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An Update on Materials Selection of Nickel-containing Materials for Various Process Industries

Hosted by: American Institute of Chemical Engineers, Susquehanna Section

Presenter: Gary Coates, P.Eng.

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This Evenings Presentation

- **Introduction to NI / current issues**
- **Stainless Steels and Nickel Alloys**
  - a tale of ancient history, current practices, and future events masquerading as education, with a few quiz questions thrown in for fun.

Questions can be taken at any time during the talk

Who is the Nickel Institute?

- **We are a not-for-profit industry association, with official head office in Toronto, Canada.**
- **We have 3 legs:**
  MARKET DEVELOPMENT - Identify and open new markets for nickel applications & defend existing markets.
  SCIENCE – Provide relevant science in respect to human health and environment.
  ADVOCACY - Advocate for public policy and regulation based on sound science, risk management & socio-economic benefit.

Market Development is just one of the functions of NI

Member companies

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Ambatovy

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VALE
Vale Canada Limited
PT Vale Indonesia Tbk
Vale Japan Limited

WESTERN AREAS NL

Approximately 85% of worldwide nickel production outside China

Geographic Distribution

Three main offices in

- Raleigh (USA) - science
- Brussels (Belgium) - advocacy
- Beijing (China) - promotion

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Issues Facing the Perception of Nickel in the World

- **Certain nickel compounds are carcinogenic by inhalation.** So far nickel metal has avoided getting that label.
- **Nickel Allergic Contact Dermatitis (NACD) – a rash or eczema on the skin resulting from contact with nickel. Once a person has a reaction in one area of the skin, he/she can react on any other skin area.** About 1-2% of men and 12-15% of women are allergic to nickel, often caused by using nickel-plated piercings at some point. Nickel-containing stainless steels are generally OK, not causing NACD. For piercings, 316 SS is advised. There are some nickel hyper-sensitive people.
- **Other metals are being currently targeted.**

Nickel and many other metals often have a negative reputation

Stainless Steels and Nickel Alloys

- **Let's begin our story.**
  Once upon a time, in a land far away…….

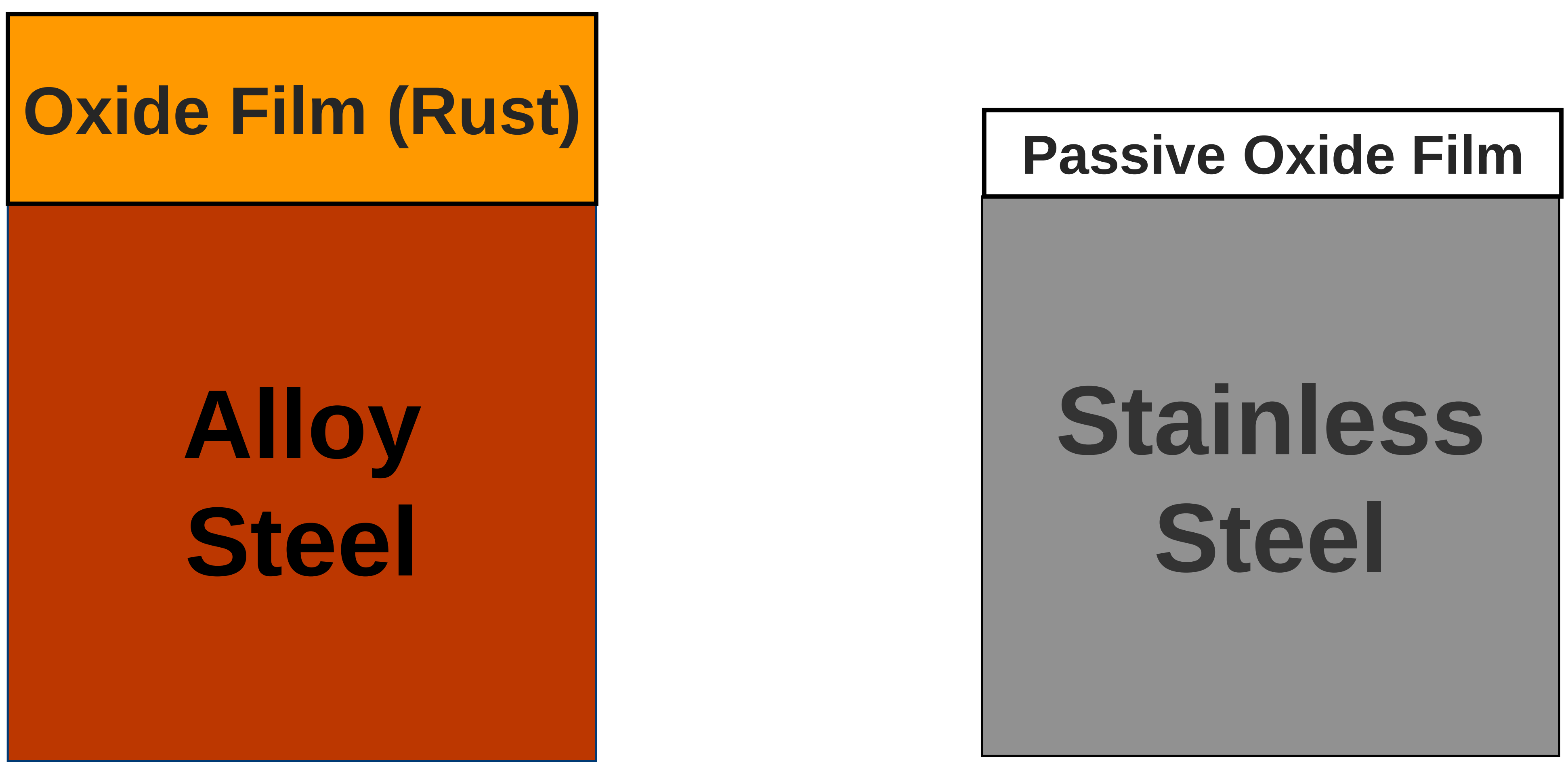
What is stainless steel?

Understood first in the first decade of 1900s.

For metal exposed to water and air

Iron + < 11% chromium

Iron + > 11% chromium



Passive means protective

Current definition of a Stainless Steel (ASTM)

An iron-based alloy with a minimum of 10.5% Cr…..

- more iron than any other element.
- previously it needed to have more than 50% iron to be called a stainless steel.
- found in ASTM A or ASME SA specifications, e.g. ASTM A240 or ASME SA240 (for plates, sheet, strip).

Current definition of a Nickel Alloy

An alloy with more nickel than any other element.

Note that there are some nickel alloys have less than 50% Ni

- previously, the definition of a Nickel Alloy was different than today.

Specifically: if the iron content of an alloy was less than 50% and there was more nickel than any other element other than iron, the alloy was called a Nickel Alloy.

- found in ASTM B or ASME SB specifications, e.g. ASTM B575 or ASME SB575.

Naming of Stainless Steels

- **AISI name** – most commonly used, even though AISI no longer is involved with stainless steel.
  ASTM has adopted the AISI names for the most part, calling them e.g. Type 316L.
  It is wrong to say, e.g. AISI 316L. It means nothing. You may get sued by AISI.
- **UNS numbers** – Unified Numbering System
  Run by ASTM and SAE, they give a unique number to all alloys and metals.
  The format is one Letter plus 5 numbers - L#####
  S = stainless N = nickel alloys W = welding alloys

316L is S31603; often for SS but not always, the old AISI name is incorporated in the UNS number.

Naming of Nickel Alloys

Most nickel alloys started out associated with one producer. Their name for that alloy became the name most people used, and has become part of the "common name" for the alloy. That common name often, but not always, forms part of the UNS number.

Trade name	Common Name	UNS Number
Inconel® 600	Alloy 600	N06600
Monel® 400	Alloy 400	N04400
Hastelloy® C-276	Alloy C-276	N10276
Hastelloy® B-2	Alloy B-2	N10665

NEVER specify an alloy by saying just Inconel or Hastelloy ALWAYS give a UNS number followed by the appropriate ASTM or ASME spec

Stainless Steel or Nickel Alloy?

Alloy 800 with 21%Cr, 32%Ni and 45%Fe was called a nickel alloy under the old definition, and was given a UNS number starting with "N". N08800 was in the ASTM B and ASME SB specifications.

Today Alloy 800 is officially called a stainless steel and in the ASTM A and ASME SA specifications.
The UNS number remains the same.
However it cannot be used as a stainless steel in ASME as it is not in the tables of allowable stress tables as a stainless steel. It remains grandfathered into the B & SB specs.

Similarly 904L (N08904), 20Cb-3 (N08020), AL6XN (N08367), etc.

Metallurgical Structures

- Austenitic
- Ferritic
- Duplex (Austenitic-Ferritic)
- Martensitic
- Precipitation Hardening

The metallurgical structures are due to the crystalline structure, that is, the arrangement of the metal atoms.

Alloying Elements Promoting:

Austenite
- Nickel
- Nitrogen
- Carbon
- Manganese

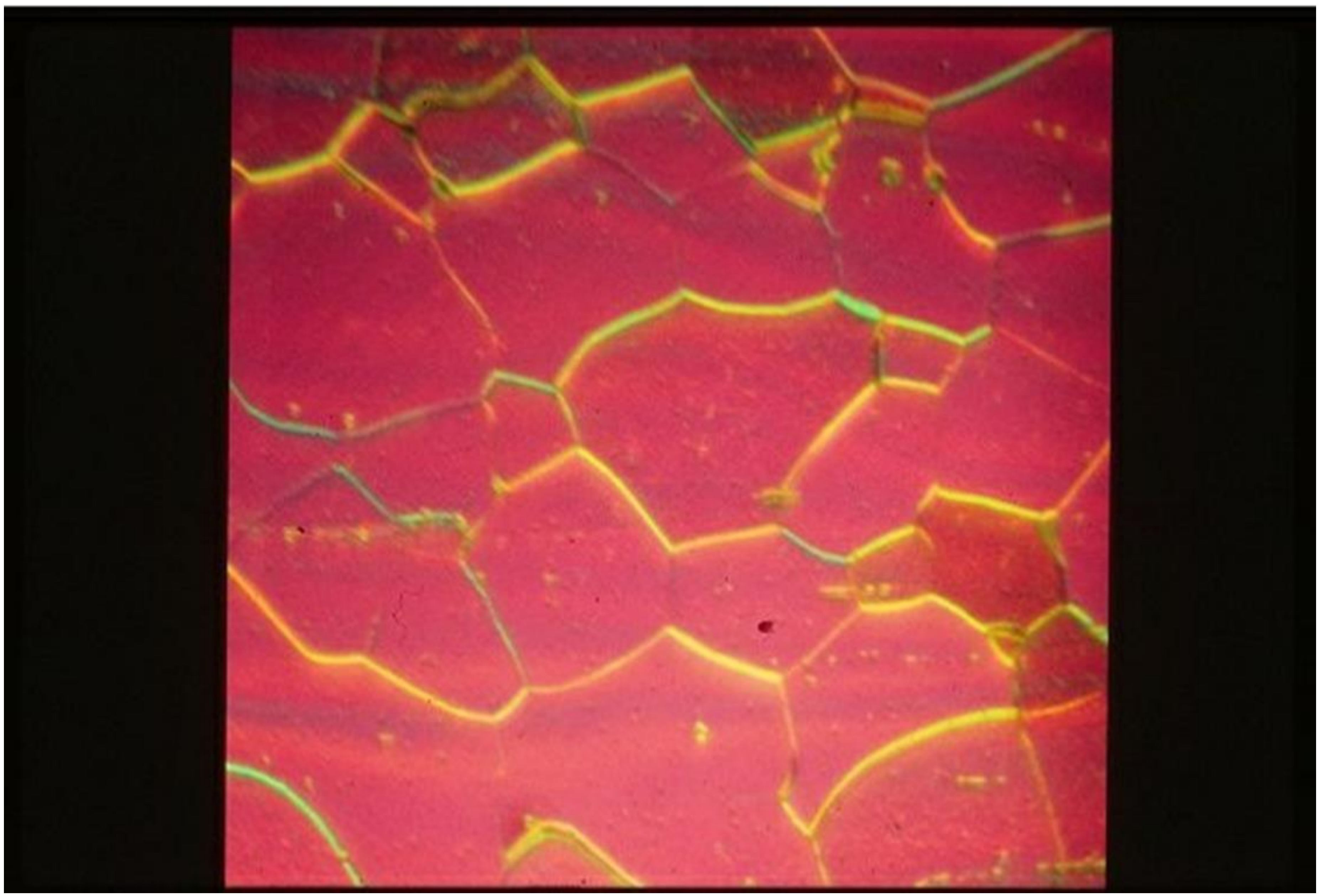
Ferrite
- Chromium
- Molybdenum
- Silicon

There are formulas for calculating what the resulting structure will be based on the composition. The austenite-forming elements are called "nickel equivalent" and the ferrite-forming ones "chromium equivalent".

