S32750	25	7	4	-	0.25	-
Nickel-base Alloys							
Alloy 625	N06625	22	62	9	-	-	3Nb
Alloy C-276	N10276	16	67	16	-	-	3W

TMR Stainless

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