The Role of Nickel in Stainless Steels

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Indian Institute of Metals (Delhi Chapter)

New Delhi, 14 December 2011

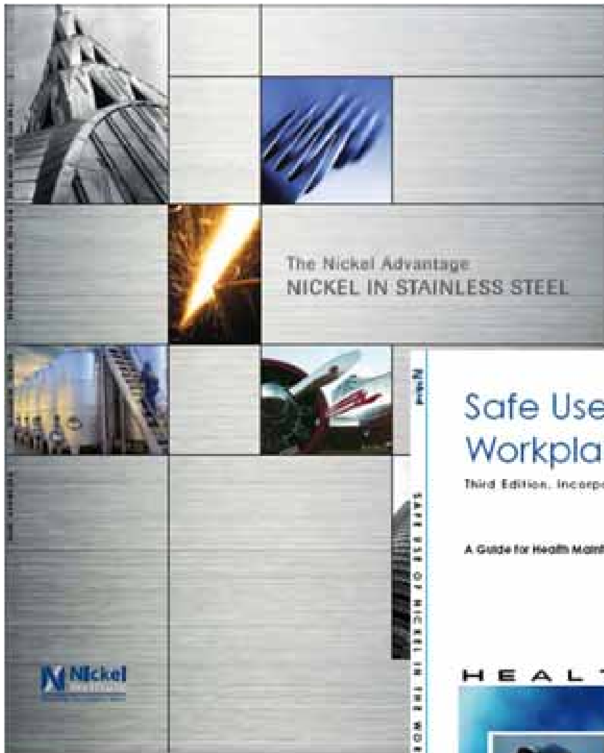
The Nickel Institute does not present forecasts or comments on nickel markets, prices or supply/demand. The Nickel Institute does promote the long term use of nickel to contribute to a sustainable future.

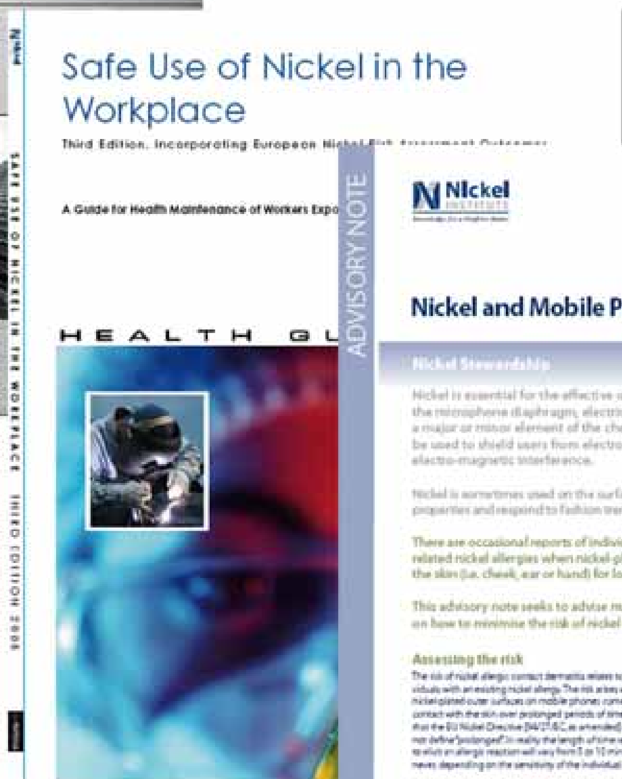
Nickel Institute

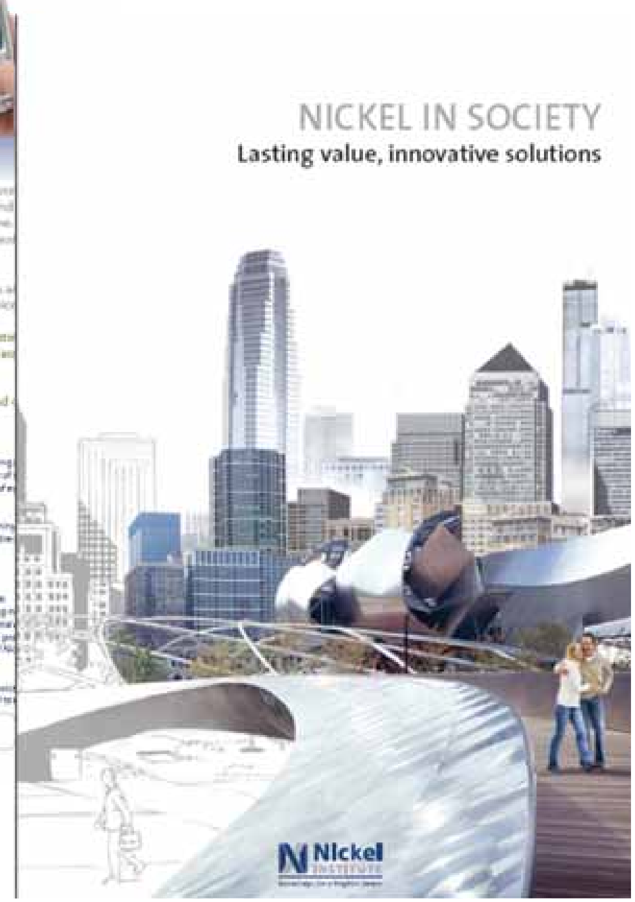
- Promote appropriate uses of nickel-containing materials
- Work towards appropriate regulation
- Offices in Toronto, Brussels, Beijing, Tokyo, Raleigh (USA, NiPERA)
- Partnerships with stainless steel development associations, e.g.ISSDA
- Not-for-profit
- Represents ~ 75% of global nickel production

Nickel - lasting value

www.nickelinstitute.org







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History of Stainless Steel

- **1751** — Axel Fredrik Cronsted (Sweden) discovers **Nickel**
- **1778** — Carl Wilhelm Scheele (Germany) discovers **Molybdenum**
- **1797** — Nicolas-Louis Vauquelin (France) discovers **Chromium**
- **1912** — Eduard Maurer (Germany) is granted a Patent on **Austenitic Stainless Steel**
- **1913** — Henry Brearley (UK) produces **Martensitic Stainless Steel**
- **1919** — Elwood Haynes (US) is granted a Patent on **Ferritic Stainless Steel**
- **1930** — **Duplex Stainless Steel** are initially produced (Sweden)

It took 115 years to produce Stainless Steel, even after the discovery of Chromium

N. Mathur, Maastricht 2011

Chrysler Building, 1927

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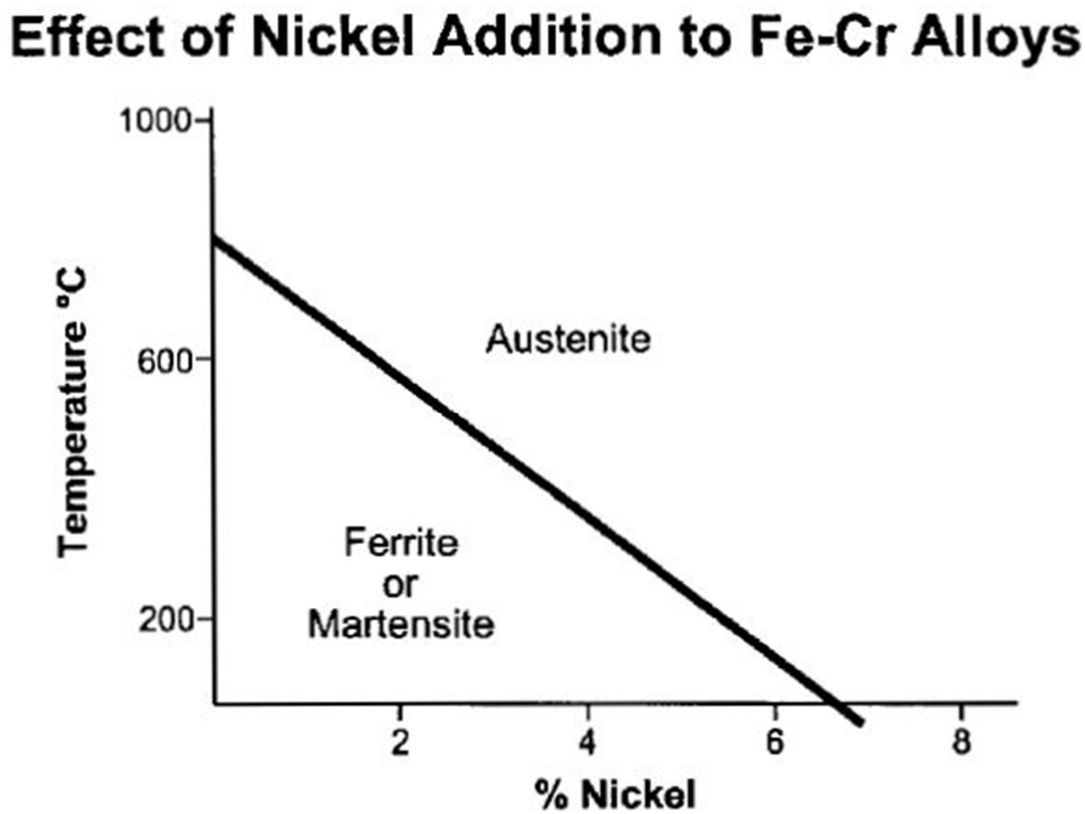
Chromium is the essential element in stainless steel.

Nickel is used in ~60% of stainless steel.

What is the role of nickel?

Nickel, an austenite stabiliser



Nickel equivalent = Ni% + 30C% + 30N% + 0.5Mn% + 0.3Cu% (by weight)

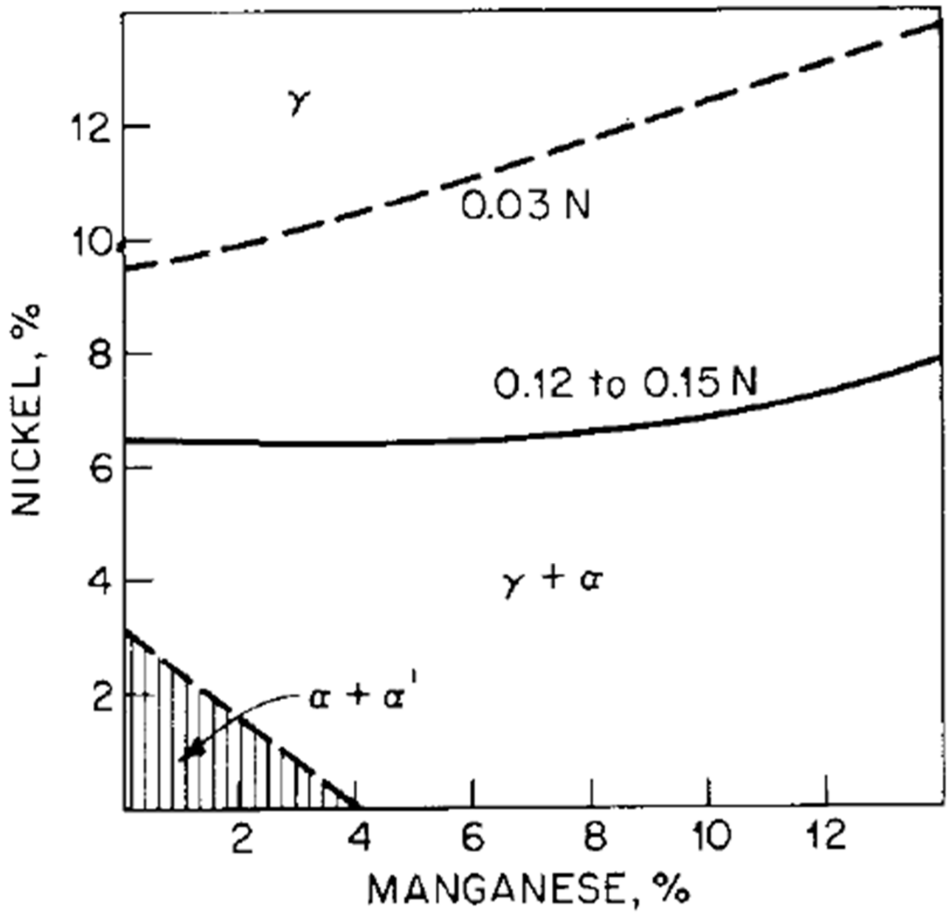


Fig. 19 Effect of nickel, manganese, and nitrogen on alloys containing 18.5% chromium at 0.05–0.08% carbon. Structure after cooling from 1075°C (1967°F).[32]

Binder et al quoted in Peckner & Bernstein

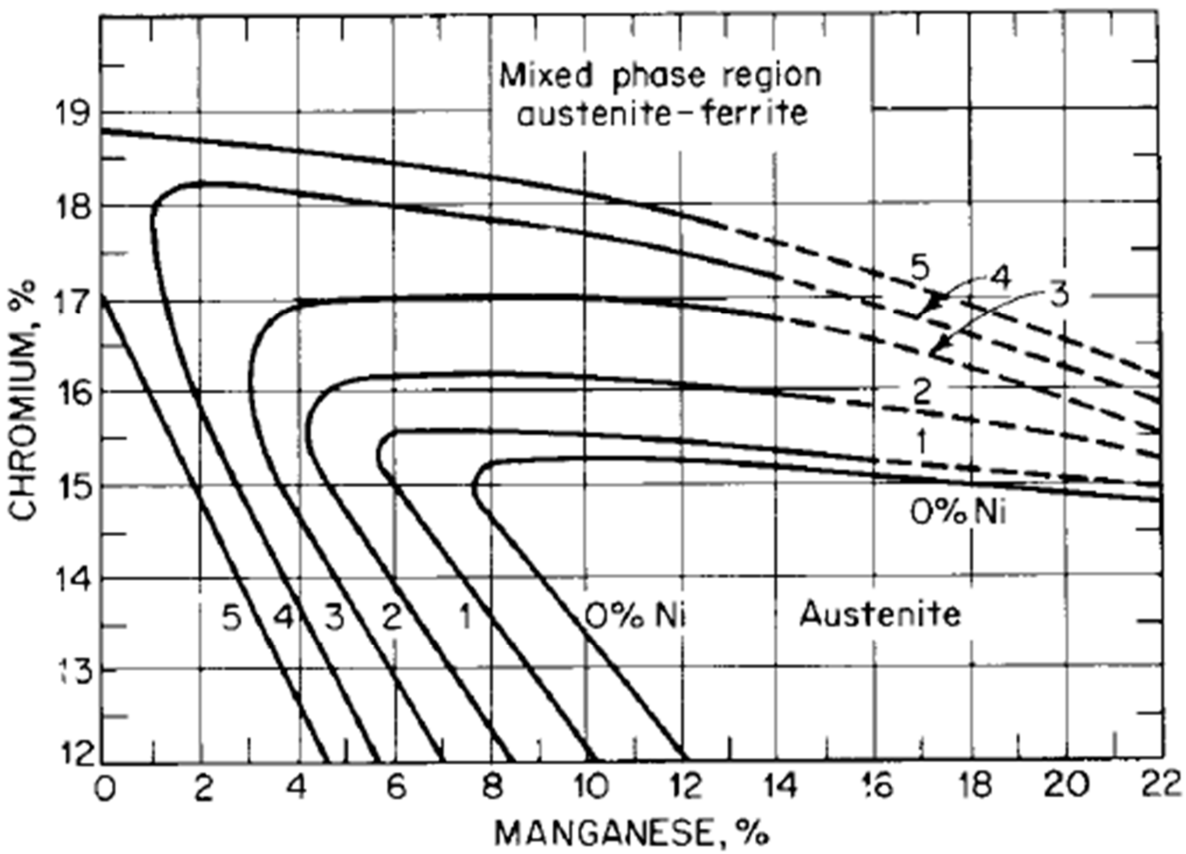


Fig. 20 Effect of chromium, manganese, and nickel on alloys containing 0.12 to 0.15% carbon and 0.08 to 0.15% nitrogen. Structure after cooling from 1075°C (1967°F).[32]