Some Properties of the Structures

Austenite	Ferrite
High Toughness	Poorer Toughness
High Ductility	Good Ductility
Good Weldability	Limited Weldability
High Formability	Good Formability
May be sensitive to Cl- stress corrosion	Sensitive to hydrogen embrittlement
High Thermal Expansion	Lower Thermal Expansion
Low Thermal Conductivity	Higher Thermal Conductivity
Non-magnetic	Ferro-Magnetic

Ferritic Stainless Steels



Form part of the 400 series of SS.
Generally no or low nickel content.

Ferritic Stainless Steels

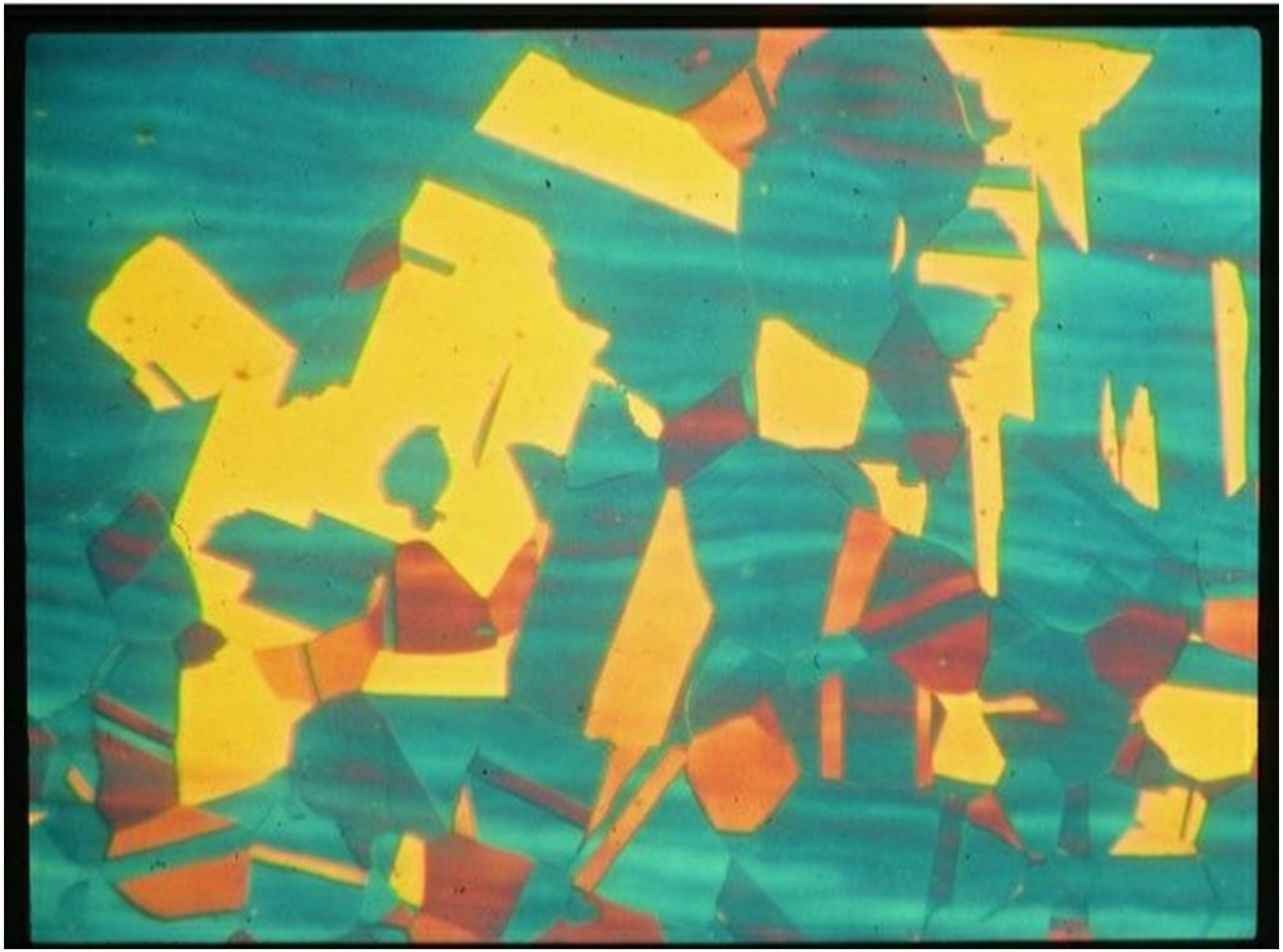
Grade	Cr	Mo	N (max)	C (max)	Other
409	11	-	0.03	0.03	Ti=6x(C+N)
409Ni*	11	-	0.03	0.03	Ni
430	17	-	0.03	0.12	
439	17	-	0.04	0.12	Ti=0.2+4(C+N)
444	18	2.0	0.035	0.025	(Ti+Nb)=0.2+4(C+N)
29-4	29	4.0	0.03	0.045	Ti
446	25	-	0.25	0.20	-

409Ni* - a weldable ferritic-martensitic grade, best known as 3CR12 or Duracorr®

Ferritic Stainless Steels

- **Ferritic SS have little or no content of elements that are austenite promoters, e.g. Ni or N.**
- **409 is barely a stainless steel with the minimum Cr content. Mostly used for certain elevated temperature applications where carbon steel is not sufficient.**
- **There are some high corrosion-resistant ferritic stainless steels, but limited thickness range and poor weldability.**

Austenitic Stainless Steels



Form the 300 and 200 series of SS.

Some 300 series Austenitic Stainless Steels

Grade	Cr	Ni	Mo	N	C (max)	Other
304	19	9	–	0.06	0.08	
304H	19	9	-	0.06	0.04-0.10	
304L	19	9	–	0.06	0.030	
321	18	10	-	0.04	0.08	Ti
347	18	11	-	0.04	0.08	Nb
316L	17	11	2.2	0.06	0.030	
317L	18	12	3.2	0.06	0.030	
904L	20	25	4.5	0.04	0.020	
Alloy 20	20	33	3.0	0.04	0.07	Nb, Cu
6%Mo*	19-20	18-24	6.2	0.20	0.020	(Cu)

*Various grades fit into these families

300 series Austenitic Stainless Steels

Quiz question #1

The specified composition of 304 and 304L in ASTM standards has changed in the last 15 years?

TRUE

or

False

Previously the specified Cr content was 18.0-20.0%, but was reduced to 17.5-19.5% to match European (and ISO) specifications for the major alloying elements.

300 Series Austenitic Stainless Steels

- **304-type materials are the most commonly produced SS grades in the world.**
- **L = low carbon, usually <0.030%**
  H = "high" carbon (usually 0.04-0.10% C)
- **Ancient History / Modern Practice: 321 and 347 were often used for corrosion services when the cost of producing an "L" grade was high, but rarely today. Today, "L" grades are inexpensive. In fact, when making an "H" grade, the carbon is often reduced to a low level, and then added back in.**
- **321/321H and 347/347H are commonly used at high temperatures.**

"H" grades also are required to have a minimum grain size

300 Series Austenitic Stainless Steels

- **Role of carbon content**
  Plus side – increases strength, especially at higher temperatures.
  Negative – may decrease corrosion resistance in the Heat Affected Zone of welds, or if exposed to high temperatures for several minutes, due to the formation of chromium carbides.
- **Generally, always specify/use L grades if the SS is going to be welded and used in corrosive service.**
- **But to take advantage of the higher strength of the non-L grade, specify "dual grade".**

300 Series Austenitic Stainless Steels

What is dual grade? i.e. dual grade 304/304L.

- **It is a stainless steel with the low carbon desired for welding, but the minimum strength level of the non-L grade.**

Values according to ASTM A240 at RT	304L	304	Dual Grade 304/304L
Min. Yield Strength (ksi/MPa)	25/170	30/210	30/210
Min. Tensile Strength (ksi/MPa)	70/485	75/515	75/515
Carbon content - max.	0.030%	0.08%	0.030%

The same is valid for 316/316L

200 Series Austenitic Stainless Steels

200 series alloys are austenitic stainless steels with higher Mn (and usually N) content, to replace some of the Ni required to form the austenitic structure.

- **ASTM 200 types – most have 16.0% min. Cr**
- **Low Cr 200 types – even lower Cr and higher Mn**

Great interest in 200 series alloys because Mn is much less expensive than Ni. The low Cr 200 series are used mostly in consumer goods.

The ASTM 200 types are not commonly used industrially. They are occasionally used in cryogenic applications or where higher demands on wear/abrasion.

200 Series Austenitic Stainless Steels

Grade	Cr	Ni	Mo	N	Mn	Other
201L	17	4.5	–	0.15	6.5	
304L	19	9	–	0.06	1.0	
N50 (Nitronic 50)	22	12.5	2.2	0.30	5.0	Nb, V
J1	15	4.0	-	0.08	7.5	Cu
J4	15.5	1.0	-	0.15	9.2	Cu

Quiz question #2

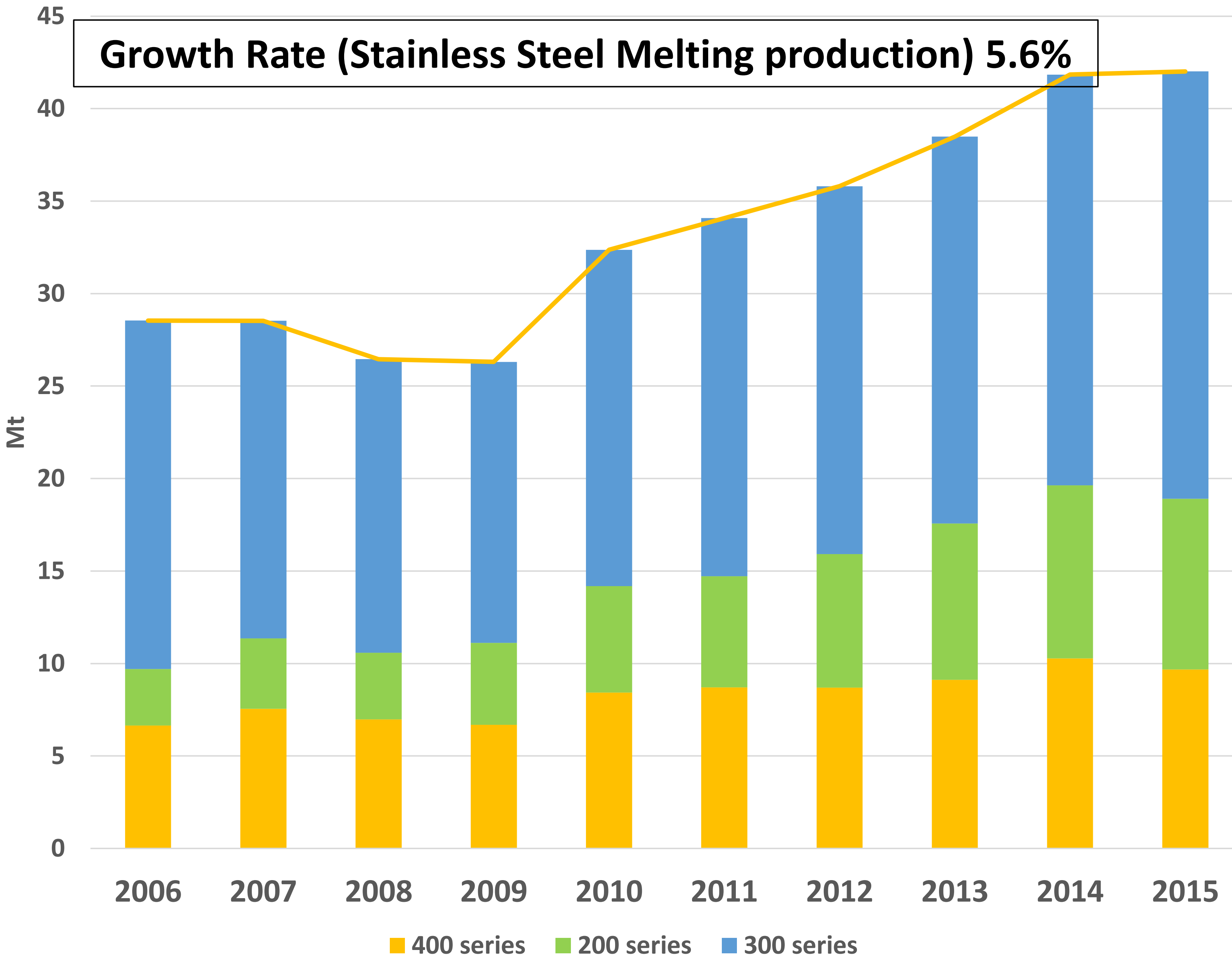
Which family of stainless steel has had the greatest growth rate in the last 10 years?

- ➡ **200 series**
- **300 series**
- **400 series**

The increase is most of the low Cr 200 series alloys, the end market being primarily consumer goods.

An Update on Materials Selection of Nickel-containing Materials for Various Process Industries

Volume and Grade Mix



	2006	2015
300 series	19 Mt 66%	23 Mt 55%
200 series	3 Mt 11%	9 Mt 21%
400 series	7 Mt 23%	10 Mt 24%
Total	29 Mt	42 Mt

Quiz question #3

Which country produces the largest amount of stainless steel?

USA

Japan

→ **China**

Today, China produces over 50% of the stainless steel in the world

Issues with 200 Series Austenitic Stainless Steels

200 series alloys – what does it have to do with me?

Previously, the lowest alloyed non-magnetic stainless steel alloy practically speaking was 304. The ASTM 200 series alloys were not common, and nearly as corrosion resistant as 304.

Today, the low Cr 200 series alloys meet that criteria, but with much lower corrosion resistance and other issues.

Issues with 200 Series Austenitic Stainless Steels

200 series alloys – what does it have to do with me?

Large tank built of supposedly 304 stainless steel. Cracks parallel to welds appeared after hydrotesting. Material test reports were 304, but material was actually a low Cr 200 series alloy.

Issues with 200 Series Austenitic Stainless Steels

200 series alloys – what does it have to do with me?

Plate material supposedly 316LN. The plate had a MTR with that composition. Material was low Cr 200 series.

Even if the material is 304, it should always be PMI tested.

Quiz question #4

304L and 316L produced in the U.S. today is not as good as those grades produced 40 years ago?

Yes

No

→ **It depends**

There are arguments for and against this. But generally, I would conclude in most applications, the quality today is generally better than the quality of 40 years ago.

Quality today vs. 40 years ago of 304L and 316L SS

Arguments for Not as good today:

1) **Today, the nickel and molybdenum contents of these alloys are at the very low end of the specifications, as the steel producers can control the composition much more tightly than previously. In fact, 316L can have as low as 1.95%Mo (the spec is 2.0% min.) Even Cr is closer to the minimum allowed.**

Reply: there was never any guarantee of a higher Cr, Ni or Mo content previously, even if that "average" content was higher.

2) **The annealing heat treatments today are shorter in time, and therefore not as good, all in an effort to save money. ASTM standards give a min. T for annealing, but not time.**
3) **Reply: With the carbon contents of the stainless lower now, one needs less time. With continuous cast slabs, the material needs less time for homogenization.**

Quality today vs. 40 years ago of 304L and 316L SS

Arguments for Not as good today:

3) **The use of scrap metal that all producers partially use as a raw material means impurities such as copper, lead, tin, zinc and who knows what else can build up to high levels, causing problems.**

Reply: much of the impurities are removed in the AOD converter. The impurity levels are being monitored closely in each heat. Copper, which cannot be removed in the AOD, is increasing. However, only a few corrosive environments are sensitive to copper of low levels in an alloy, the most common being hydrogen peroxide.

Quality today vs. 40 years ago of 304L and 316L SS

Arguments for Better today:

1) **With everyone using AOD converters, the carbon contents of "L" grades are much lower than before, often less than 0.020%, so that intergranular corrosion caused by chromium carbides after welding is almost ancient history. Also most producers now desulfurize which means the sulfur content is often lower than 0.001%. AOD refining gives a much cleaner steel with regards to inclusions.**

Reply: Intergranular corrosion after welding was never a problem in most environments with L-grades, even if the C content at the max. of 0.03% or slightly higher. Today the sulfur content is often so low that is causes problems in GTA welding.

Quality today vs. 40 years ago of 304L and 316L SS

Better today:

2) **With automation and better process control, the steel from any one producer is more uniform in nature, similar corrosion resistance and mechanical properties.**

Reply: There is still significant variations in many cases between various steel producers, and even within a steel producer that has various lines for cold rolling.

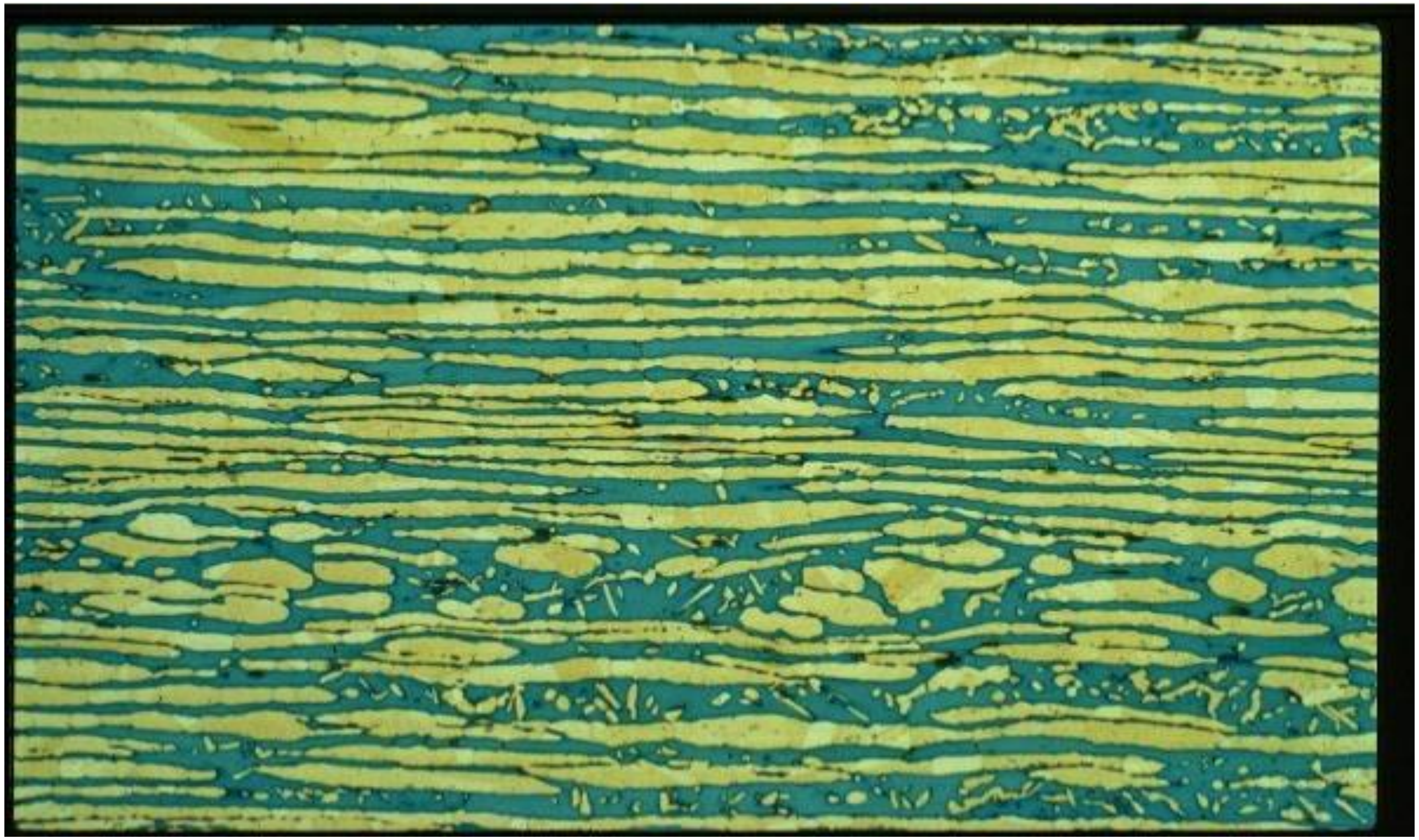
Martensitic Stainless Steels - Properties

- High hardness and high strength, but low ductility.
- Soft in the annealed condition but with heat treatment, quench and temper they become hard, just like a tool steel.
- Corrosion resistance less than 304 SS, often much lower.
- Good for knives, tools.
- Poor formability and poor weldability.
- Part of the ASTM 400 series – 410, 416, 420, 440C
- About 1% of the total SS produced

PH (Precipitation Hardenable) SS - Properties

- Various types - martensitic, semi-austenitic, etc. (quite a complicated family)
- Hardenable, but by a precipitation mechanism. Heat up to a certain temperature for a certain time period, no need to quench.
- High hardness and high strength, and low ductility.
- Slightly better weldability than martensitic alloys.
- Corrosion resistance somewhat close to 304 SS.
- Most common grade is 17-4PH (AISI 630)

Duplex Stainless Steels



The first duplex SS was used around 1930, in the AISI series it was given a 300 series number, 329. Today they are given a common name, e.g. 2205 or 2304.

Duplex = 2 phases = austenite (light) and ferrite (dark) phases, usually in roughly equal amounts

Duplex Stainless Steels

- **Combine some of the advantages of the austenitic family some of with the advantages of the ferritic grades. Also have some of the disadvantages of the austenitic and ferritic grades.**
- **The 2 phase (duplex) structure obtained by having an intermediate % of nickel.**
- **Nitrogen is beneficial for the obtaining optimum properties, so today always an alloying element.**
- **Seen as problem-solving alloys**
- **Semi-ferro-magnetic**

Duplex Stainless Steels – Good Properties

- **High strength** (higher than ferritic or austenitic)
- **Good chloride SCC resistance** (better than austenitics, not as good as ferritics)
- **High corrosion resistance in many environments**
- **Good formability** (not as good as austenitics)
- **Good weldability** (different and not as easy as austenitic alloys)
- **Better erosion-corrosion resistance**

Duplex Stainless Steels – Not So Good Properties

- Lower ductility
- Embrittles in hydrogen
- Embrittles at low temperature
- Embrittles at high temperature (>300^{o}C)
- Learning curve for fabricators/welders
- Sensitivity to detrimental changes in the structure during welding or heat treatment
- May have limited availability

Sub-families of Duplex Stainless Steels

- **5 sub-families – lean, low alloyed, standard, super and hyper**
- **There are many different wrought alloys in most of these families, plus many different cast alloys.**
- **All modern duplex SS contain nitrogen as an intentional addition.**

Quiz question #5

What percentage of all stainless steel produced are duplex alloys?

→ **~ 1%**

~ 3%

~ 5%

For the last 10 years, the % of duplex was 1.1%.
The % of papers written on duplex stainless steels as a % of all stainless papers is much higher.

Quiz question #6

In what form is nitrogen in stainless steels?

- **N_2 (diatomic)**
- → **N (monoatomic)**
- **N^- (ionic form)**

As monoatomic nitrogen, it behaves just like an alloying element such as carbon, i.e. interstitial.

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Sub-families of Duplex Stainless Steels

Family	Example	Cr	Ni	Mo	N	Other
Lean	2101	21.5	1.5	0.3	0.22	Mn
Low alloy	2304	23	4.5	0.1	0.12	
Standard	2205	22.5	5.5	3.2	0.17	
Superduplex	2507	25	7	4.0	0.28	
Hyper	3207 HD	32	7	3.5	0.5	Mn

Some Main Uses of Duplex Stainless Steels

Chemical / Petrochemical / Power / Oil & Gas

- **corrosion under insulation (CUI) in coastal environments**
- **heat exchangers for brackish water**
- **structural components, including in the nuclear industry**
- **certain organic acids, caustic environments**
- **RO (reverse osmosis) plants**

- **~~FGD~~** ✖

Quiz question #7

Duplex 2205 stainless steel was used extensively in FGD scrubbers at coal-fired power plants in the first decade of the 2000. It failed miserably in many installations, causing the power industry millions of dollars in repairs. Why?

The data showing it was suitable was wrong

The material delivered was of poor quality

There were problems with welding on-site

➡ **The FGD process was slightly changed**

To make better use of the gypsum product, forced oxidation (air) processes were developed, which changed the conditions in the scrubbers significantly.