Binder et al quoted in Peckner & Bernstein

Chrome-Manganese Stainless Steel : Historical Development

- 15% Cr-Mn-1.5Ni. Stainless Steels were in use in Germany in 1940's
- Used in Dairy Industry, Beer Industry and House-hold Appliances.
- In early 50's during Korean War, U.S. Government restriction of 1% Nickel (max.) for Stainless Steel in certain applications.
- Following Grades developed by ALLEGHENY termed **IA 201**

Cr. (Min.)	Mn. (Min.)	C (Max)	Ni. (Max)	N (Max)	Substitute for AISI
14.5	**15**	**0.15**	**0.99**	**0.25**	**301**

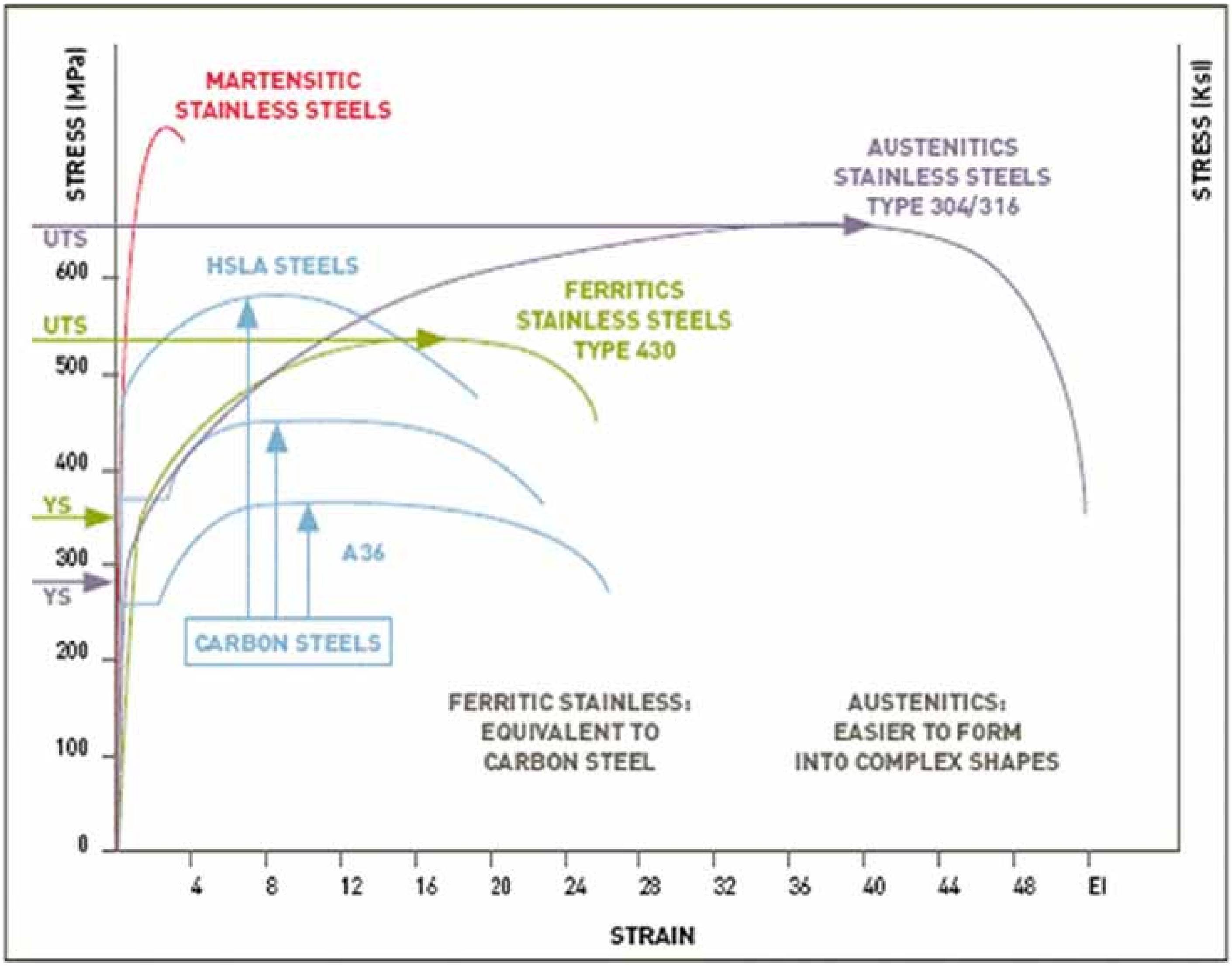
Chrome-Manganese Stainless Steel : Post Korean War Scenario

Post Korean War Scenario

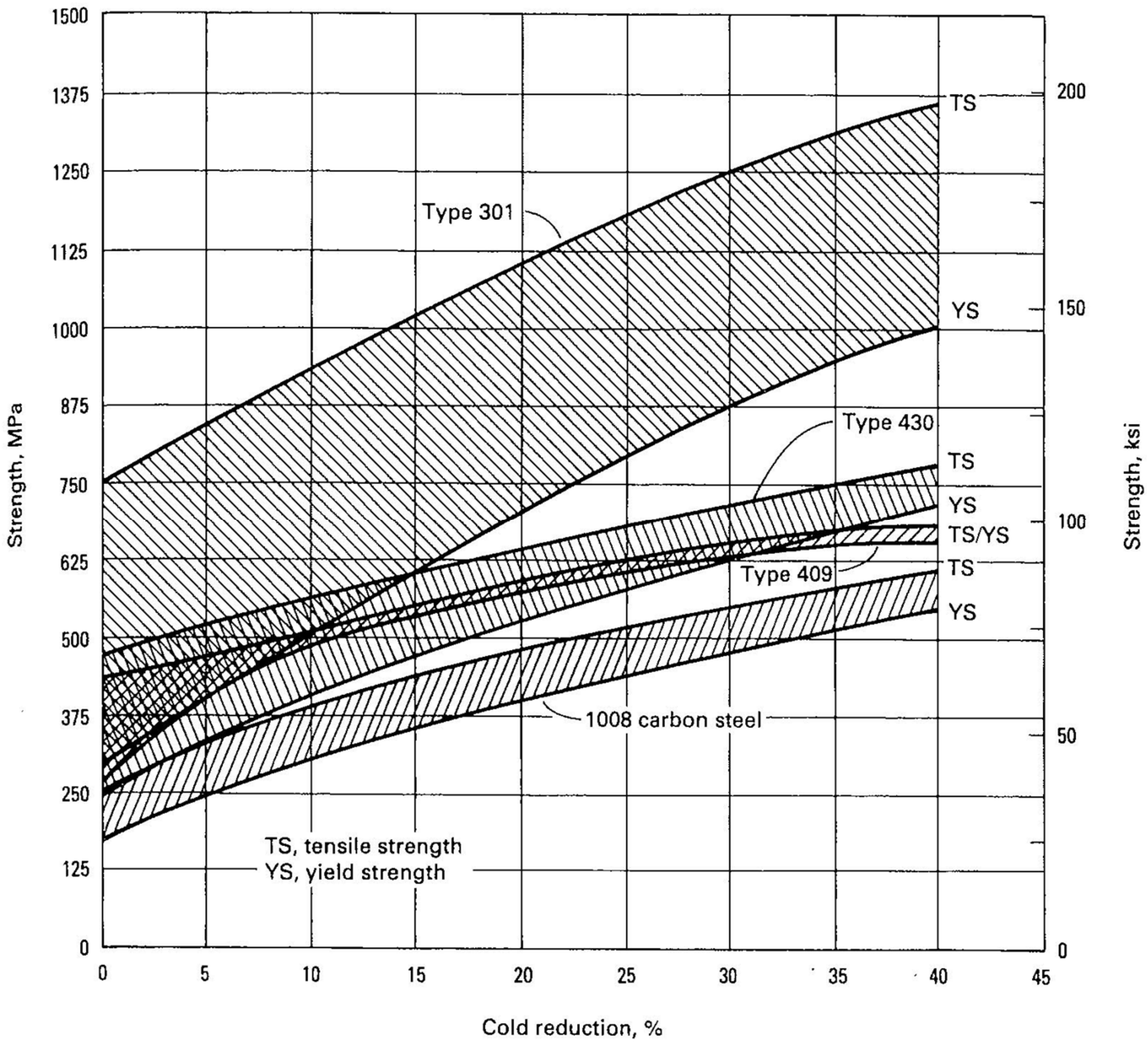
- Softer Alloys preferred
- Half of Nickel only replaced by Mn. and N.
- AISI designation in 1955 to 201 and 202

Grade	C	Cr.	Mn.	N	Ni.
201	0.15 Max	16.0 – 18.0	5.5 – 7.5	0.25 Max	3.5 – 5.5
202	0.15 Max	17.0 – 19.0	7.5 – 10.0	0.25 Max	4.0 – 6.0

Strength and ductility



Work hardening



Energy absorption - bus frame roll-over test

Centro Inox

Energy absorption

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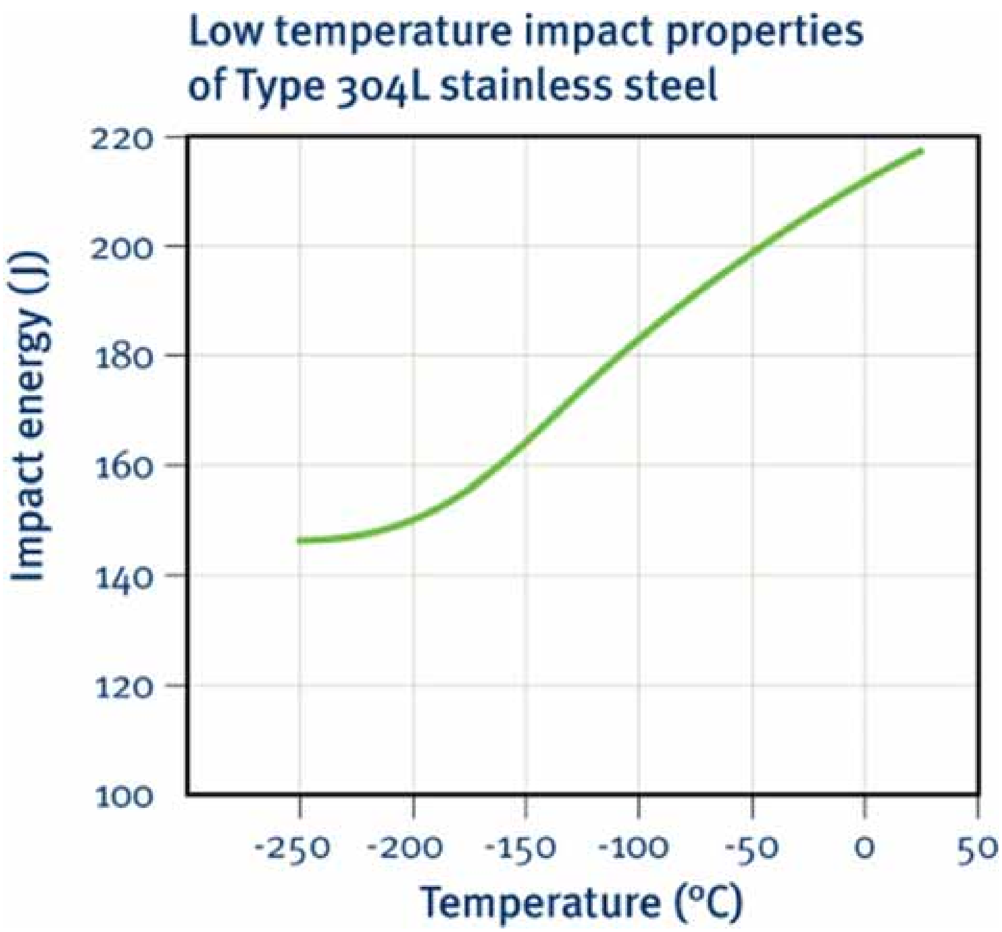
Nickel and toughness



Large Hadron Collider, CERN

NICKEL IN FERRITIC STAINLESS STEEL

- The DBTT is often above ambient temperature
- The DBTT will often limit the maximum thickness for practical use
- The DBTT will be even higher for welded steel
- The DBTT may have an influence on production yields of a grade

Poor toughness is the biggest drawback to ferritic stainless steels

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NICKEL IN FERRITIC STAINLESS STEEL

Effect of Nickel on Mechanical Properties

Effect of nickel on the toughness of 3 different 28Cr-2Mo ELI (extra low interstitial) ferritic SS alloys

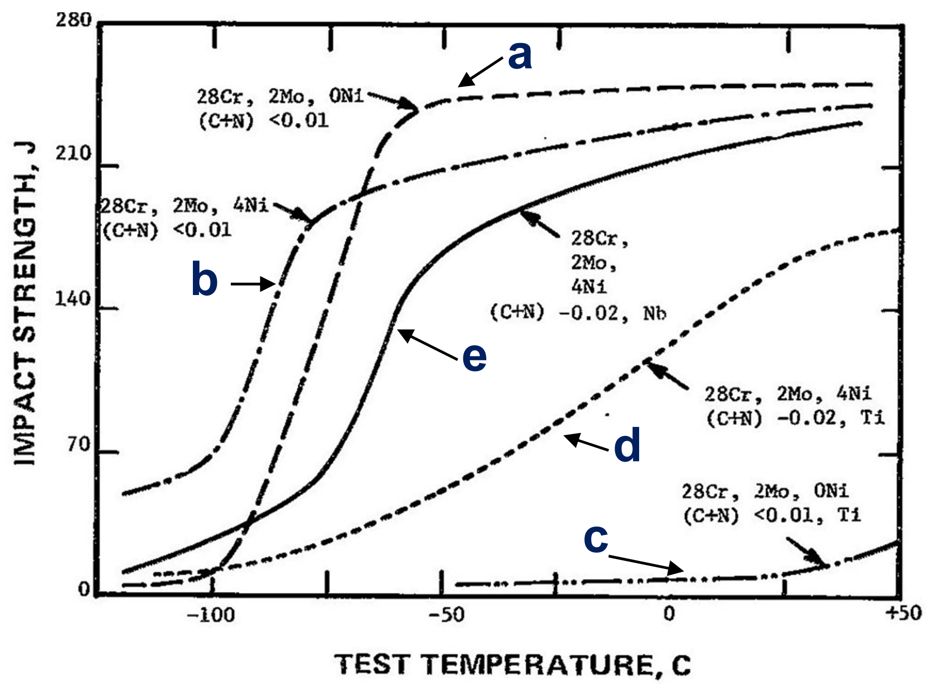
a) without Ni

b) with 4%Ni

c) with Ti & no Ni

d) with Ti & 4% Ni, higher interstitial

e) with Nb and 4%Ni, higher interstitial



NICKEL IN FERRITIC STAINLESS STEEL

Effect on Mechanical Properties

<u>409Ni (S40975) with 0.5-1.0% Ni</u>

In the low alloyed ferritic stainless steels, a small nickel addition gives favourable properties

- grain size control, especially important in welded constructions and thicker material, leading for example to higher toughness
- increased yield strength including at higher temperatures (to 500^{o}C)