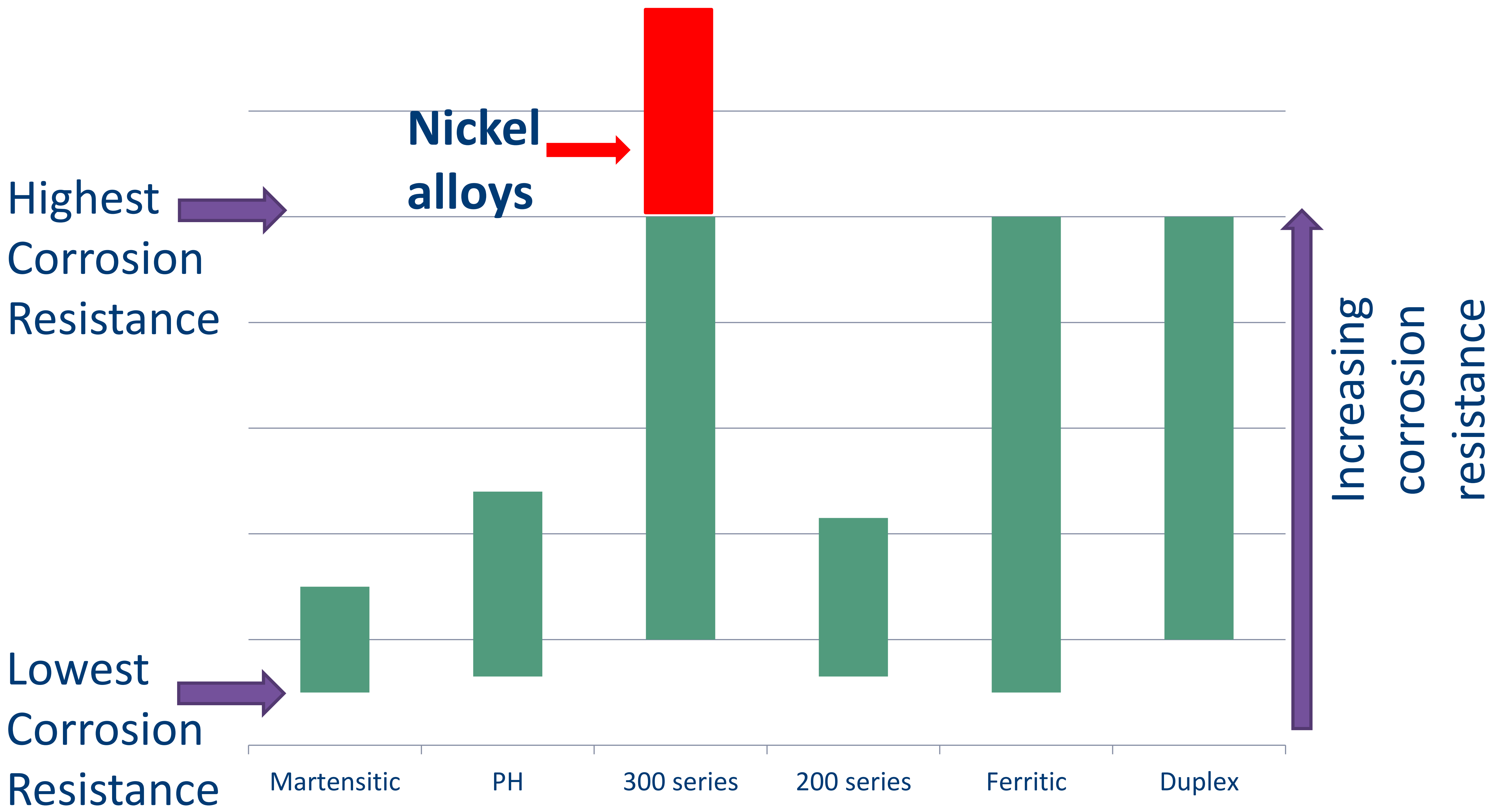
Strength of stainless steels

Examples of minimum strength levels (ASTM A240 except PH)

SS family	Grade	Yield Strength MPa	Tensile Strength MPa	% Elong.
Austenitic	304	205	515	40
Austenitic	6%Mo	310	655	30
Ferritic	430	205	450	22
Duplex	2205	450	655	25
Martensitic	410 - A - H&T400	205 (1000)	415 (1310)	20 (16)
PH	17-4PH –A - H900	(900) 1170	(1100) 1310	(15) 10

A = Annealed; H&T 400 = hardened then tempered at 400°F
H900 – heat treated at 900°F for 1 hour
Values in brackets are typical values

Corrosion resistance of the Families



Standard versus Special Stainless Steels

- By standard, we are talking about the 304L, 316L, 321, 347, 2205, and a few other alloys that are stocked by a number of different distributors.
- By special alloys, we are talking about proprietary alloys, alloys developed for certain limited applications, and alloys that are not common.
- In the UNS book, there are over 350 stainless steel alloys listed. This does not include cast stainless steels nor welding alloys. Nor does it include many foreign alloys.

Standard versus Special Stainless Steels

- **Ancient history: 50 years ago, stainless steel producers had their own brand name for e.g. 316L, and would say that their 316L was better than the competitors 316L. There was some truth to that. With that advent of AOD refining processes, those differences became minimal.**
- **Stainless steel producers developed many of their own proprietary grades, which were different in composition than their competitors. It was an era of innovation. It may take 10 years or more from the time an alloy is introduced into the market before it become commercially profitable (assuming it would be used in large quantities), but SS producers were prepared to take that time. Their reputation as an innovative supplier was important.**

Standard versus Special Stainless Steels

- **Modern Practice: In the last 40 years, the size of a heat of stainless steel has gone from about 25T to between 150-250T or more, at least for plate & sheet producers. The cost of producing small quantities of special SS can be very high – not many companies want to do that. Availability can be poor to non-existent, price can be very high.**
  Note that seamless tube producers have smaller heat sizes.
- **Few Western companies are doing research into new stainless alloys. They are not willing to spend 1-2 million $ in the hope that the product will be successful. Even if the new alloy is patented, other companies will ignore the patent or at worst be forced to pay a small fee to the patentee for every ton sold.**

Standard versus Special Stainless Steels

Examples:

- **310L for nitric acid, 310LMoN for urea – very difficult to find in plate/sheet**
- **6%Mo grades (254 SMO®, AL6XN®) – have established markets of reasonable size, so product availability is still OK.**
- **7%Mo grades (654SMO®, 27-7Mo®, B66®) – fantastic grades, promoted well, but difficult to produce. Needed in relatively small quantities. Came on during the mid 1990s to 2000, did not establish themselves, today uncommon to non-existent.**
- **Some of the duplex grades are being heavily promoted, such as lean duplex 2101, and gaining reasonable acceptance, but getting products in all forms can be a challenge.**

Nickel Alloys

Quiz question #8

The production of nickel alloys is smaller than stainless steels. How much smaller?

- One tenth of SS production.
- One fiftieth of SS production
- ➡ One hundredth of SS production

Quiz question #9

Which country produces the greatest tonnage of nickel alloys?

- ➡ USA
- Japan
- China

•

Nickel Alloys

Estimated Production of Nickel Alloys in 2008 in thousands of tonnes.

Market	Tonnage
Corrosion	102.0
Aerospace	83.0
Electronic	38.5
Total	223.5

Families of Nickel Alloys

Ni-Cr-Fe – e.g. Alloy 800
Ni-Cr – e.g. Alloy 600
Ni-Cr-Fe-Mo – e.g. Alloy 825, "G"-types
Ni-Cr-Mo – e.g. 625, "C"-types

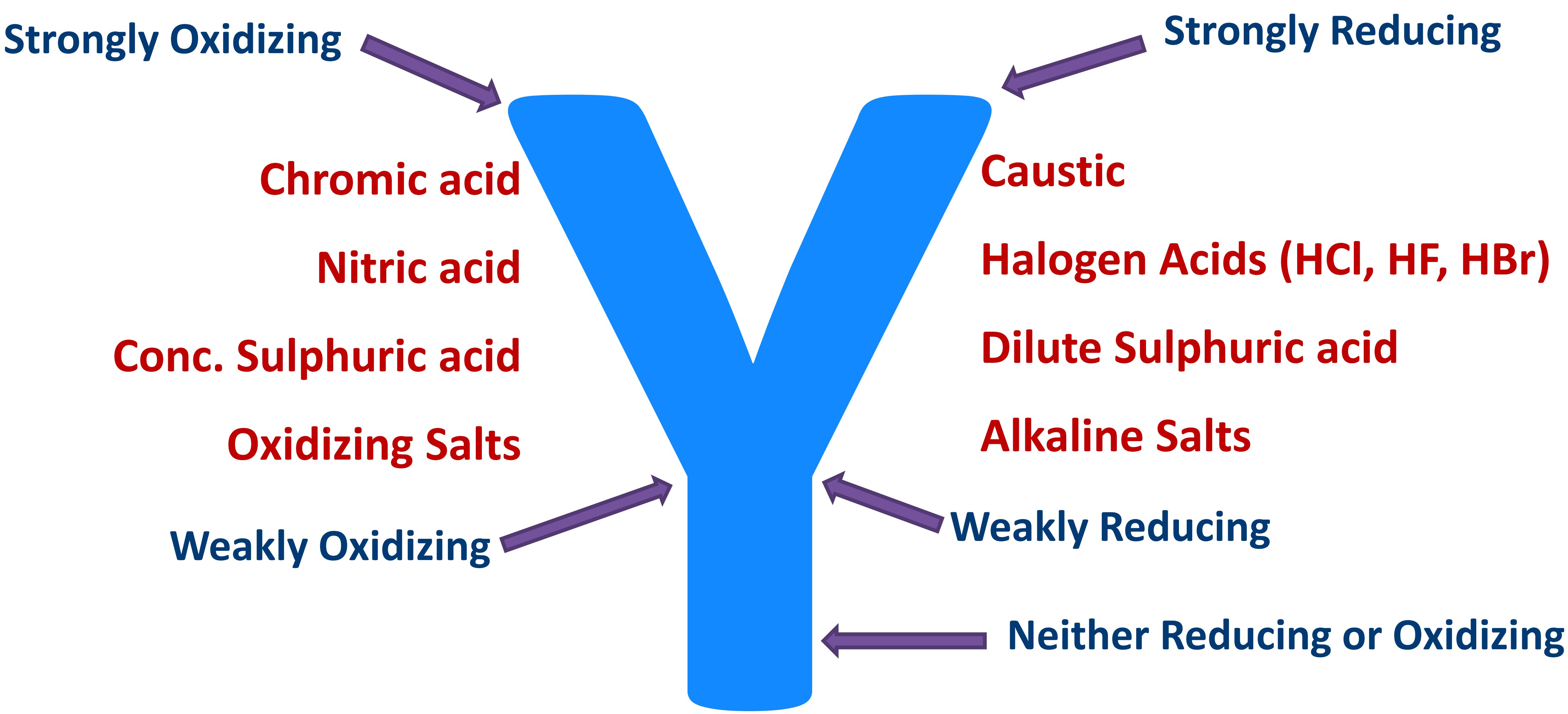
Contain Cr

Ni-Mo – e.g. "B"-types
Ni-Cu – e.g. Alloy 400
Commercially Pure (C.P.) Nickel – e.g. Alloy 200

Do not contain Cr

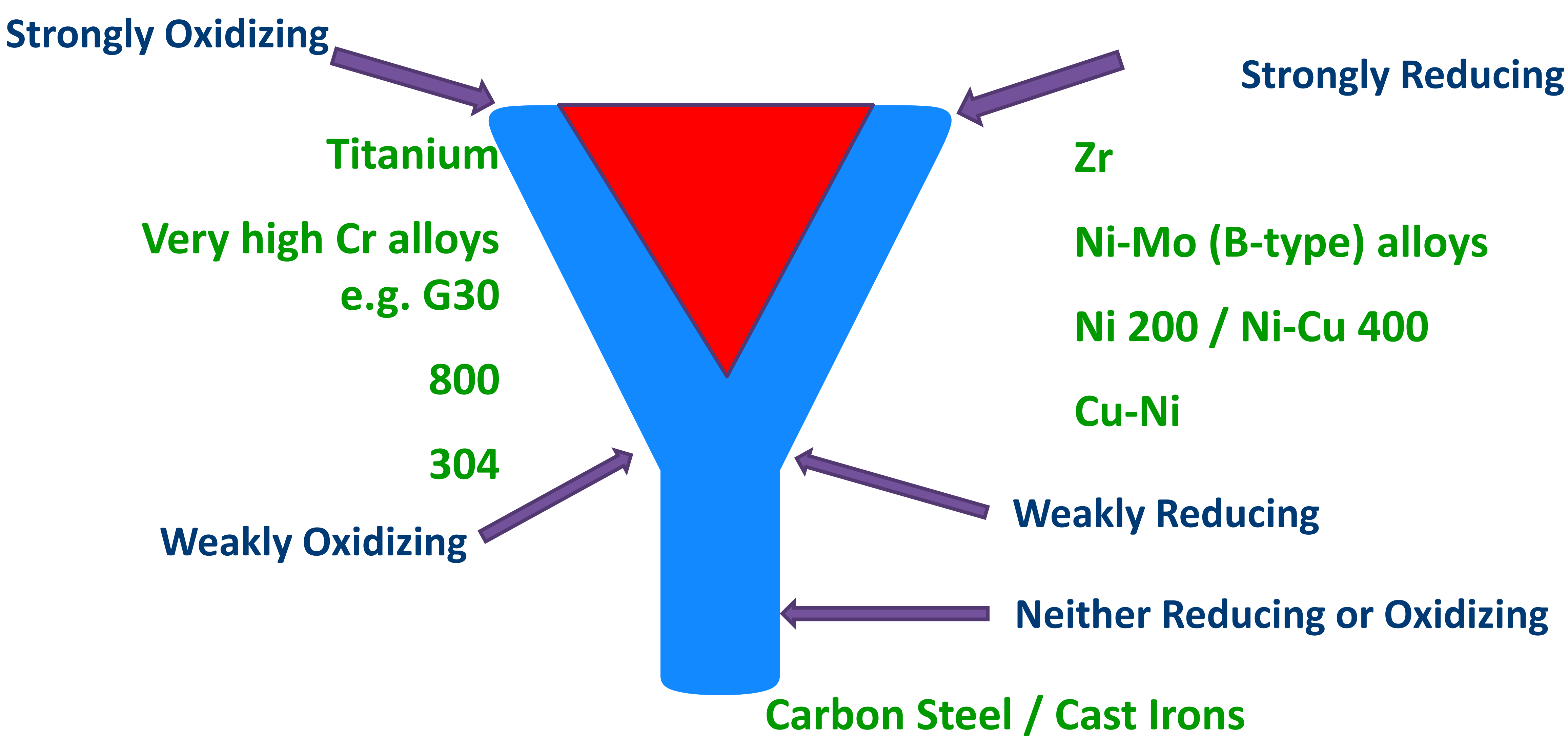
General (Uniform) Corrosion

The "Y" of Corrosion



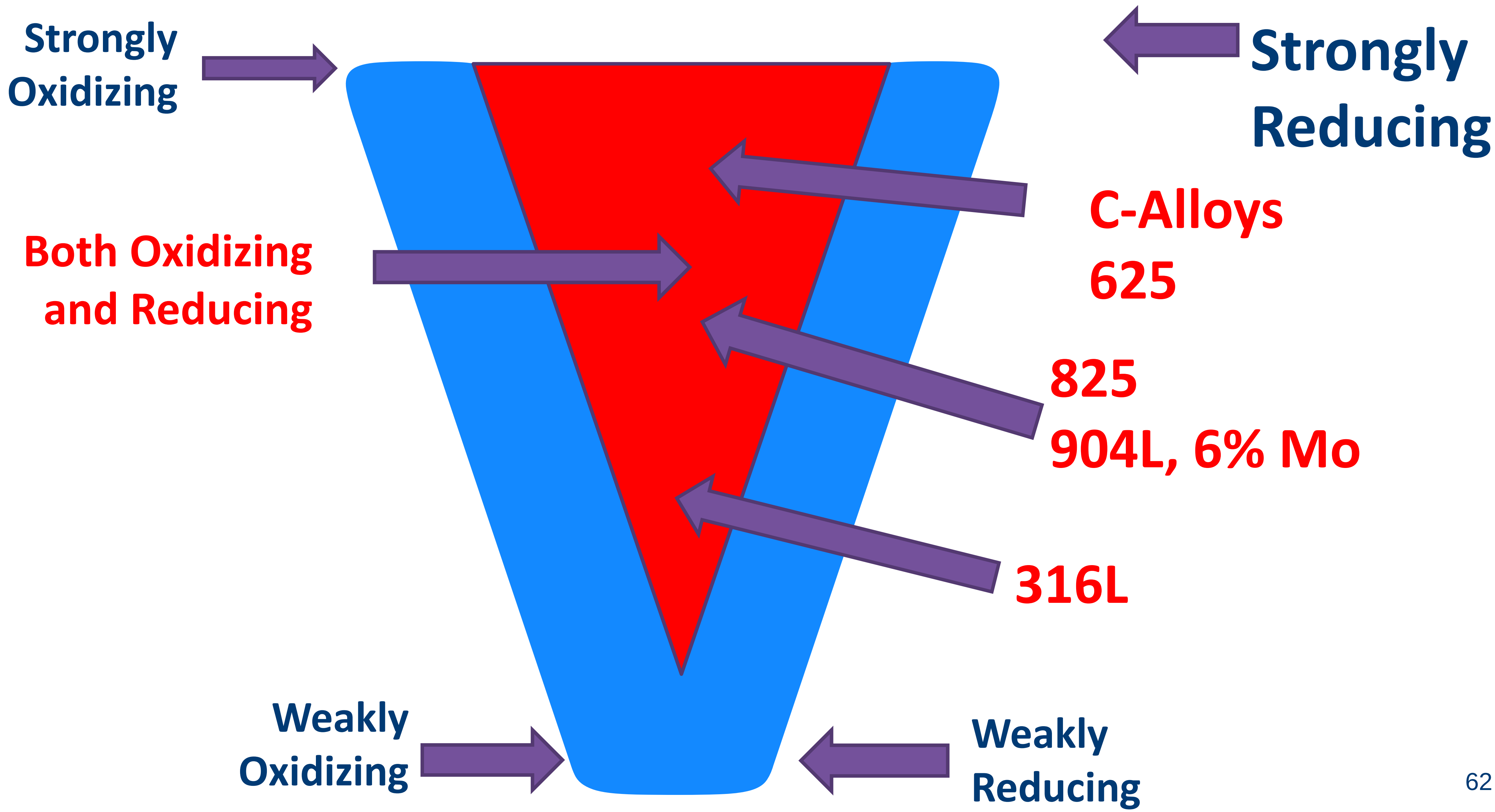
General (Uniform) Corrosion

The "Y" of Corrosion



General (Uniform) Corrosion

The "Y" of Corrosion – the middle ground

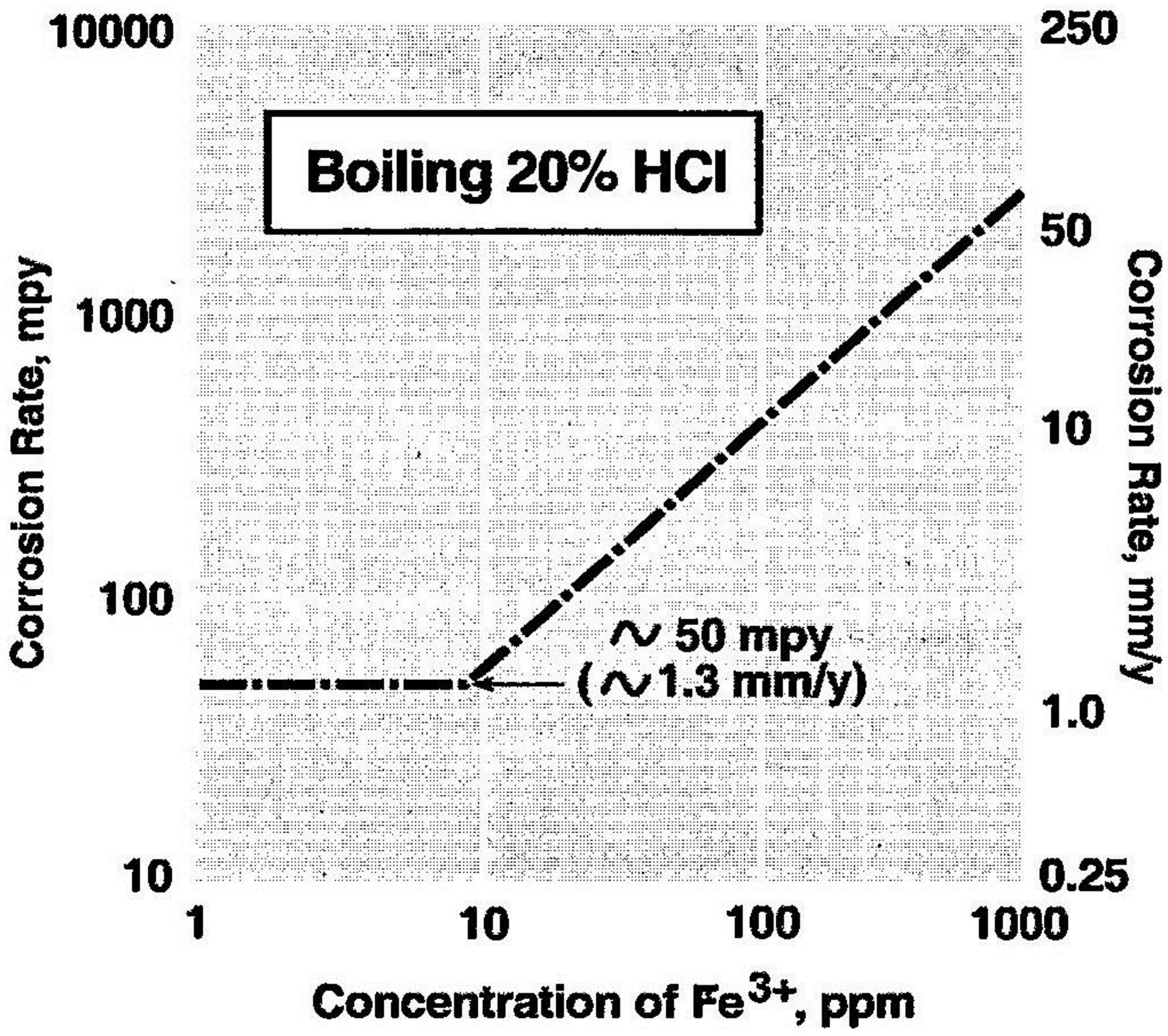


The "Y" of Corrosion

Hydrochloric Acid

Effect of ferric ion concentration on corrosion rate of B-2 in HCl

Hydrochloric acid is strongly reducing.
Even a very small amount of oxidizing ion will cause significant increase in corrosion rate.



Nickel Alloy Development

Example 1. Constantly improving the C-alloy

At first there was C-276 (or in Europe C-4). Then came C-22. Then came Alloy 59. Then came 686. Then came C-2000.

And they are still working on improving them further.

Common name	UNS number	%Cr	%Mo	Comments
C-276	N10276	16	16	Slightly better in reducing env.
C-4	N06455	16	16	European version of C-276
C-22	N06022	22	13	Slightly better in oxidizing env.
686	N06686	21	16	,,
59	N06059	23	16	,,
C-2000	N06200	23	16	,,

Nickel Alloy Development

Example 2.

Goal: to have improved resistance to oxidizing ions in reducing acids, or where conditions are alternatively oxidizing and reducing.

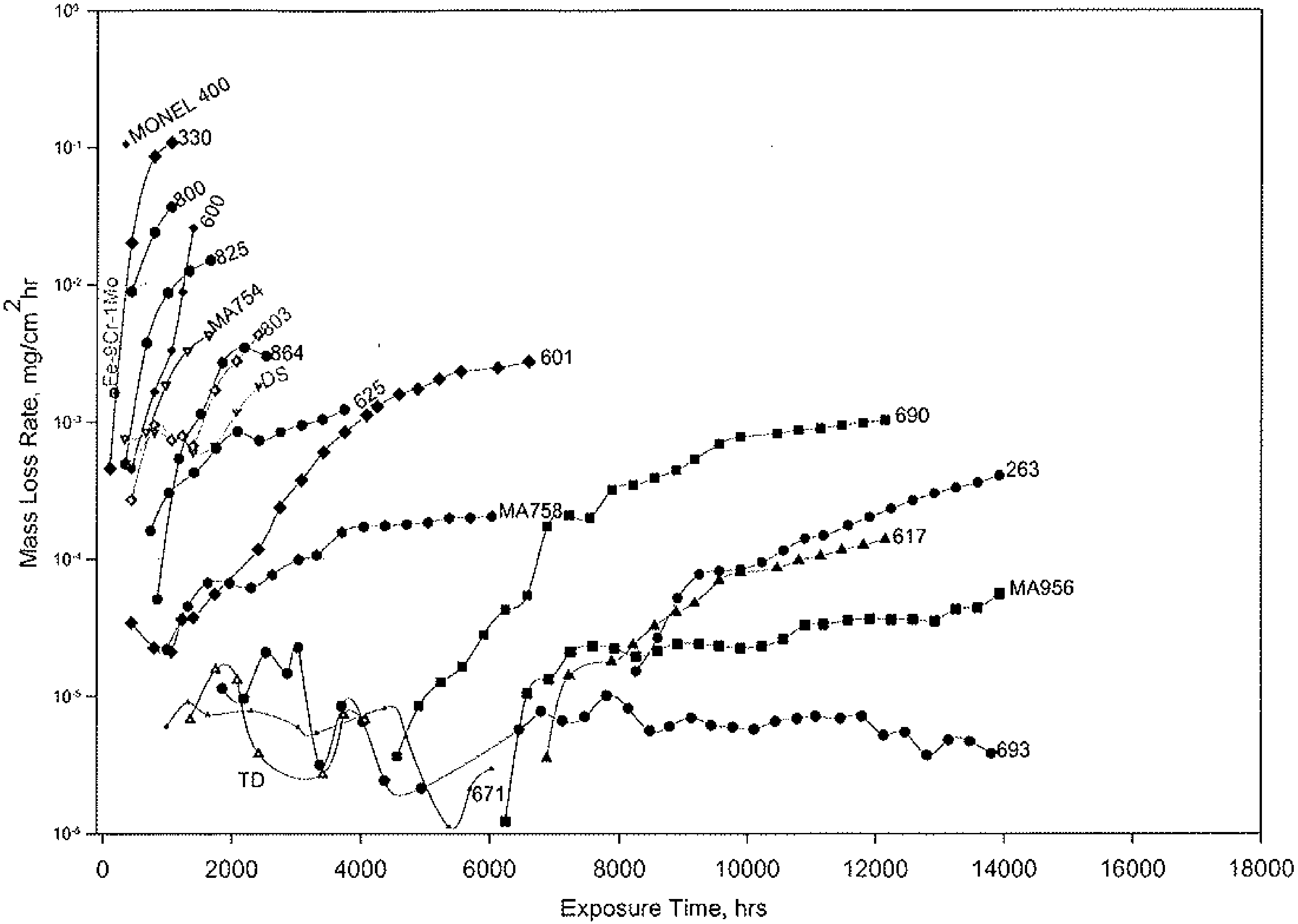
Haynes Hybrid BC-1

Common name	UNS number	%Cr	%Mo	Ni	Comments
B-2	N10665	-	28	Bal.	
C-276	N10276	16	16	Bal.	
BC Alloy	N10362	11	22	Bal.	Hybrid of a “B” and “C” alloy

Nickel Alloy Development – Metal Dusting

Mass loss vs. exposure time for various alloy samples exposed to CO-20% H_2 at 621°C.