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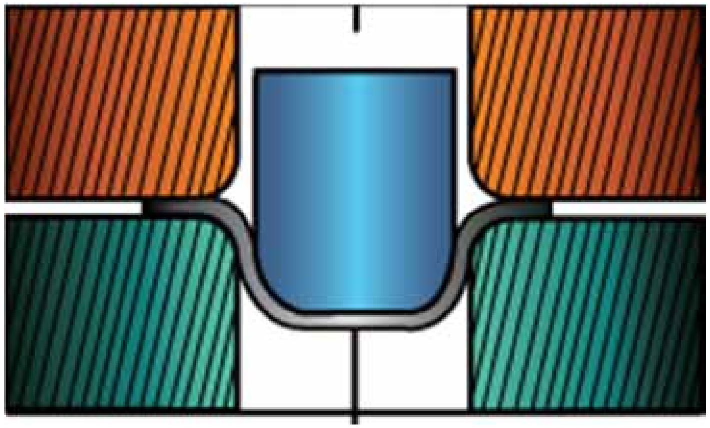
- In the railway wagon sector, NI and ISSDA have been providing active help, although the alloy 409M contains only about 1% nickel. But this is a high tonnage application (14,000 wagons of 8 tonnes each this fiscal year)

Formability

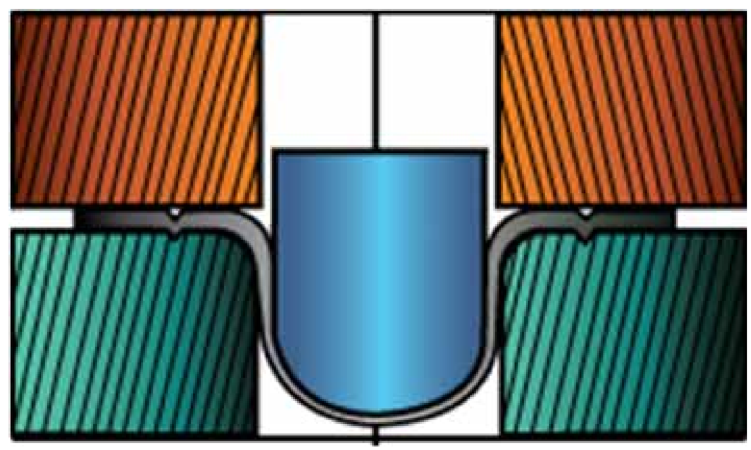
Stala

Formability

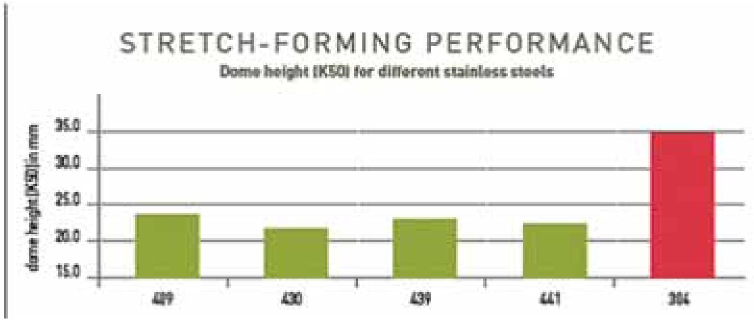


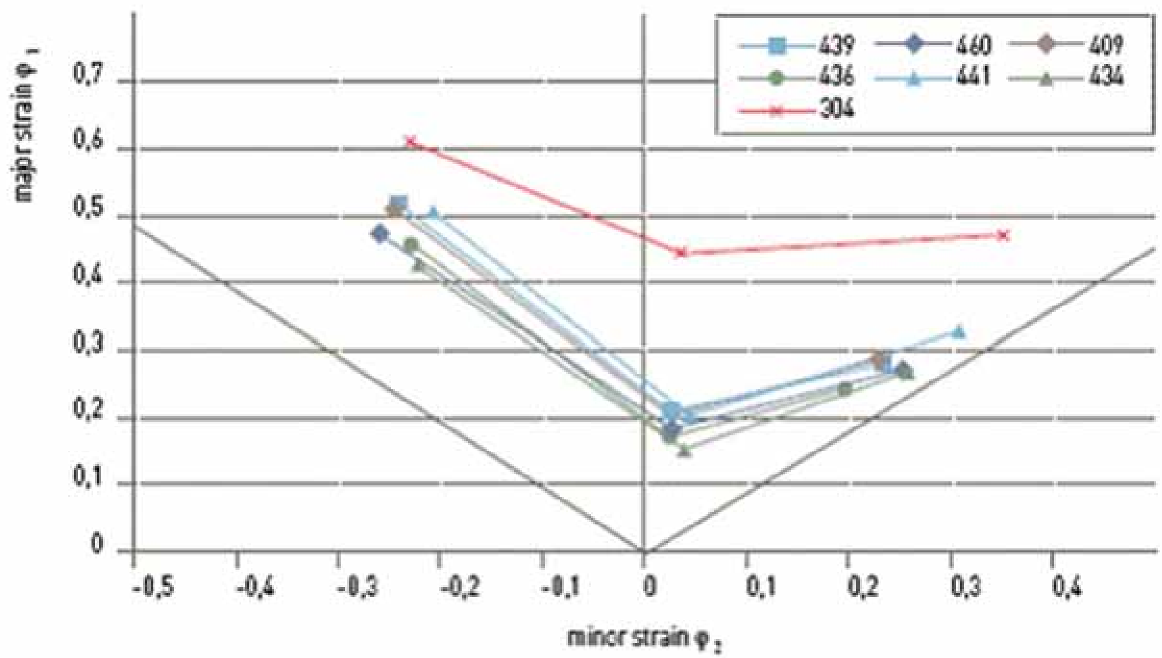
Deep drawing

Stretch forming



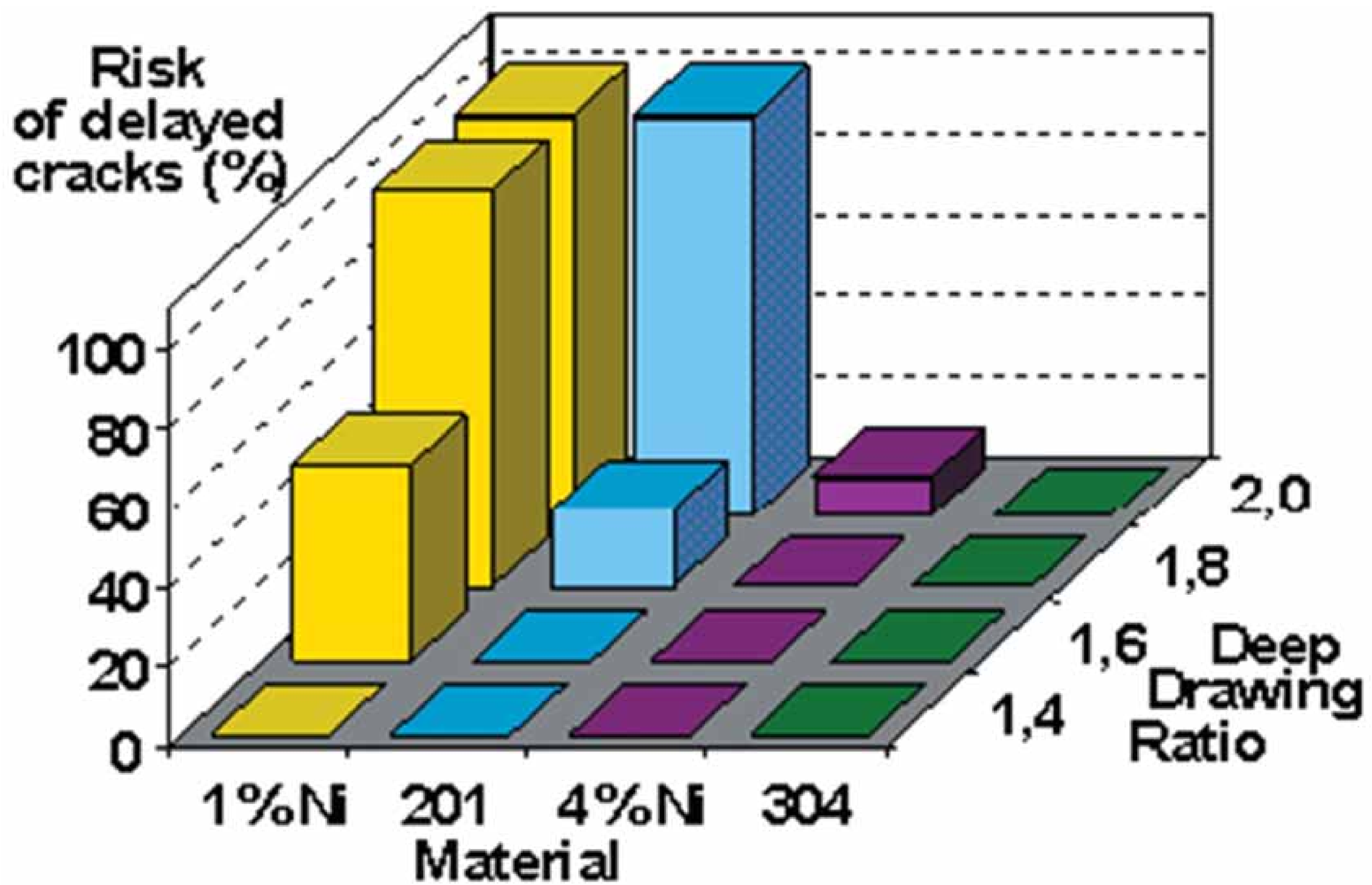
Formability





ISSF/ICDA

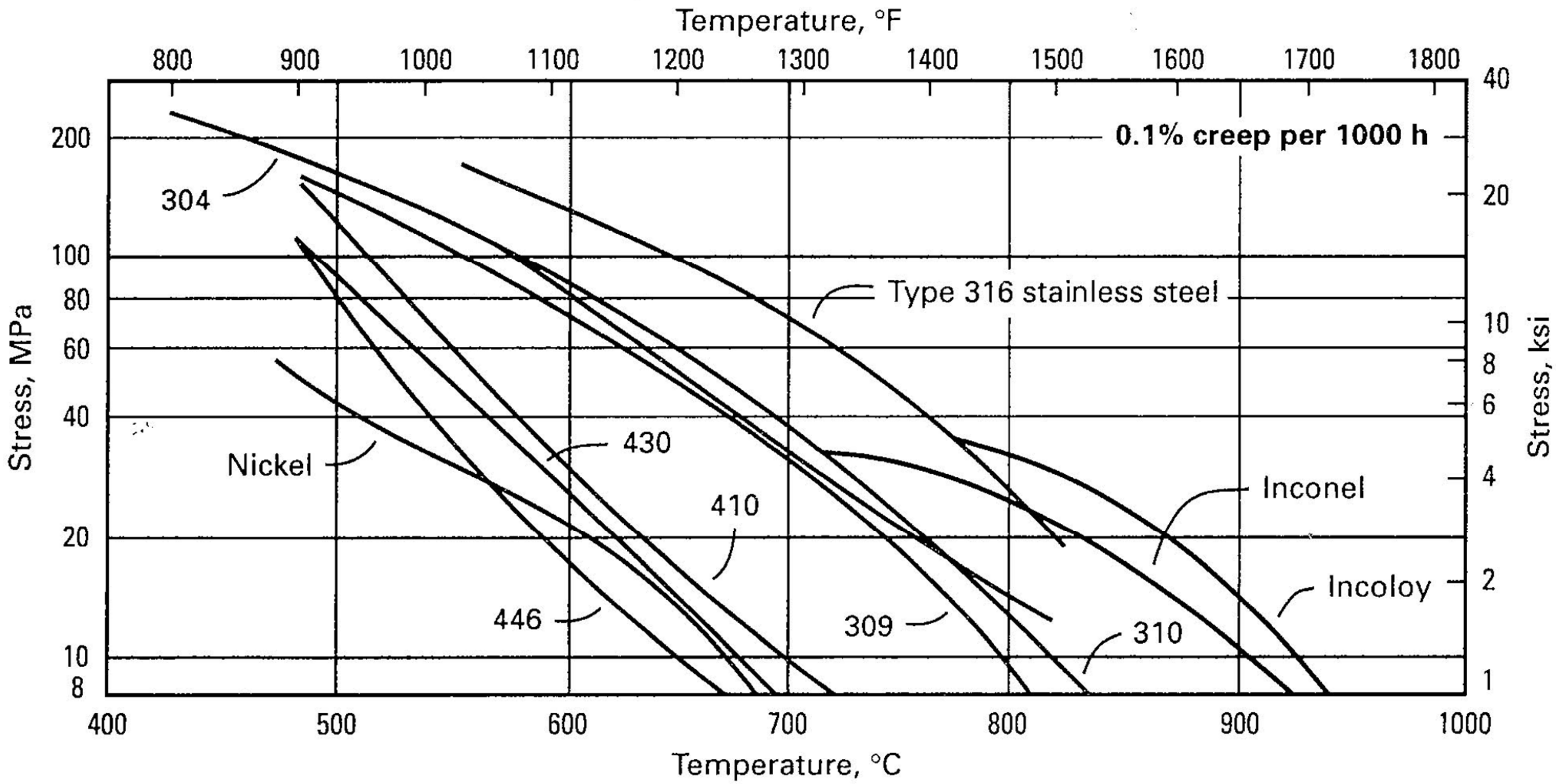
Delayed cracking



Weldability

Austenitic grades generally have good weldability

High temperature properties



Toughness after elevated temperature exposure

Stainless Type	Room Temp. Charpy Keyhole Impact Strength after 10,000 hr			
	Unexposed (J)	480C (J)	565C (J)	650C (J)
304	123	107	84	64
316	108	118	66	28
321	145	119	98	84
410	45	53	4	28
430	62	1	4	5

From stainless steels to nickel alloys

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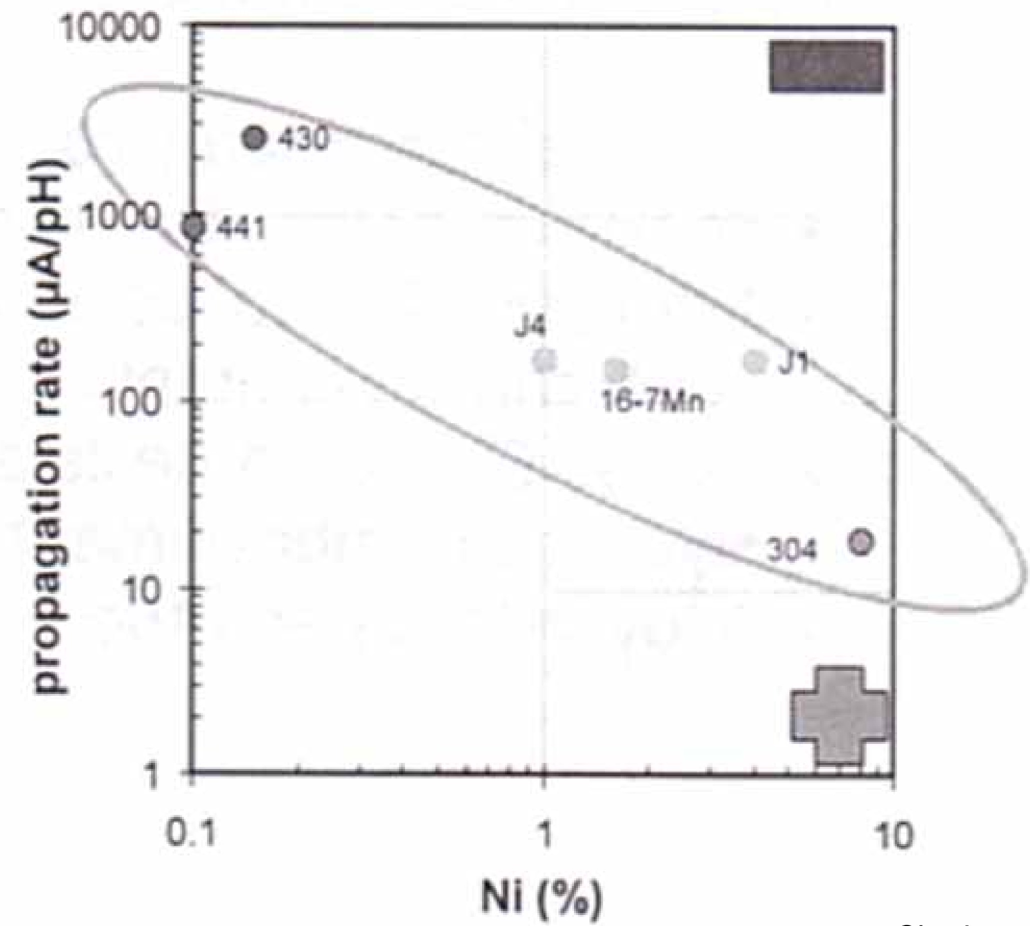
Corrosion resistance

Pitting Resistance Equivalent

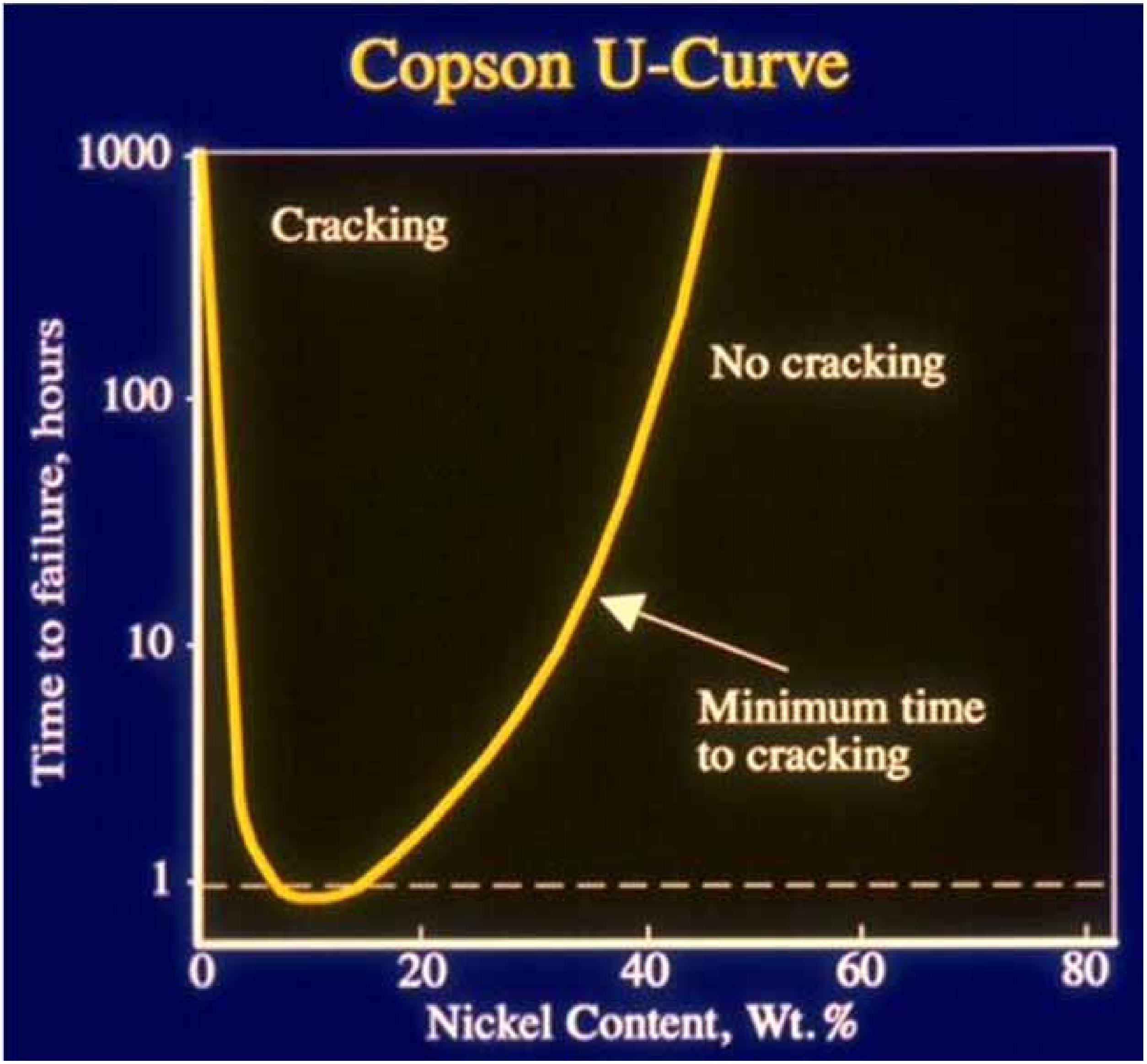
$$PRE = Cr\% + 3.3Mo\% + 16N\%$$

Nickel and corrosion propagation

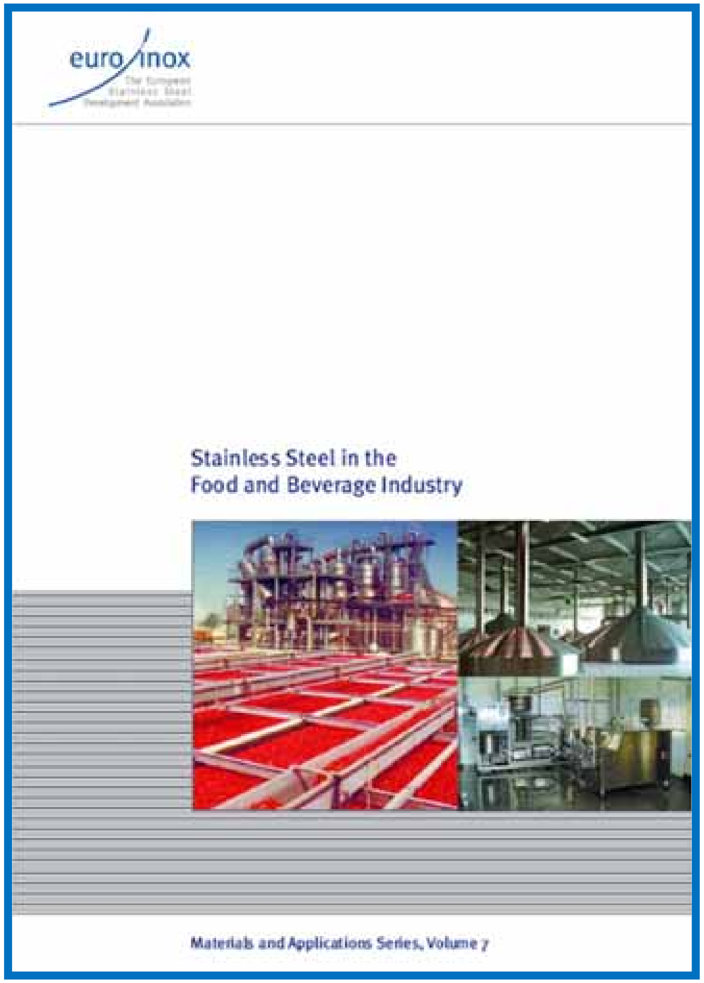


Charles

Nickel and Chloride Stress Corrosion Cracking



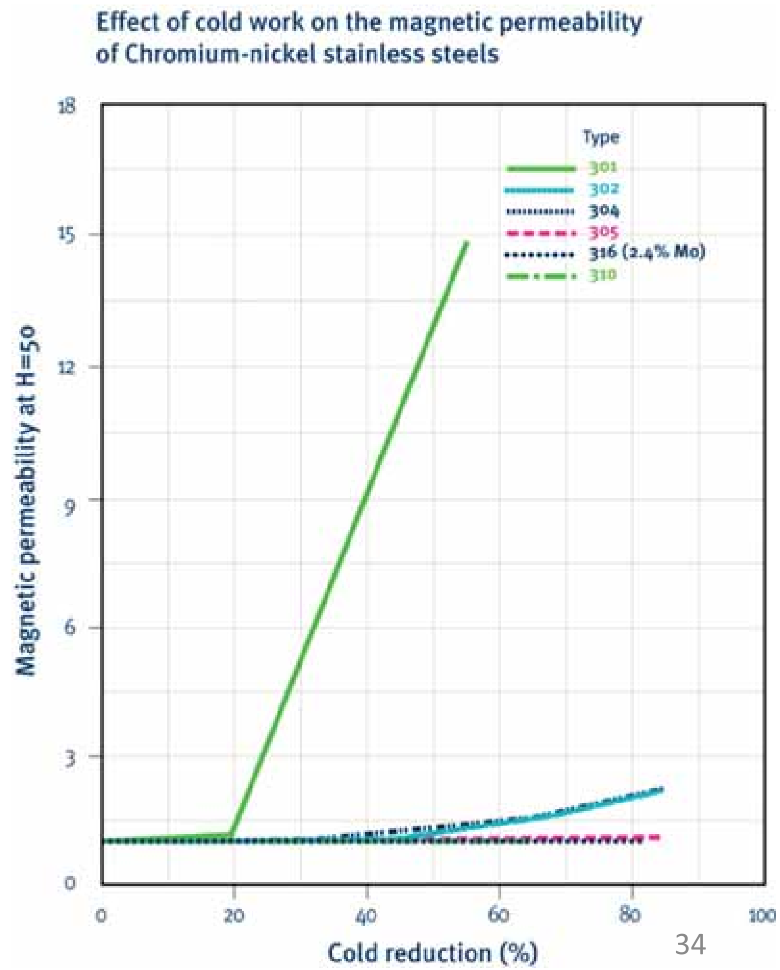
Hygienic



304 wine tanks, Italy

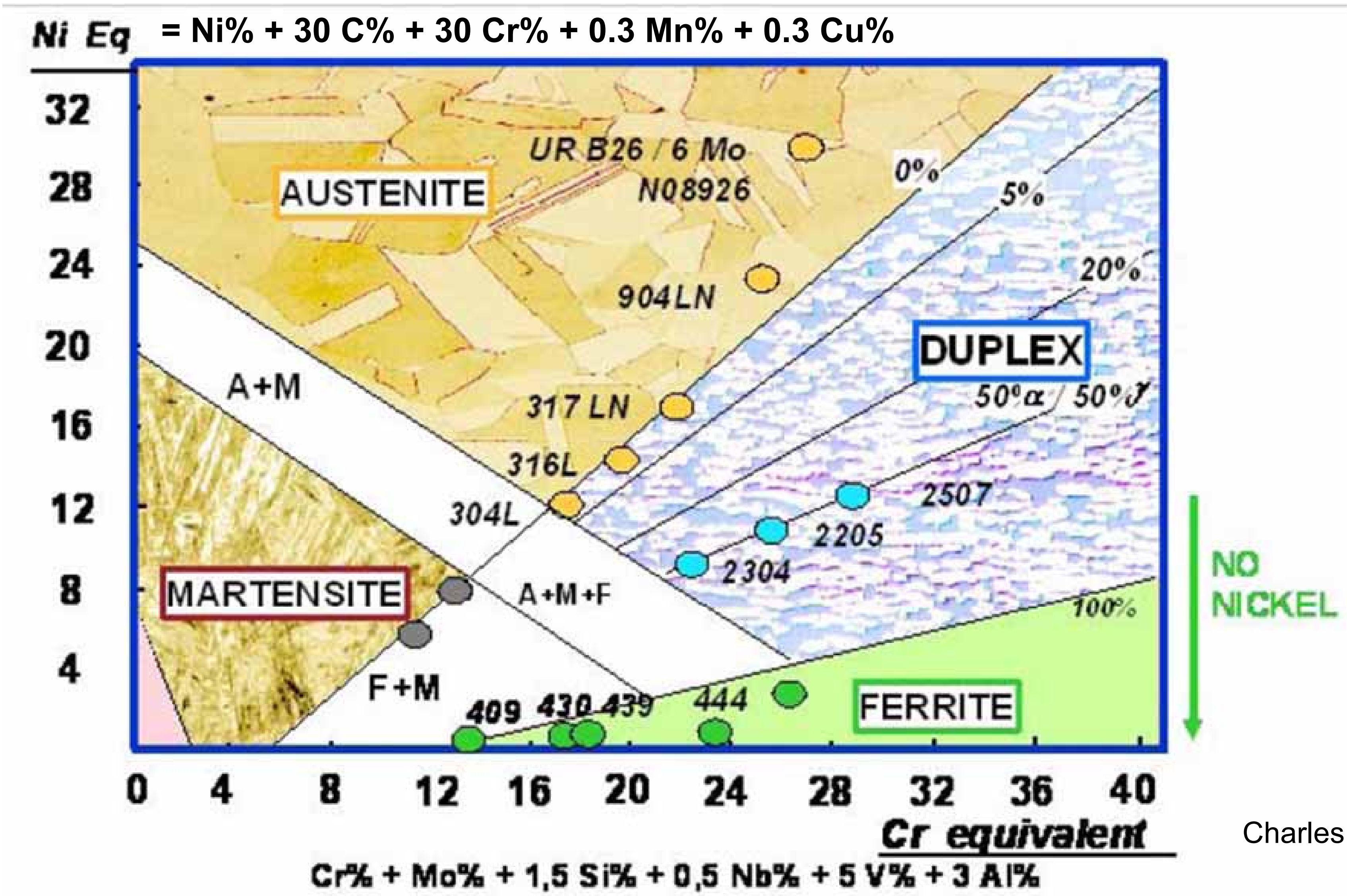
Ferromagnetism

- Austenitic grades are generally not ferromagnetic
- Special applications
- Impact on recycling



Duplex grades

Nickel stabilises the austenitic structure



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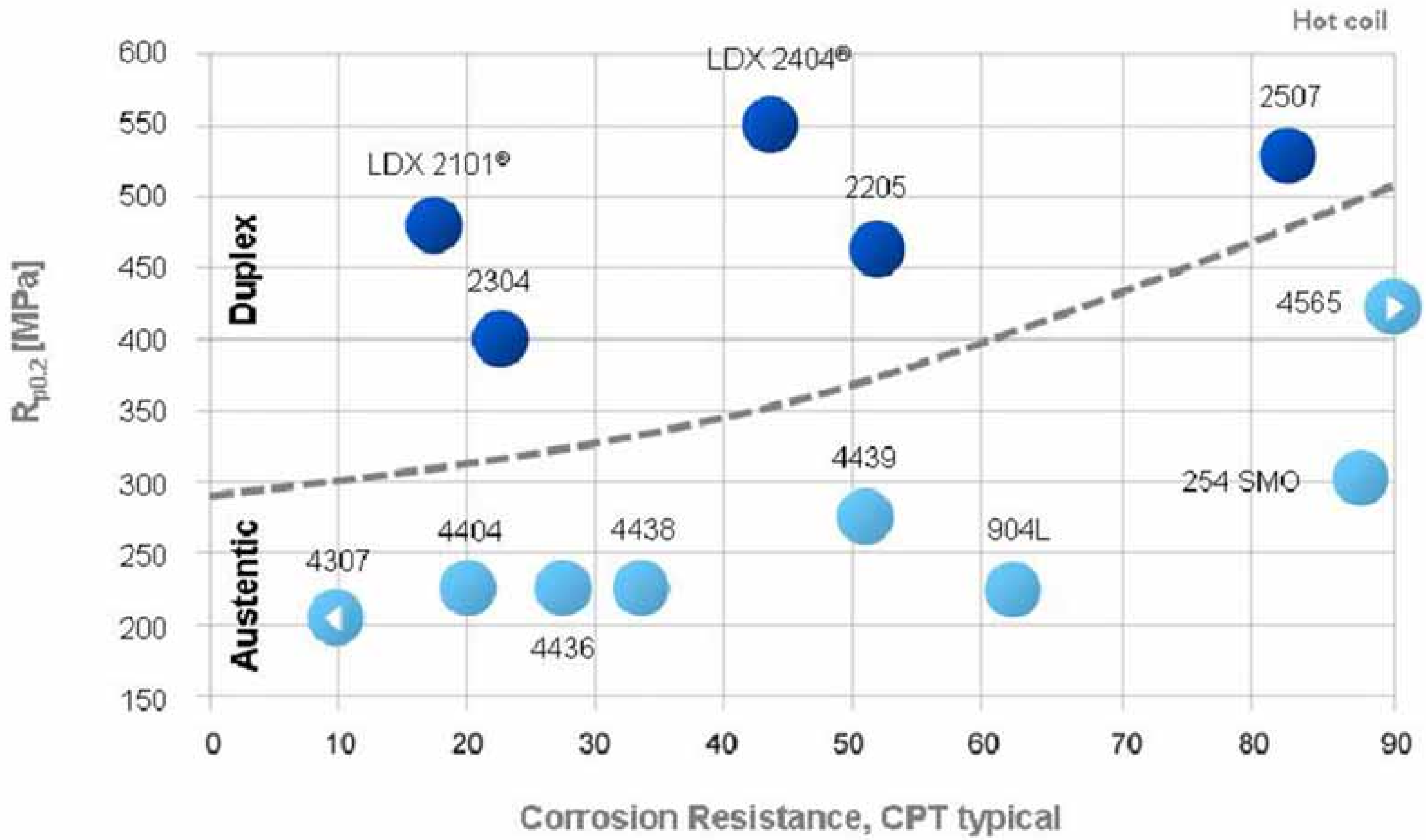
Why duplex stainless steels are used