Courtesy: Special Metals



Standard versus Special Nickel Alloys

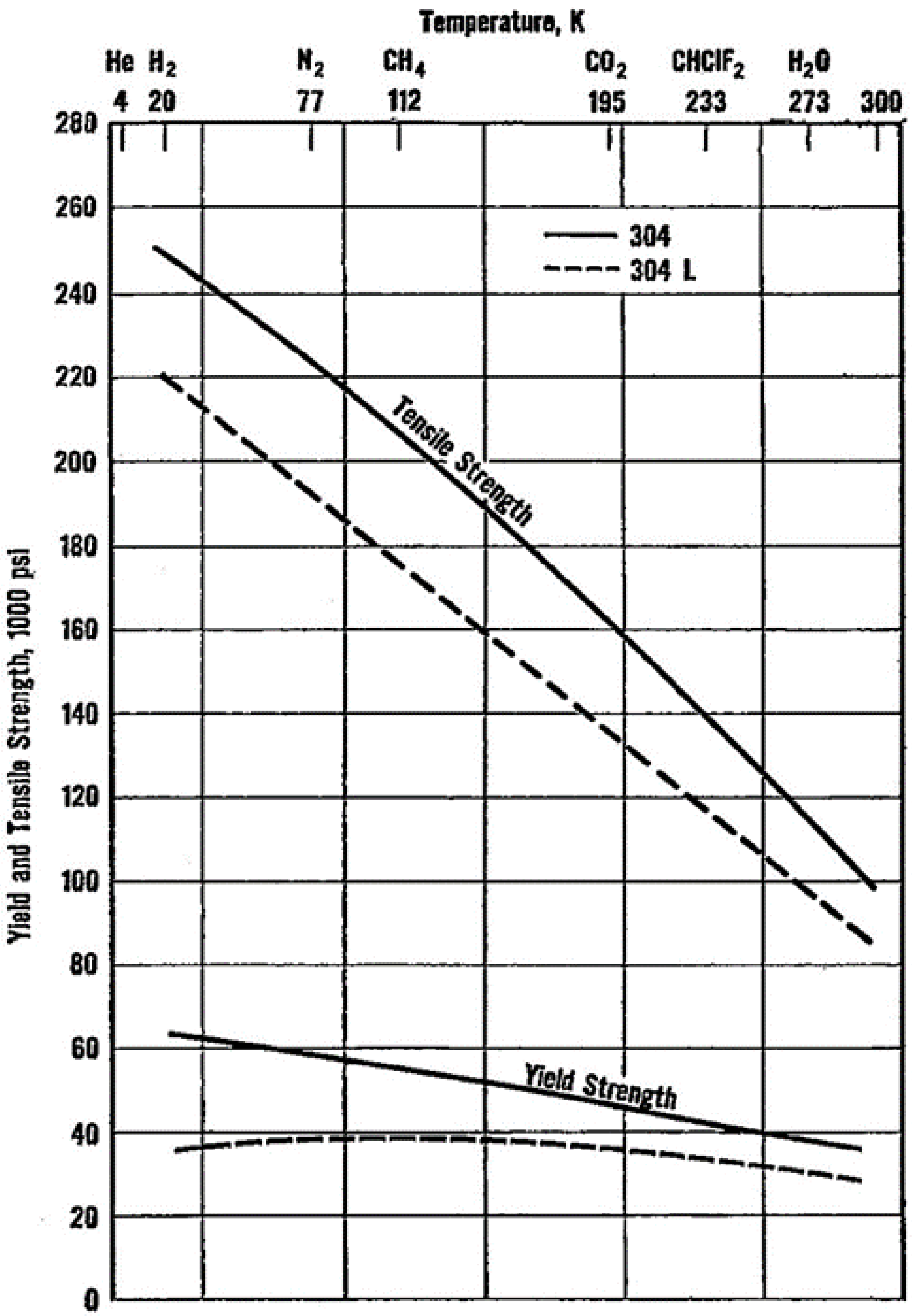
- **Ancient history: In many ways, most nickel alloys are special, not produced in large quantities. Like stainless steels, 50 years ago nickel alloy producers promoted that their version of an alloy was better than their competitors, with some truth to that. Few companies were involved with nickel alloys.**
- **Nickel alloy producers developed many of their own proprietary grades for very specialized applications. At one time, Inco Alloys had many (7?) different versions of CP nickel, each version optimized for a special application.**

Standard versus Special Nickel Alloys

- **Modern practice: Many of the small volume nickel alloys are no longer produced, with mills concentration on the higher volume alloys.**
- **Producers are still developing new alloys, but at a much slower pace than previously. The cost of developing and commercializing a new alloy is very high, taking 10 year (if successful).**
- **More producers are copying other producers alloys, although sometimes with small tweaks to show that they have "developed" an improved alloy.**
- **China is starting to produce nickel alloys. (Drum roll please.)**

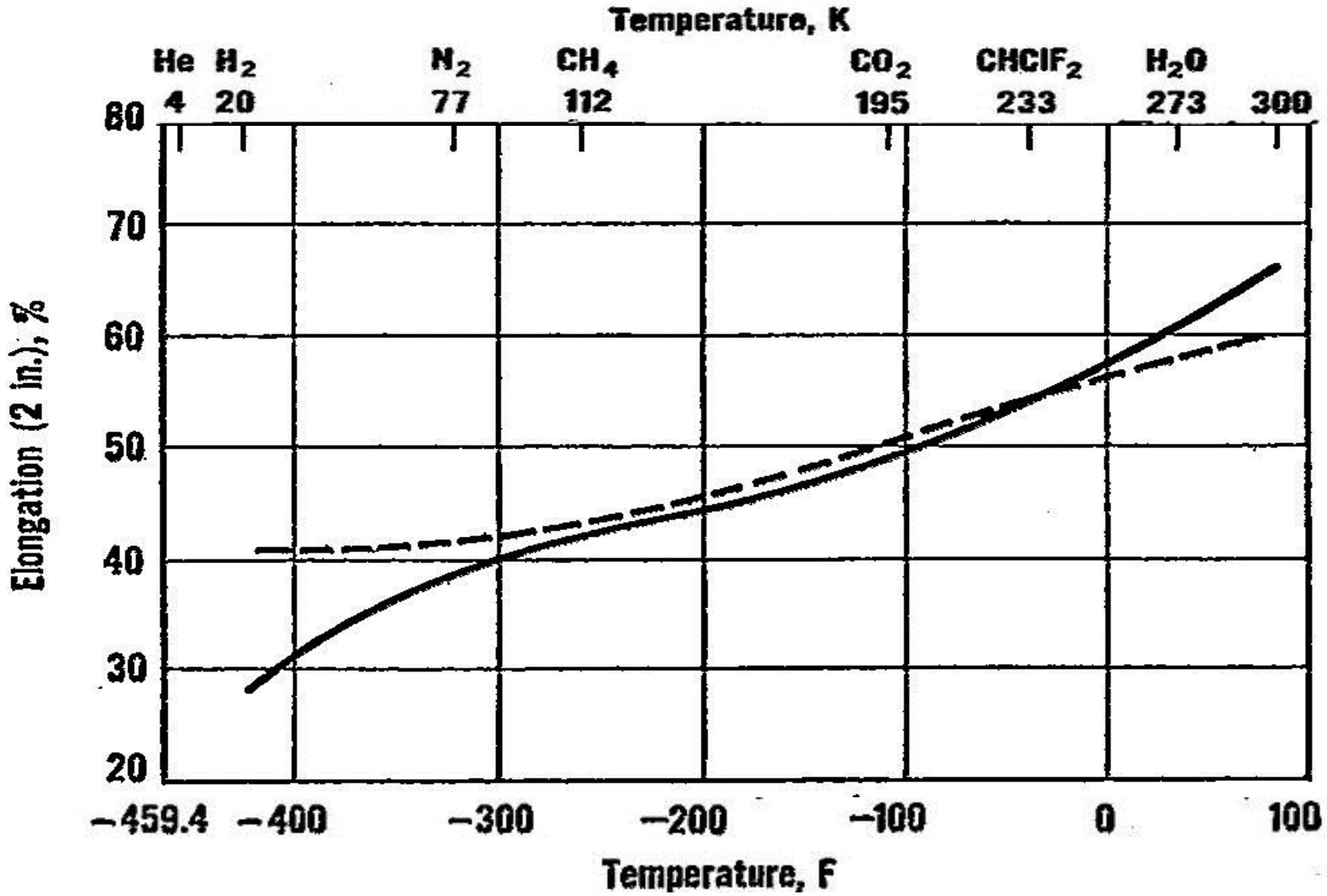
Cryogenic Applications

Yield and tensile strength of 304 and 304L increases with decreasing cryogenic temperatures