- Duplex grades are ~ 1% of stainless steel production
- A lot of work has gone into their development and they are well-characterised
- Used because of the combination of:
  - Corrosion resistance - including to stress corrosion cracking
  - Mechanical properties - particularly strength
  - Fabricability
  - Economical overall

Positioning of Duplex grades

An excellent combination of high strength and corrosion resistance



OUTO KUMPU

Phase balance

- In duplex grades, aim is around 50/50 austenite/ferrite
- This requires approximately $Ni_{eq} = 0.5\ Cr_{eq} - 2$
- $Ni_{eq} = Ni + 0.5\ Mn + 0.3\ Cu + 25\ N + 30\ C$
- $Cr_{eq} = Cr + 1.5\ Mo + 0.75\ W$

Partitioning of elements between ferrite and austenite

- Broadly similar for all alloys
- N has low solubility in ferrite so is concentrated in austenite

Lean duplex 2101

Cr 1.14
Ni 0.62
Mn 0.84

GRADE	T°	Cr	Ni	Mo	N	Si	Cu	Mn	W	P
AF 22	1000	1.20	.54	1.65	-	-	-	-	-	-
*UR 35 N	960	1.19	.61	1.65	-	1.16	.68	.89	-	2.38
*UR 35N3Cu	975	1.2	.60	1.7	-	1.19	.66	.87	-	-
*UR45N	980	1.1	.61	1.66	-	1.16	.67	.86	-	2.31
SAF 2205	980	1.2	.58	1.72	.2^{o}	-	-	-	-	-
DP3 (SEM)	1020	1.1	.74	1.49	-	1.19	-	1.01	2	-
*UR52N	1040	1.15	.65	1.6	-	1.19	.69	.87	-	2.9
*UR52N^{+}	1060	1.11	.66	1.49	-	1.15	.71	-	-	-
SAF 2507	1060	1.13	.70	1.3	.125^{oo}	-	-	-	-	-
*SAF 2507	1060	1.12	.60	1.58	-	1.19	-	.95	-	-
*ZERON 100	1080	1.16	.65	1.57	-	1.10	.73	.94	-	-
*X (Table III)	1040	1.12	.61	1.58	-	1.18	-	.86	-	-
*Y (Table III)	1040	1.17	.62	1.61	-	1.21	.60	.82	-	-
*Z (Table III)	1040	1.17	.61	1.66	-	1.21	.63	.88	-	-

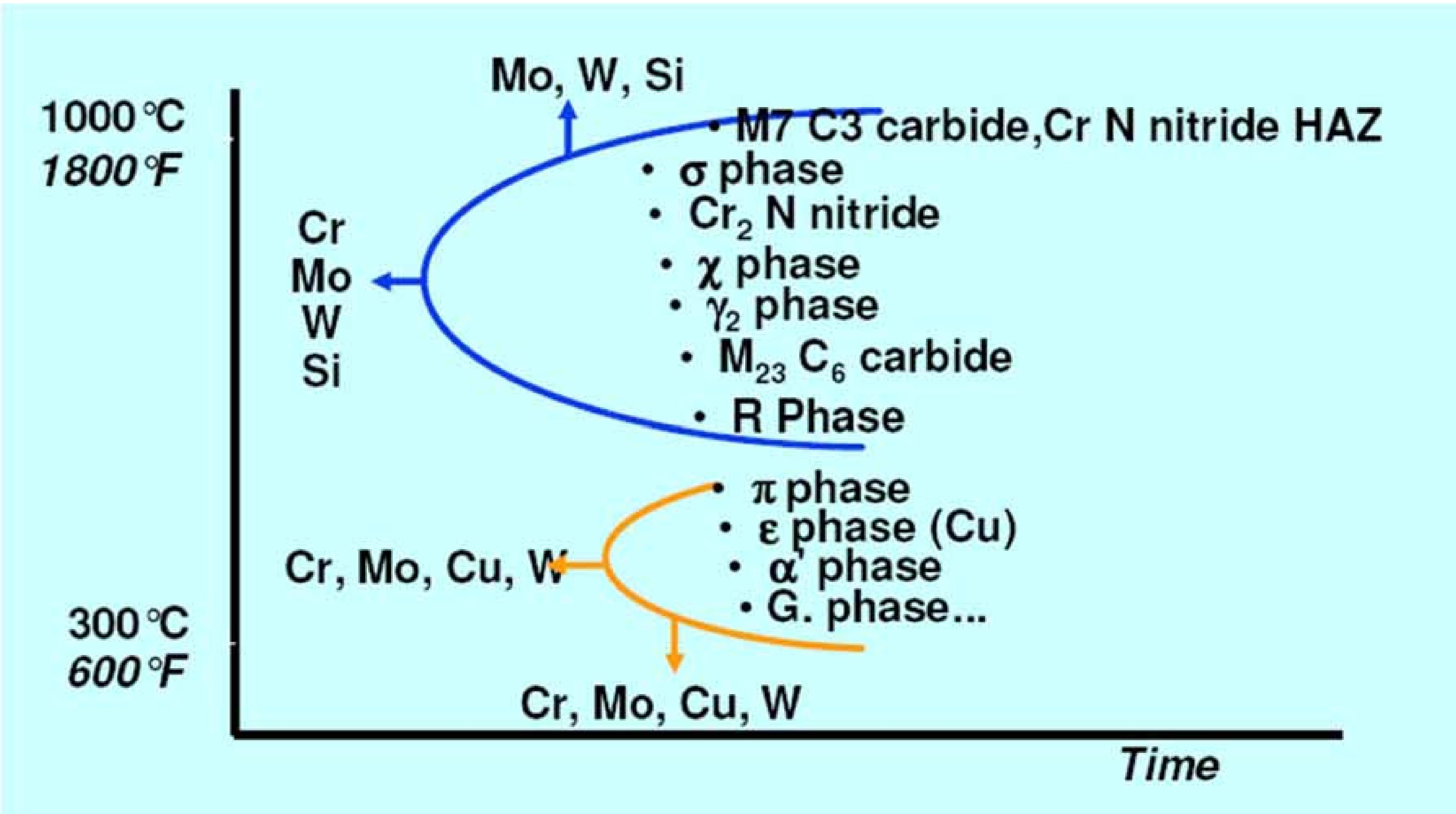
o : [N] = .05 in α and [N] = .25 in γ
oo : [N] = .06 in α and [N] = .48 in γ
* : CLI/CRMC results

Charles

Ranking for pitting resistance

- PRE = Cr + 3.3 Mo + 0.5 W + 16 N
- Compositions balanced so that commercial duplex grades have similar PRE for both phases

Precipitation reactions which may occur in duplex grades (Charles)



The New extended duplex family.
After Beaune 2010 and COMO 2011.

No clear fully equivalent grades are developed by the different Stainless steels Producers; individual marketing strategy are developed.
We can nevertheless consider the following families:

- The lean duplex grades (no Mo duplex grades) PREN : 22-27 !
  Typically : 2001/ 2101 / 2202 / 32304. (with possible Cu additions).
- The 'low Mo" grades (Mo lower than 3 typically 1.5%) PREN 30-34
  Typically 2003 / 2404.
- The "Standard" 2205 PREN 33-36
- The "classical" Super-Duplex Grades PREN >40-42 (25Cr / Cu / W)
- The Hyperduplex grades PREN 46-…56!
- Yes but! What about a Mn duplex family to reduce Ni? What about Cu, W, REM, Ba… ??? Yes complexity is there !

Welding of duplex grades

- Duplex stainless steels solidify as ferrite.
- Ni encourages the formation of austenite on cooling.
- Most filler metals are over-alloyed with about 2% extra Ni to help formation of sufficient austenite (>30%) to provide toughness.
- Filler metal with 7-8% Ni has been shown to be suitable for lean duplex, where it also helps with low temperature toughness.
- Further details are in recently revised publication “Fabricating Duplex Stainless Steels” from IMOA.

Duplex stainless steels – weld filler

Wrought material

Alloy	%Cr	%Ni	%Mo	%N
S32101	21.5	1.5	0.4	0.22
S32205	22.5	5.5	3.2	0.17
S32750	25.0	7.0	4.0	0.28

Weld filler metal for above

Alloy	%Cr	%Ni	%Mo	%N
2101	23.0	7.0	0.2	0.14
ER2209	23.0	8.5	3.2	0.17
25-10-4L	25.0	9.5	4.0	0.25

2205

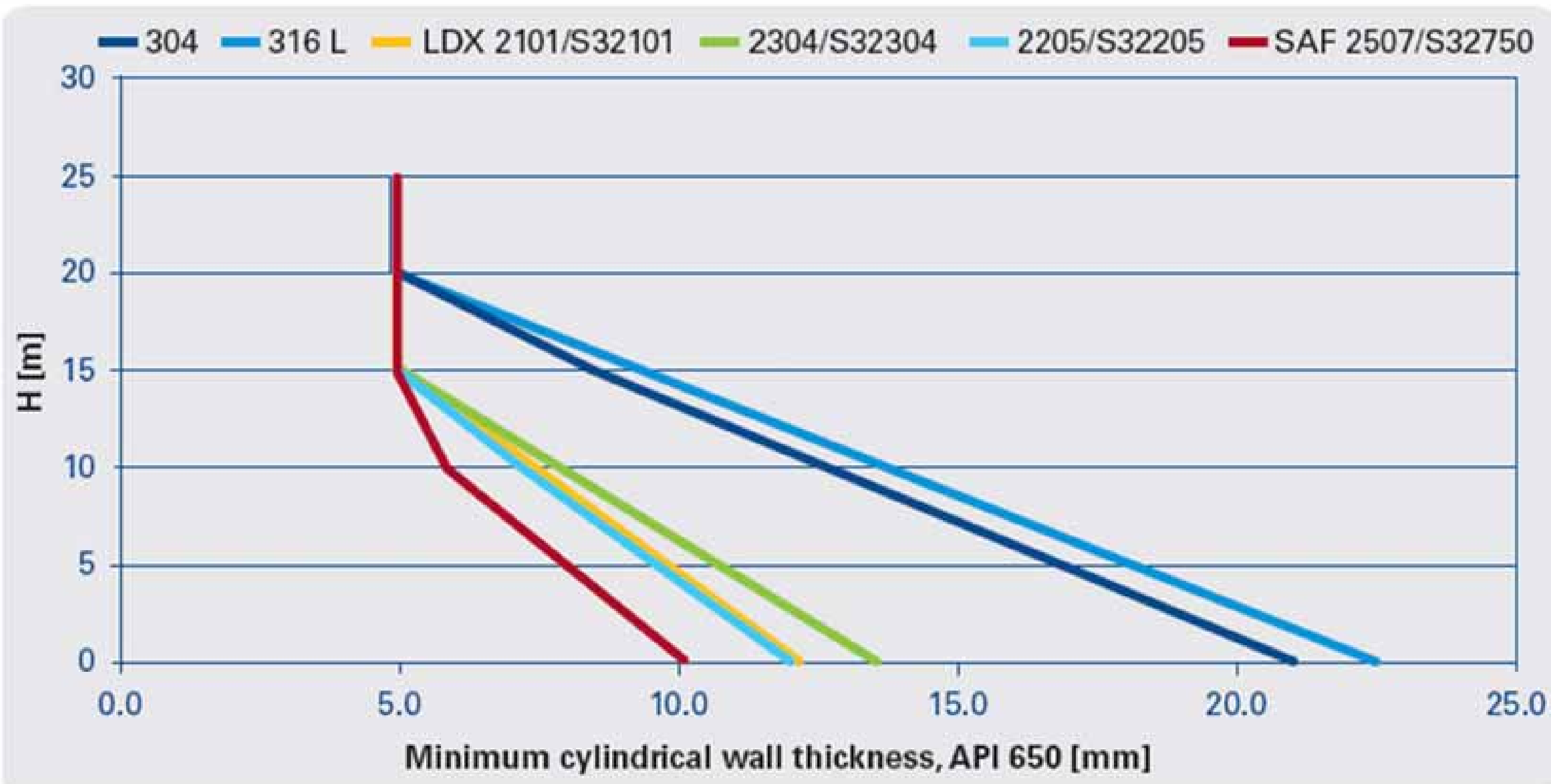
Design

- A full range of duplex stainless steels are now contained in a number of design codes, e.g. ASME, API.

- Higher proof strength compared with similar austenitic grades offers weight-saving advantages, up to ~50%.

- Full advantage of higher strength may not be gained if the design is limited by elastic modulus, which is similar for all grades of stainless steel.

Minimum tank wall thickness, API 650 standard, Outokumpu data



Municipal water storage tank – Matsuyama, Japan

Stonecutters bridge, Hong Kong

- 2,000 t of hot-rolled 2205 duplex stainless steel plate used for top 120 m of towers
- Structural requirements and zero maintenance

Doha International Airport, S32003

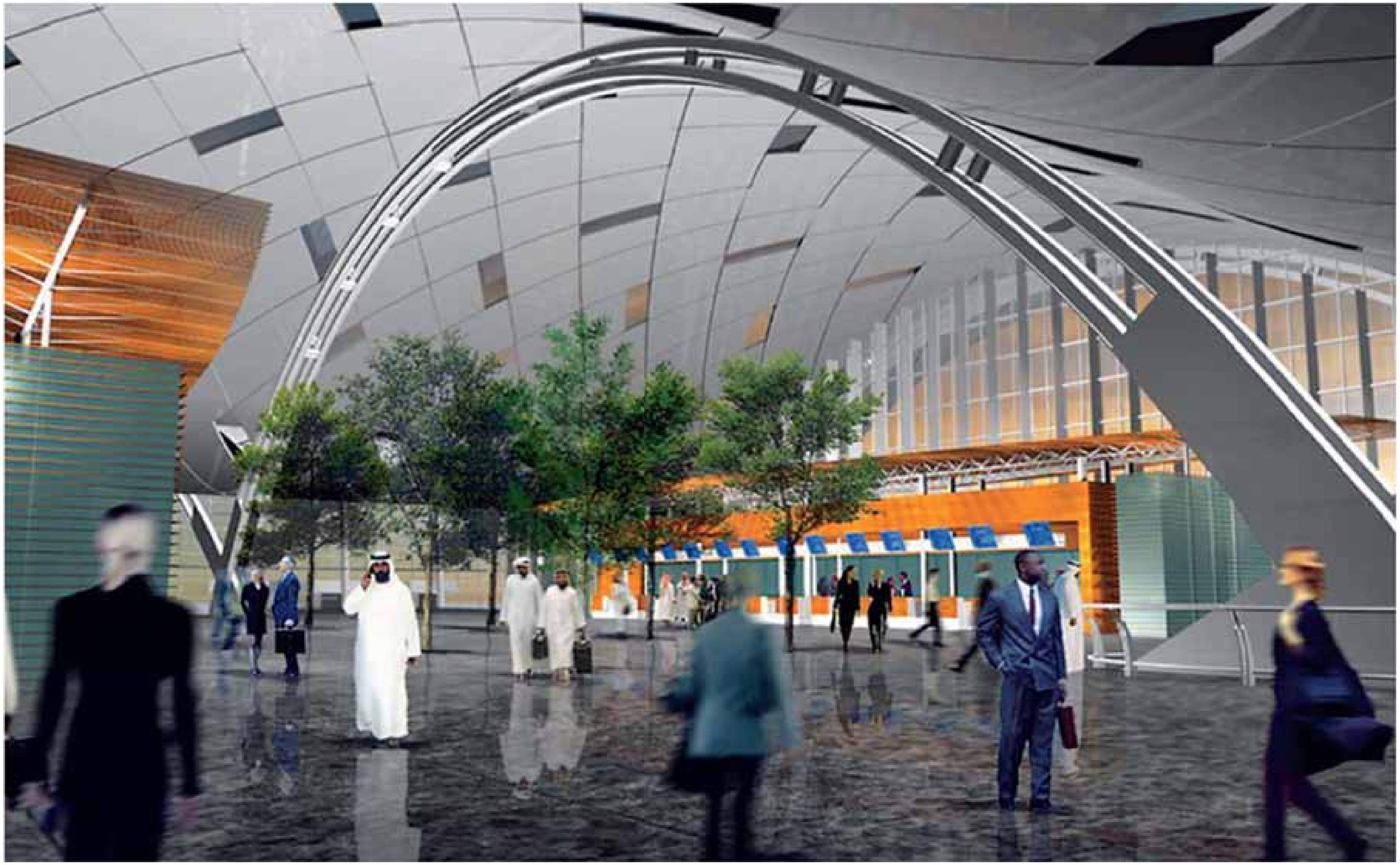


Image: Qatar Airways

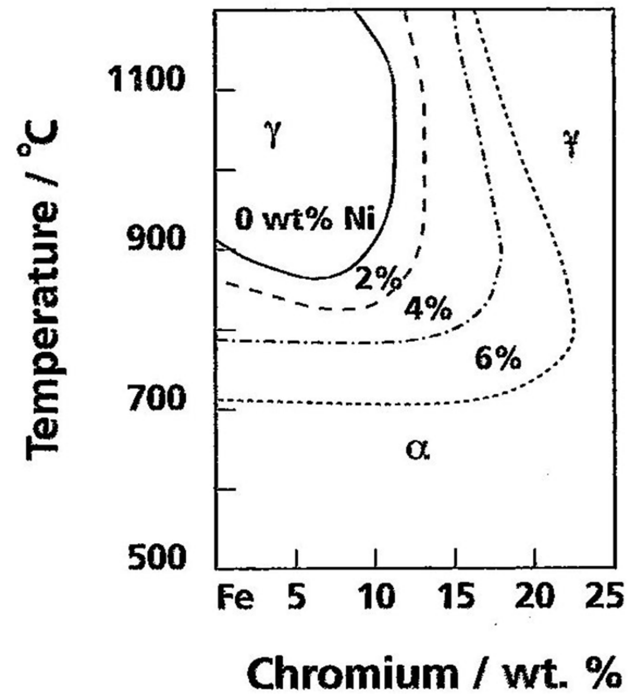
Other grades

- Martensitic
- Precipitation hardening

NICKEL IN MARTENSITIC STAINLESS STEEL

Effect on Microstructure

Nickel is one element that increases the amount of Cr that can be added and still form austenite at high temperatures, necessary to get martensite formation when quenched



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NICKEL IN MARTENSITIC SS

Effect on Corrosion Properties

1. Most standard martensitic SS have relatively low Cr content, 11.5-13.5%, and thus have relatively low general corrosion resistance compared to austenitic grades with higher Cr content
2. Nickel increases the corrosion resistance of the martensitic grades to both general corrosion and localized corrosion. The higher Cr S43100 has the highest corrosion resistance of any of the standard martensitic SS

Note: all the martensitic SS have their best corrosion resistance in the hardened and tempered condition; corrosion resistance is much poorer in the annealed condition

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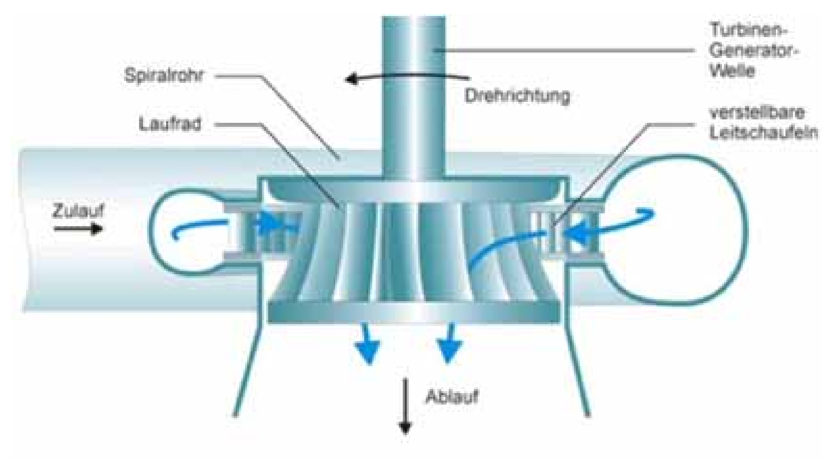
NICKEL IN MARTENSITIC STAINLESS STEEL

Martensitic-ferritic-austenitic grades (triplex)

1. 1.4418 grade is typically 65% martensite, 30% austenite and 5% ferrite in the tempered condition
2. It is a weldable martensitic SS with corrosion resistance, good strength and good ductility
3. Major use in small to medium-sized water turbines (Francis, Kaplan),
   also used in Pulp & Paper industry



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NICKEL IN MARTENSITIC STAINLESS STEEL

Super-Martensitic grades

1. Super-martensitic grades were developed specifically for high pressure, generally sweet gas applications for offshore use
2. There are grades with 2.5-6.5% nickel, some containing Mo, some without
3. They are produced as seamless or welded pipe, but they must be welded on an offshore pipe-laying platform
4. A short Post Weld Heat Treatment is usually performed (e.g. a few minutes at 600^{o}C)

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NICKEL IN PH GRADE STAINLESS STEEL

Some nickel-containing PH SS

UNS / EN	Common Name	Type	Cr	Ni	Mo	Other
S17400	17-4PH	M	15.0-17.5	3.0-5.0	-	Cu, Nb
S13800	PH13-8Mo	M	12.25-13.25	7.5-8.5	2.0-2.5	Al
S45000	C450	M	14.0-16.0	5.0-7.0	0.5-1.0	Cu, Nb
S17700	17-7PH	SA	16.0-18.0	6.5-7.75	-	Al
S35000	AM350	SA	16.0-17.0	4.0-5.0	2.5-3.25	N
S66286	A286	A	13.5-16.0	24.0-27.0	1.0-1.5	Ti,V,B,Al

Types: M= Martensitic
SA = Semi-austenitic
A = Austenitic

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NICKEL IN PH GRADE STAINLESS STEEL

Role of Nickel in PH Grades

1. All PH grades contain nickel, which is needed to obtain austenite to martensite transformation
2. Nickel gives higher corrosion resistance (general corrosion, localized corrosion, stress corrosion cracking)
3. Nickel gives improved ductility and notch toughness

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NICKEL IN PH GRADE STAINLESS STEEL

Mechanical Properties of 17-4PH

Minimum values at room temperature acc. to ASTM A564 for some possible heat treatments

Condi-tion*	Thickness (mm)	Yield Strength (MPa)	Tensile Strength (MPa)	Elong. (%)	R of A (%)	Hardness (Brinell)	Charpy V-notch (J)
H900	≤ 75	1170	1310	10	40	388	-
H925	≤ 75	1070	1170	10	44	375	6.8
H1025	≤ 200	1000	1070	12	45	331	20
H1075	≤ 200	860	1000	13	45	311	27
H1150	≤ 200	725	930	16	50	277	41
H1150M	All	520	795	18	55	255	75

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***The condition refers to the aging heat treatment; e.g. H900 is heating to 900°F (482°C) for 1 hour, then air cool**

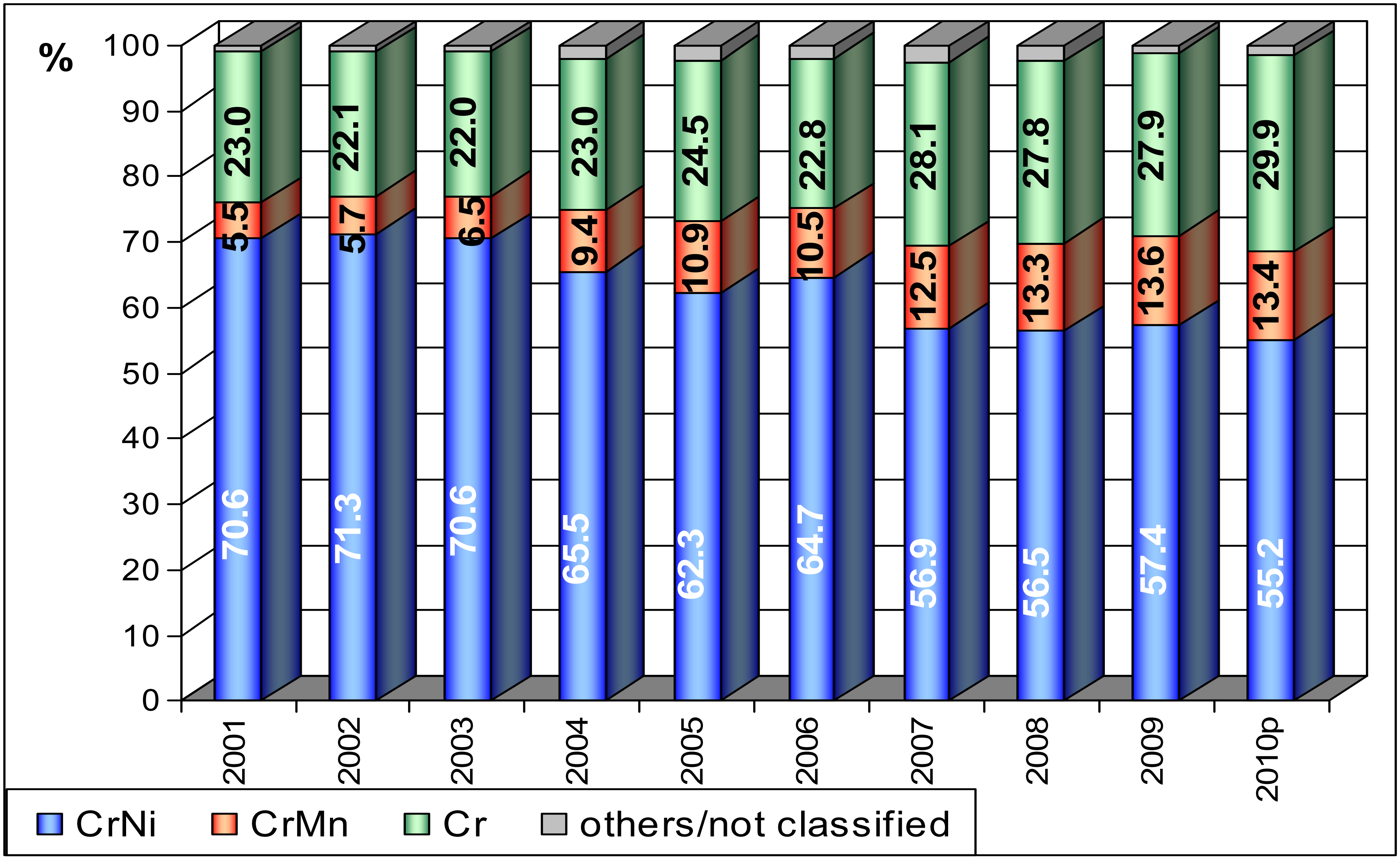
Lustre - an intangible quality

Olympic hockey stadium, Torino

Centro Inox

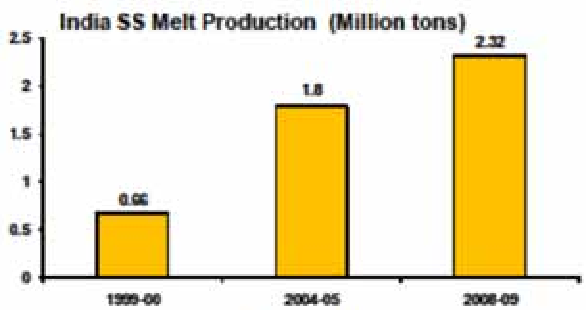
Stainless Crude Steel Production

(ISSF data)



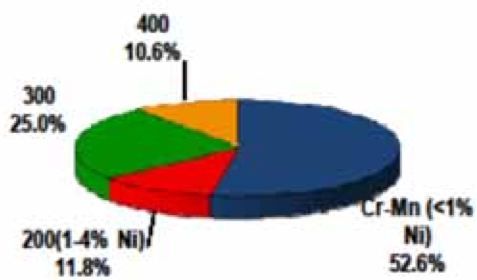
Source: ISSF

Stainless steel Production status-India



Source: Mindsight Analysis

Stainless steel melt producion by grades (2008-09)



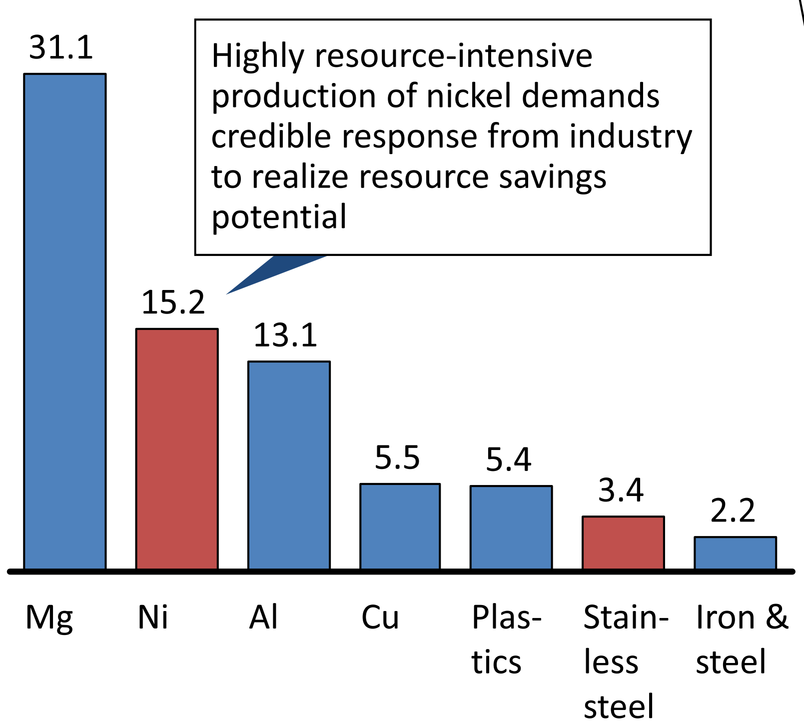
- Growth of **Long products** annually at **20.5%** compared to **Flat products** annually at **8.8. %** (over last 8 years)
- Within flats **coils and plates** have grown much faster at **19.8%** per yr
- **Flat products now** account for **72%** of the total production.
- Almost **64.5%** of the total production is in **200 series.**
- Fastest Growth in **400 series (34%)** followed by **300 series (18.5%);**
- Overall **200 Series** growth at nominal **7.7%** annually. Within 200 (1-4%Ni) growth at **16.4%** per yr

Environmental aspects

Nickel, stainless steel and CO_2 "content"

kg CO_2 equivalent*/kg material

Primary nickel has a high CO_2 equivalent output ...