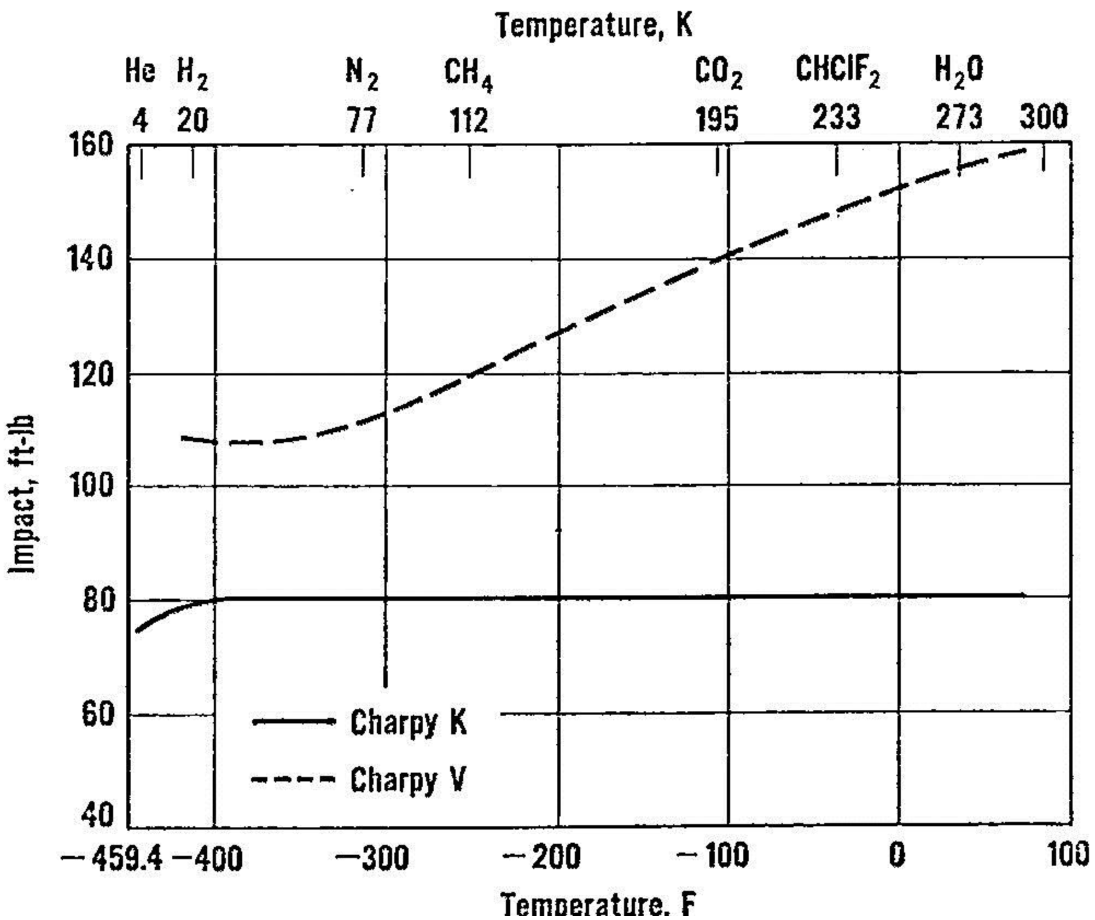


Cryogenic Applications

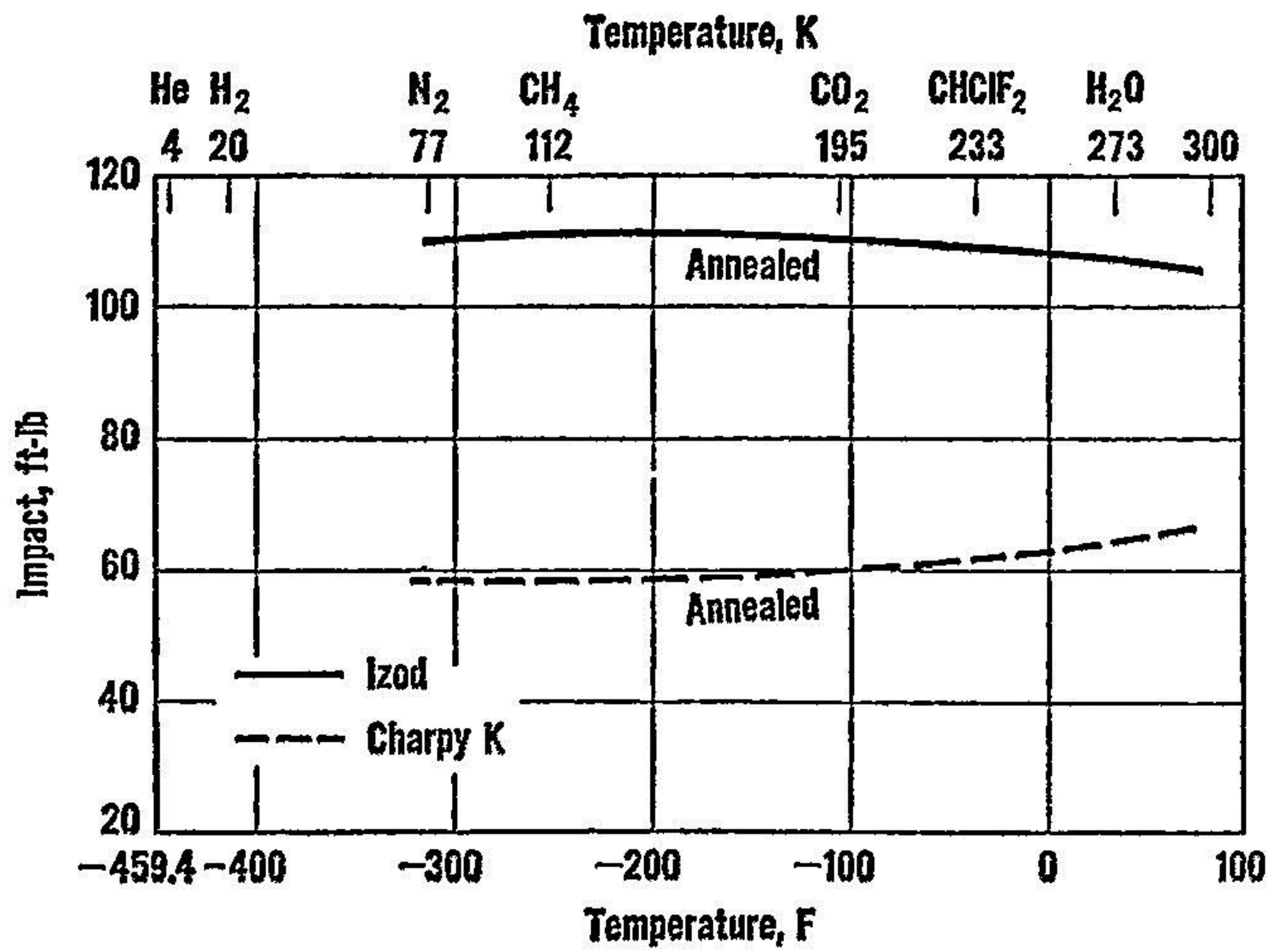
Ductility as measured by % elongation in the tensile test of 304 and 304L at cryogenic temperatures decreases, but still very ductile.



Cryogenic Applications



Impact toughness of 304 at cryogenic temperatures



Impact toughness of 316 at cryogenic temperatures

Cryogenic Applications

ASME Section VIII, Div. 1

- **For most <u>wrought</u> 300 series alloys, impact testing is required only with MDMT is below -196°C.**
- **For all 300 series cast components, the equivalent MDMT is -29°C.**
- **For all welds, whether autogenous or with filler, the equivalent MDMT is -104°C.**

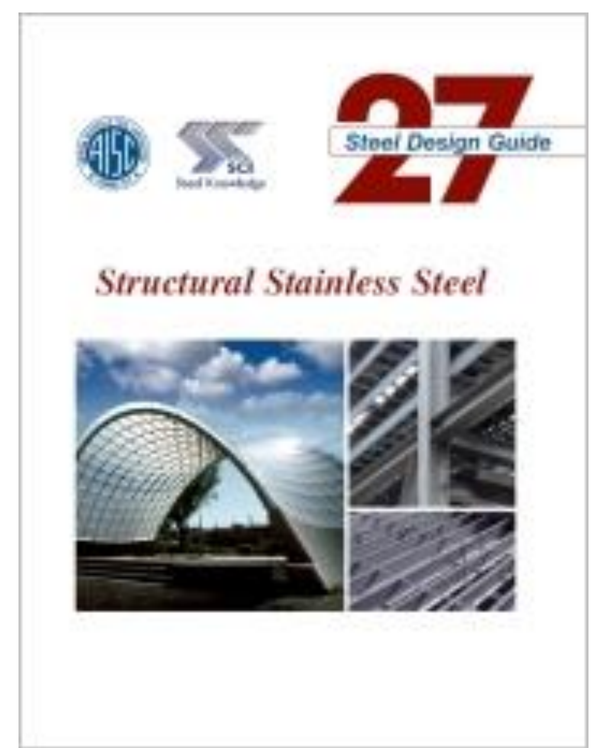
- **Key to good cryogenic quality in castings and welds is:**
  - **low ferrite**
  - **low oxygen content (oxides) – e.g. for welding, use GMAW or GTAW rather than processes that use a flux**

Materials suitable for LNG (~ -162ºC)

- **9% Ni steel**
- **300 & 200 series SS**
- **36%Ni-Fe (Invar)**
- **Aluminium**

Use of Stainless Steels in Structural Applications

- In 2013, AISC issued DG27, Design Guide for the use of stainless steels in structural applications.
- Generally for stainless steel, but specific reference to 304, 304L, 316, 316L, duplex SS – 1 lean, 1 low alloyed, 1 standard – and 17-4PH.
- More work needs to be done on this to create a code, but….
- Used more now in food & pharmaceutical industries, as well as chemical industry, transportation as well as structural applications in building and construction.



Fabrication of Stainless Steels and Nickel Alloys

- **The standard stainless steels such as 304L and 316L are relatively easy to fabricate, and rather "forgiving" of such fabrication practices such as heating to red heat to shape, improper welding practices, etc.**
- **Special SS alloys are less forgiving and may require slightly different procedures, which may not be known to many fabricators. The result may not show up before installation or quickly after installation.**
- **SS and Ni alloy producers are reducing the number of technical staff who can assist with those issues.**

Pharmaceutical

At one time, in the ASME BPE code, 316L was the standard stainless steel material, with no other alloys specifically included.
Today, many other stainless steels and nickel alloys are included, making them easier to specify.
The use of Alloy C-22 has become quite common.
Drug producers worldwide are relying on the BPE code for reliable manufacturing of pharmaceuticals.

Food Industry

An existing market for stainless steels, but many different voluntary standards.

The Food Safety Modernization Act (FSMA) is putting more demands on the whole food chain, especially on documenting that food products are actually safe through proper hygiene.

Big international companies take existing standards and adopt for their own use.

As the food industry is very international in scope, there is a need for an international standard that all food can be produced to.

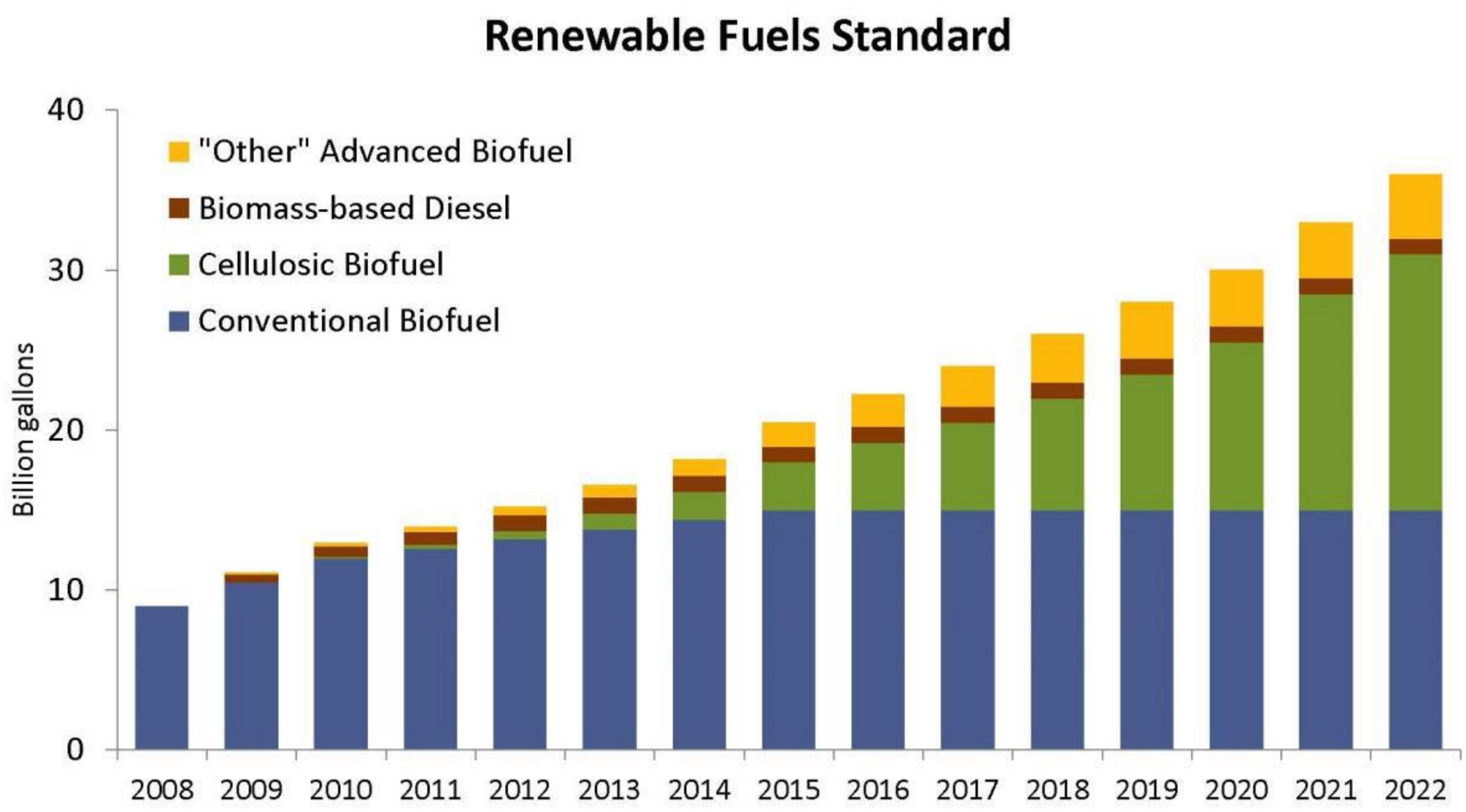
Biofuels

- The U.S. DOD is the largest fossil fuel user in the world, with the Navy/Marine Corps responsible for ~1/3 of total. The latter has a commitment for half of all fuel used on-land or at-sea be from renewable sources by 2020. They have already met that requirement for on-land fuel consumption, expect to meet it in the next few years for at-sea.
- In the U.S., 211 ethanol-from-corn plants currently in production (Apr. 2015), representing about 280,000 MT of SS (mostly 304L), or about 24,000 MT of nickel.
- In the U.S., 15 large scale cellulosic ethanol (CE) plants started up last year or this year. CE plants are both more SS-intensive and require higher Ni-containing SS alloys, including nickel alloys.