Source: Leiden EU report 2005, Eurofer, EU Webpage, ISSF

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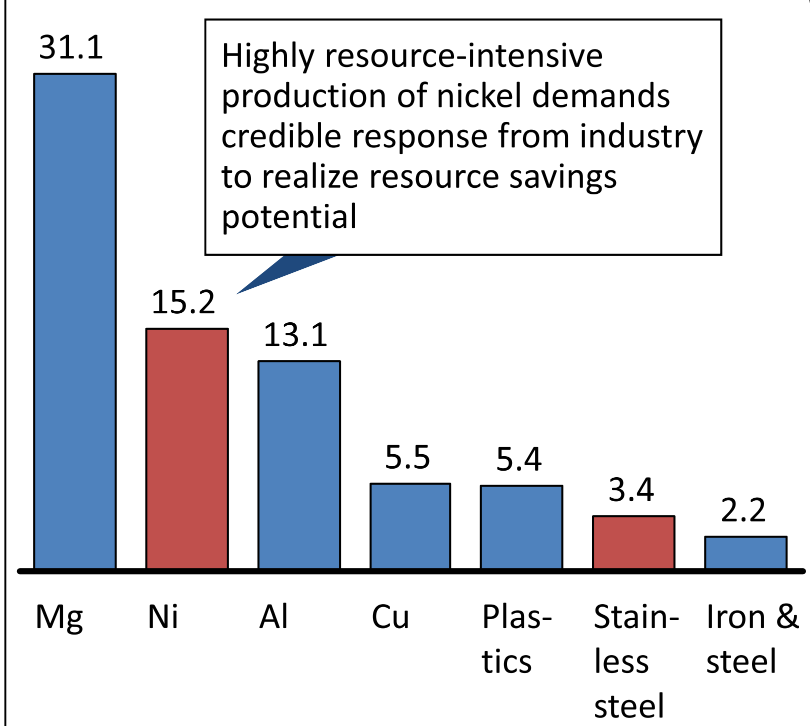
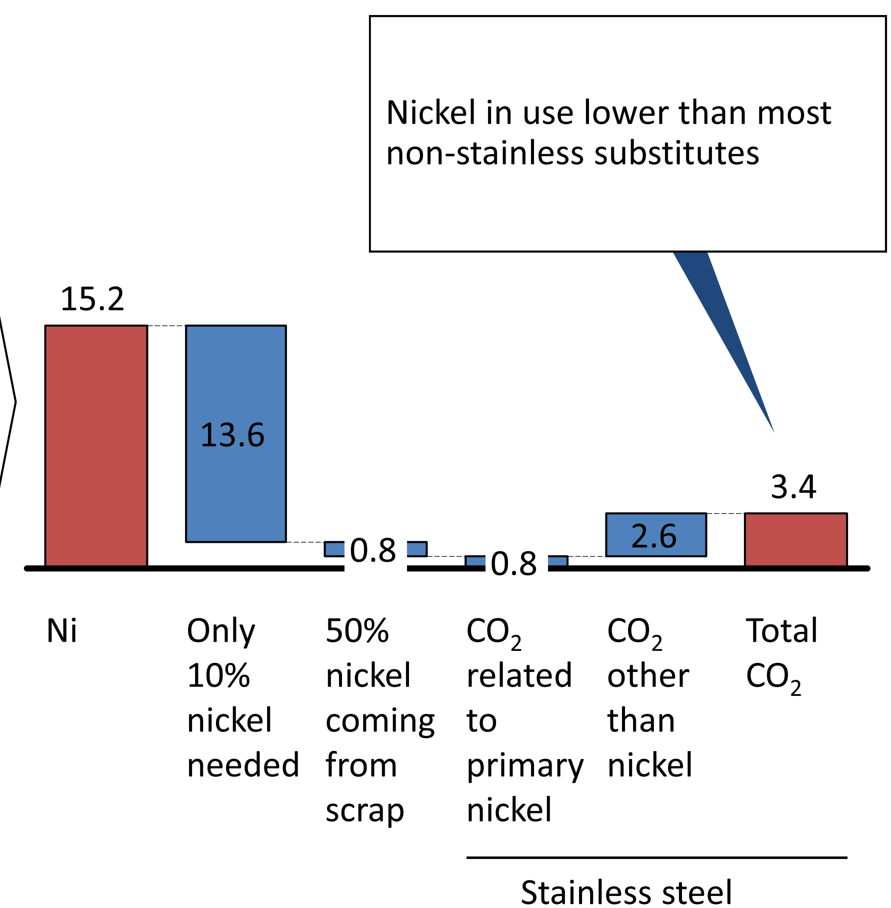
Nickel, stainless steel and CO_2 “content”

kg CO_2 equivalent*/kg material

Primary nickel has a high CO_2 equivalent output …



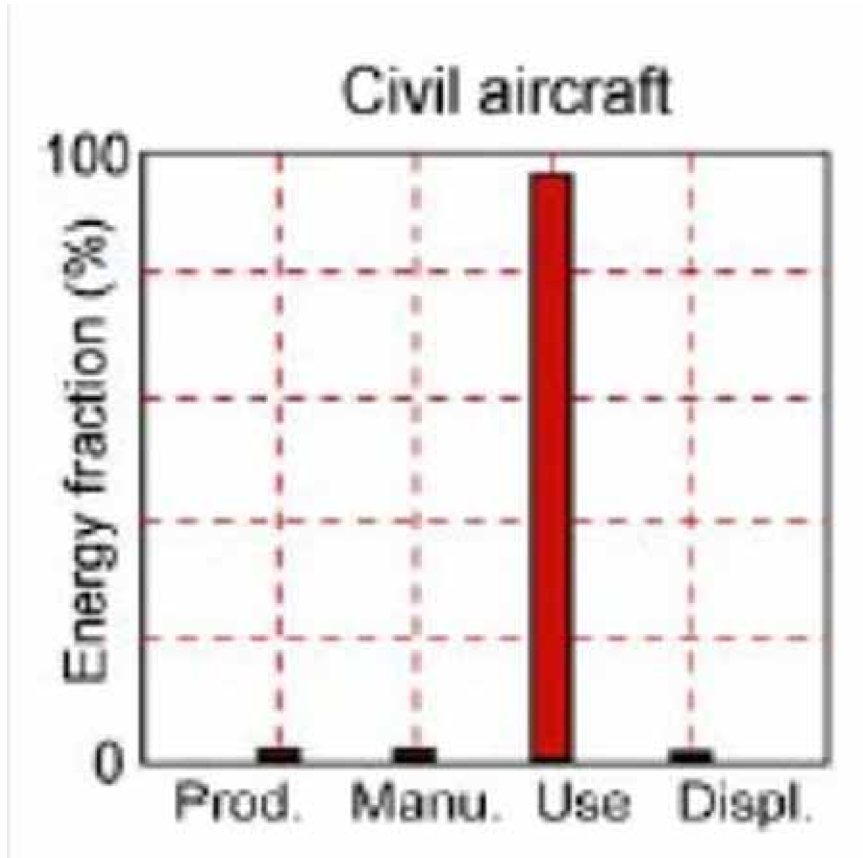
… but in its major use its CO_2 output is lower than that of aluminum, copper or plastics



: Leiden EU report 2005, Eurofer, EU Webpage, ISSF

Energy use and carbon footprint through the whole life cycle

- Important to consider the whole life cycle
- Yes, more energy is needed to produce 1 kg of nickel compared with the production of 1 kg of other metals
- BUT for a civil aircraft, > 95% of the energy involved in its whole life is during use (fuel). That is where nickel helps engines to be efficient and so makes a huge contribution to reducing the total energy used.



Ashby

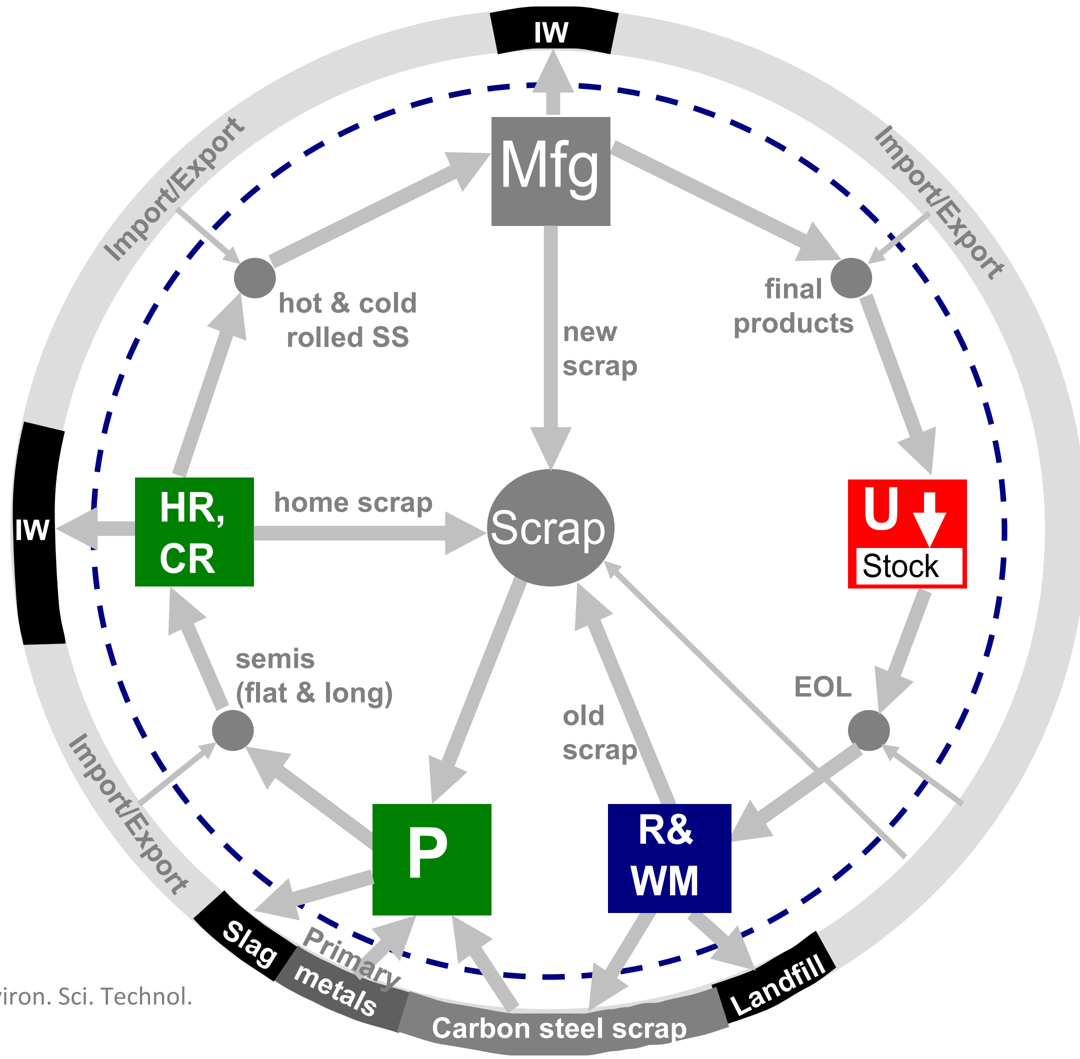
Example of Nickel as critical raw material in technologies for Mitigating the Climate Change and Low Carbon Economies

Mitigation strategy	Nickel´s contribution
More fuel efficient vehicles	**Batteries:** nickel metal hydride batteries are used in hybrid electric vehicles and all electric plug-in vehicles.
Fuel switching from coal to natural gas	**Sweetening of sour gas:** due to their corrosion resistant properties, nickel containing alloys are critical in the cleaning, or 'sweetening' of sour gas–natural gas that contains significant amounts of sulphur.
Carbon capture and storage (CCS)	**Piping and vessels:** long term storage of the CO2 is envisaged either in deep geological formations, such as saline aquifers or oil fields, in deep ocean masses, or in the form of mineral carbonates. Nickel containing alloys would be required in the piping and vessels of each of these processes as they all involve corrosive environments.
Nuclear power	**Tubing in steam generators:** specialized nickel based alloys are used as tubing for steam generators in nuclear power plants, as they perform well in these high temperature, high pressure environments.
Wind power	**Tough steels:** many of the components of a wind turbine, such as the rotor hub, are cast in ductile iron, with 1% nickel added for added impact strength at low temperatures.
Solar power	**Tower systems:** the heat transfer fluid used in solar power tower systems is typically molten salt. Due to the corrosive nature of this material, nickel containing alloys are typically used in the tubing that contains the salt.
2nd generation biofuels	**Pre-treatment:** sulphuric acid is commonly used as a pre-treating agent in cellulosic ethanol production, necessitating the use of stainless steels. Other processes use high temperature, requiring higher nickel containing alloys.

Introduction to Yale's nickel and stainless steel studies

- Professor Tom Graedel & Barbara Reck (Yale University, USA) work since early 2000 on metal flows and stocks through society
- Yale University has gained an outstanding reputation in this area
- Nickel Institute cooperated with Yale University to assess nickel and stainless steel flows

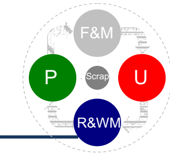
The stainless steel life cycle



P	Crude Production
HR,CR	Hot rolling, cold rolling
Mfg	Manufacturing
U	Use
R&WM	Recycling & Waste Management
EOL	End-of-Life flows
IW	Industrial Wastes

Source: Reck et al. (2010), Environ. Sci. Technol.

Using the Stocks and Flows Models to calculate recycling rates



- Recycling Rates are an important indicator for various stakeholders, particularly regarding sustainability:
  - Nickel producers and recyclers to identify potential for improvement throughout the whole value chain
  - Analysts and marketing people to identify regional and global trends
  - Authorities to identify areas for regulatory measures

- Stocks and Flows models build the basis for any recycling rate calculation

- Sound data ensure that adequate measures are taken within industry but also by regulatory environment around industry

Using the Stocks and Flows Models to calculate recycling rates

- **2006:** Declaration by the metals industry on recycling principles signed by 14 associations (Al, Cu, Pb, Ni, Zn, Sn, Co, …)

Recycling input rate

$$\text{RIR} = \frac{\text{Metal recycled}}{\text{Total metal production}}$$

Overall Recycling Efficiency Rate

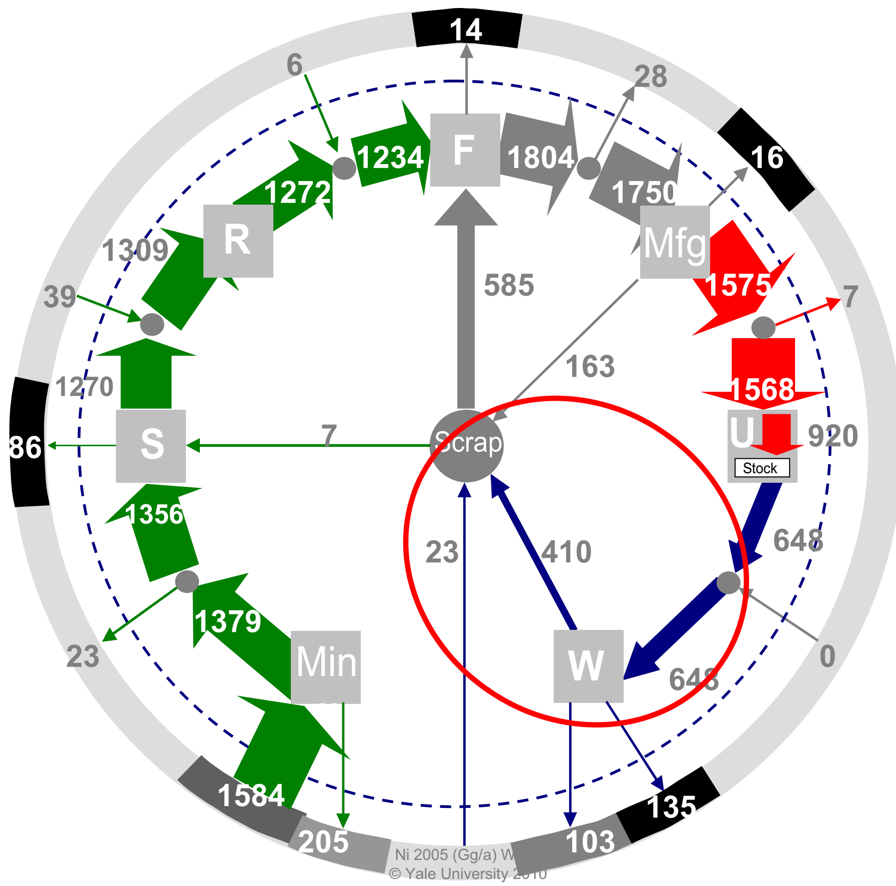
$$\text{RER} = \frac{\text{Recycled metal}}{\text{Metal available for recycling (old + new scrap)}}$$

End of Life Recycling Efficiency Rate

$$\text{EOL/RER} = \frac{\text{Metal recycled}}{\text{Metal available for collection (old scrap)}}$$

Using the Stocks and Flows Models to calculate recycling rates: End of Life Recycling Efficiency Rate

EOL Recycling Efficiency Rate
(2005):
63,3%



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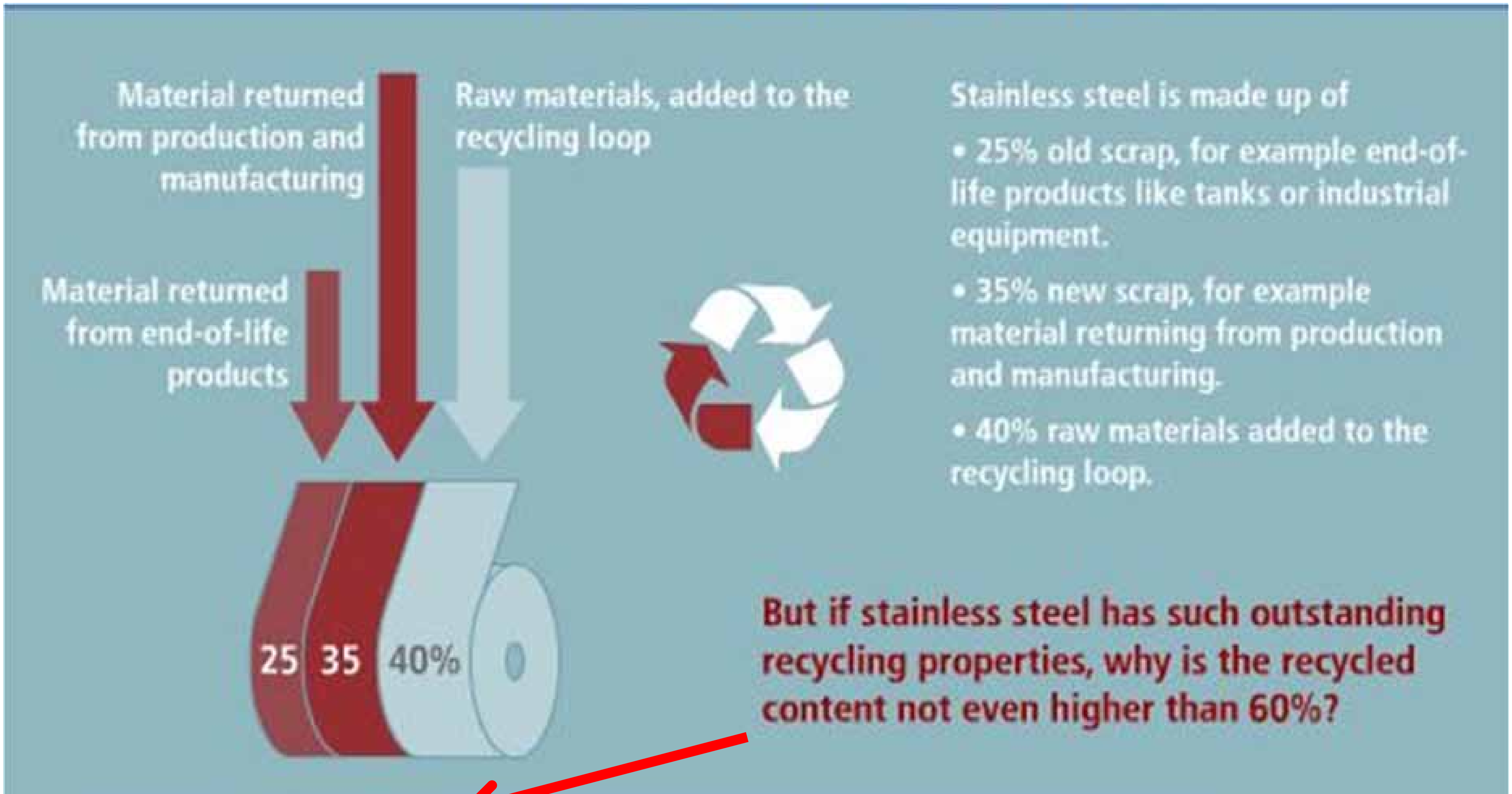
Importance of recycling

For a metal like stainless steel, which has a long service life, "recycled content" does not reflect the true extent of recycling. It makes much more sense to talk about the "recycling ratio", that is the proportion of end-of-life scrap which is actually recycled. Stainless steel is then one of the World's most recycled materials.



Because so much stainless steel is still in use and is not yet available for recycling

ISSF

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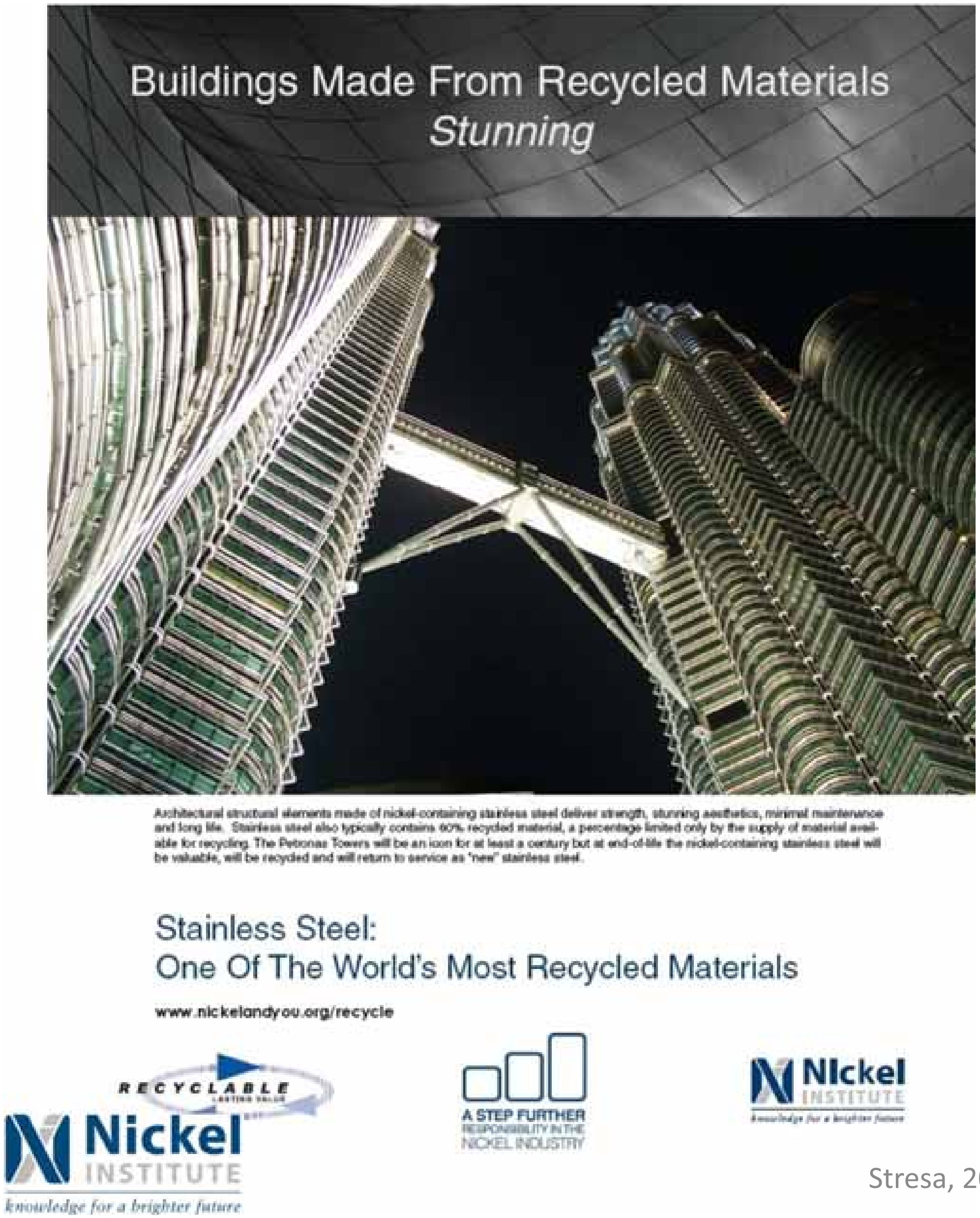
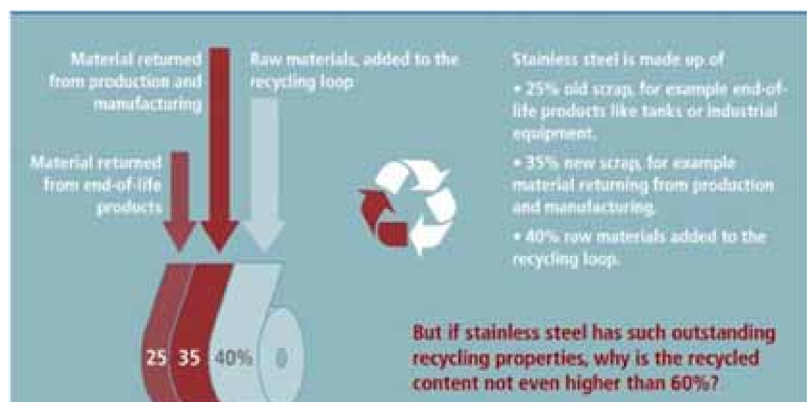
Importance of recycling





Waste water treatment - Life Cycle Cost

← Old

Huddersfield, UK

Waste water treatment

New ↓

- 98% reduction in maintenance costs
- 25% extra plant capacity

Life Cycle Cost Example

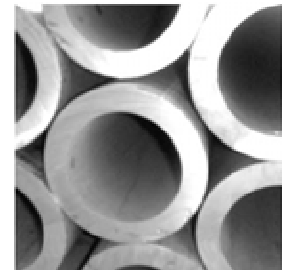
- First stainless steel raw water pipe in India (Mettur dam, 1998)
- No corrosion allowance
- 300 mm x 3 mm grade 304 stainless steel replaced 900 mm x 13 mm cast iron
- Lightweight meant easy installation in hilly country
- >50 year life expected (2 replacements of cast iron in that time)
- Smooth and smaller bore meant sustained low pumping costs
- Very low maintenance costs
- **LCC analysis: >60% saving over 50 years**

300 series is available in many forms

This is one reason why they are so widely used









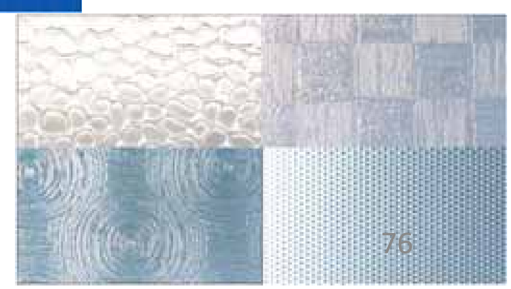










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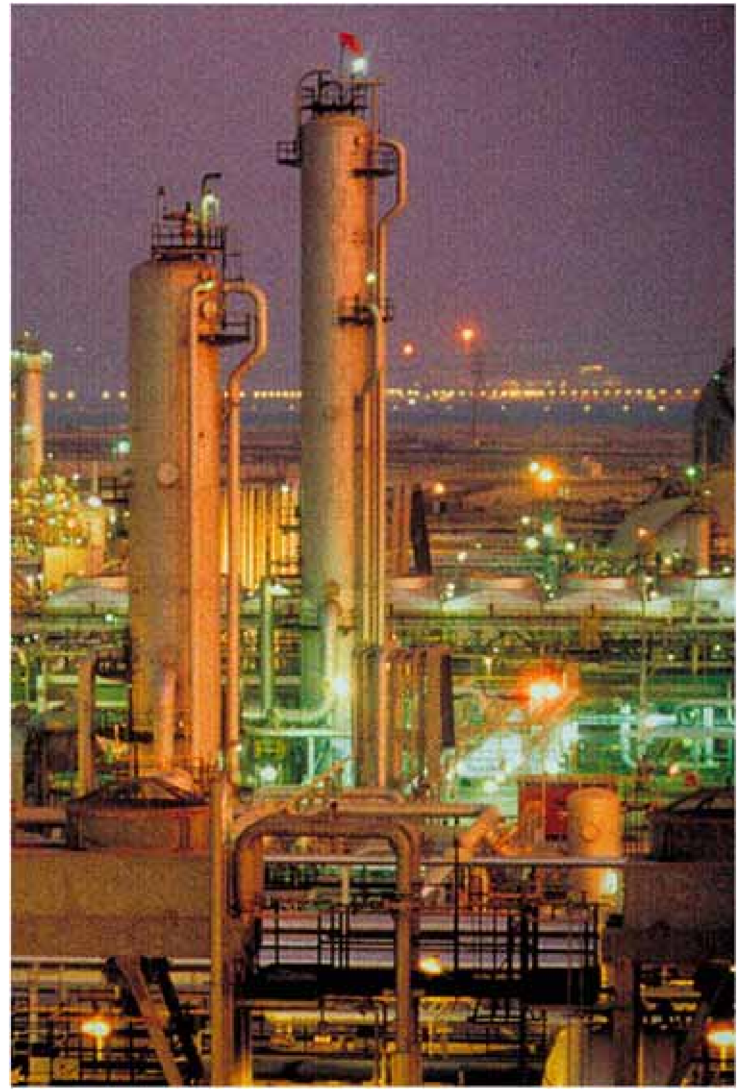
Consider all the factors when selecting a grade

- Corrosion resistance
- Operating temperature
- Strength - influences thickness & weight
- Other mechanical properties
- Fabrication and welding
- Physical properties
- Appearance
- Tooling costs
- Life cycle costs
- Availability: confidence in suppliers
- Familiarity
- Recyclability, environmental impacts and benefits
- Degree of comfort (risk, insurance)



Delhi metro coach – 301L for structurals, skin & furnishings

Local railcar interior, Mumbai, India - 304

Nickel in Stainless Steels - summary

- Nickel-containing stainless steels have a continuing role because of their combination of characteristics
- **Select appropriate grades for appropriate applications**

↓

- Performance
- Customer satisfaction
- Shareholder value
- Enhanced image
- Market growth

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