Biofuels

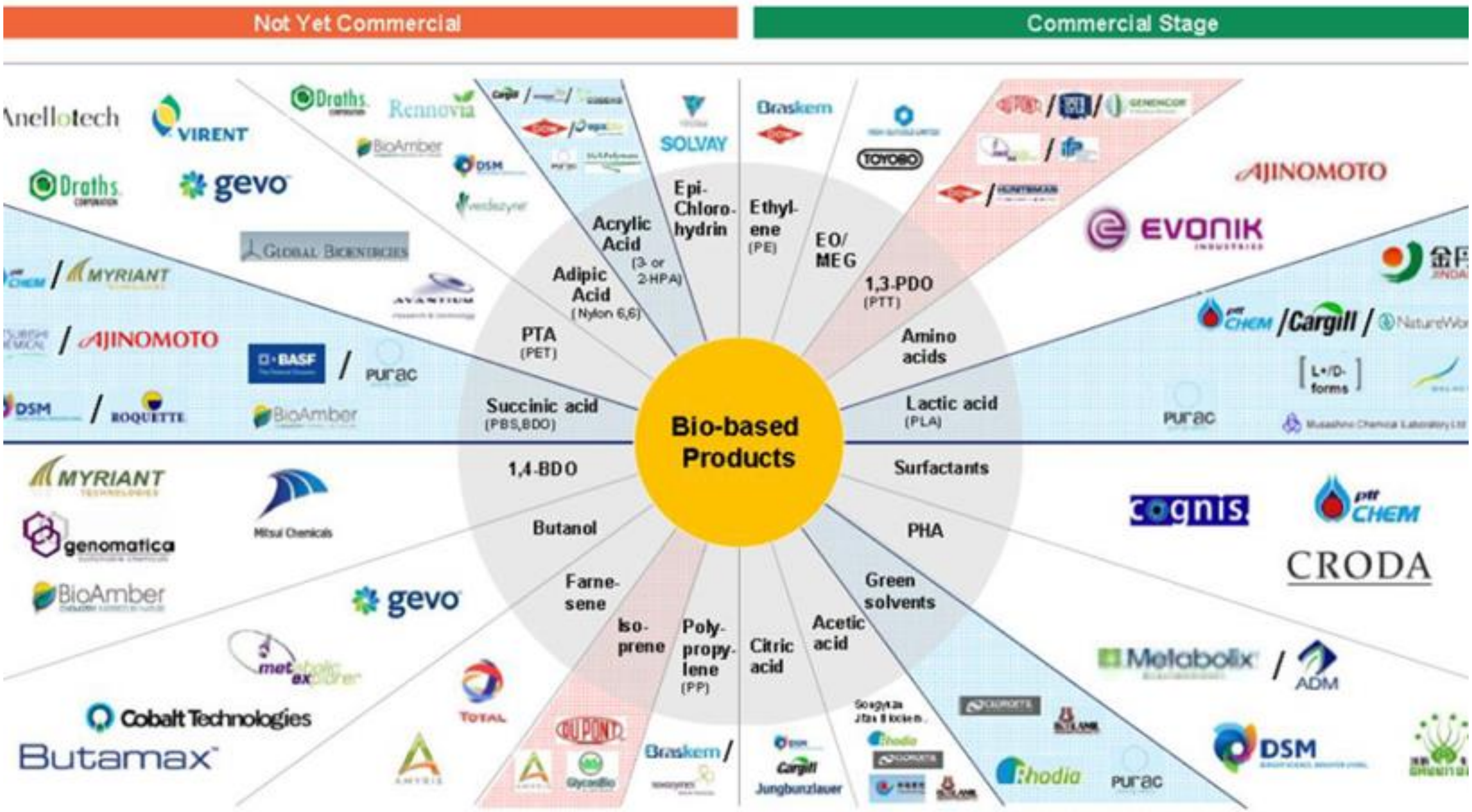
Ethanol from corn – mostly 304L and 316L equipment

Cellulosic Ethanol – pre-digestion section needs nickel alloys or high alloyed SS.



Source: EISA 2007 (RFS2)

Bio-chemicals



Bio-chemicals

- more than 25 **renewable chemicals bio-refineries** in the U.S., using biomass feedstocks: wheat straw, corn stover, bagasse, energy crops, wood waste products, landfill waste, used cooking oils, etc., have opened or are under construction in 2015.
- several bio-refineries in Brazil, Europe, China etc.
- these plants require modification in design and materials over fossil-fuel based plants, due to differences in the bio-feedstocks, leading to a challenging materials selection process, i.e. information gaps, needed to be filled to make equipment & processes cost-effective.
- suppliers report no change in demand for equipment / processes despite low oil prices. There may be a change in end use, from e.g. ethanol as fuel to ethanol as a feedstock for other high value chemicals.

Newer Applications – Water Distribution

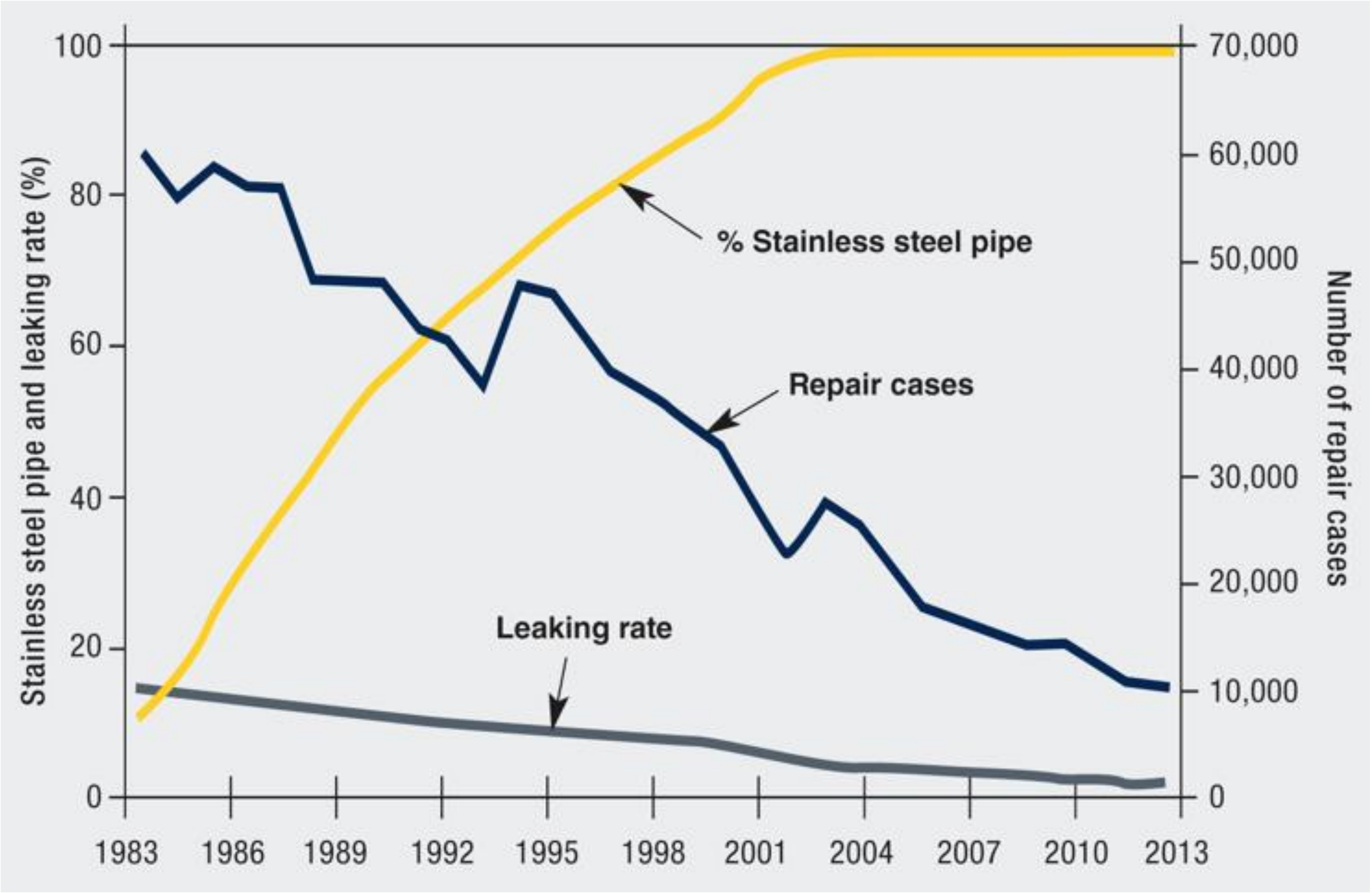
- buried pipes between water mains and building, small leaks but can account for 90% or more of water loss.
- earth movements (both from seismic and other) can lead to leaks at joints
- lead pipes need replacement for health reasons

Lead line in Tokyo showing leak

Corrugated stainless steel solution

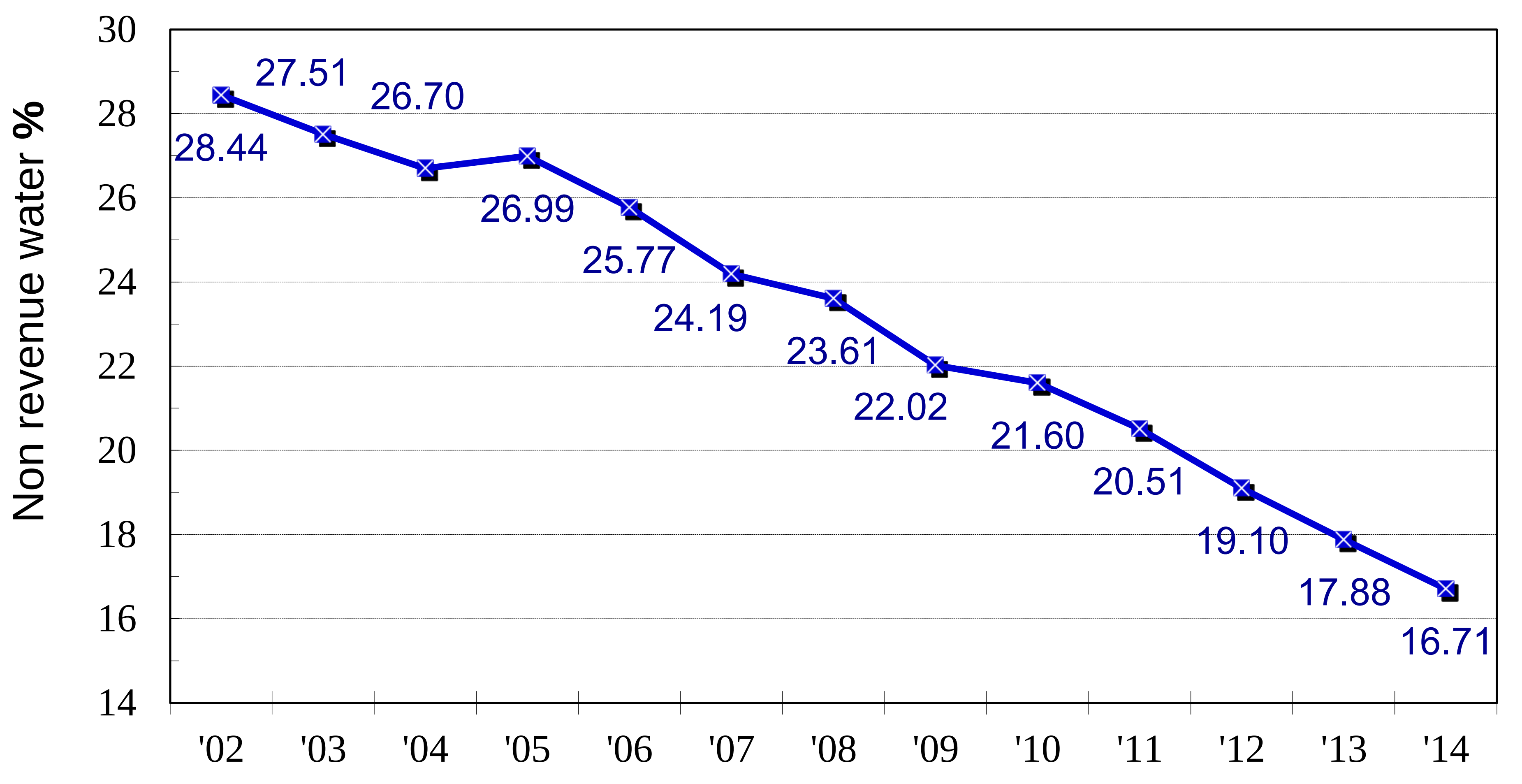
Newer Applications – Water Distribution

Tokyo: a reduction from 15.4% non-revenue water (1983) to 2.2% (2013). Saved building a new dam. Major reduction in costs.



Newer Applications – Water Distribution

Taipei: Started their programme in 2003 following a drought in 2002 where water tankers had to be brought in to supply residents. Reduced leakage rate from 27% to 17%, after 35% implementation of stainless steel service pipe. A worse drought occurred in 2014, but no water rationing needed.



Newer Applications – Rebar for Bridges, etc.

Newer Applications – Rebar for Bridges, etc.

Epoxy-coated rebar in bridge decks in northern states and in Canada last only ~20 years before spalling of concrete. Stainless steel rebar can be easily guaranteed for 75 years, and even 125 years.

The cost of SS rebar is perhaps 3X the cost of epoxy-coated, but cost on a project is usually only 1-3%.

First use of SS rebar in the U.S. was near Detroit in 1984. Later it was used in NJ, NY, OR, VA, MD, RI, IL and many others. Commonly used in Ontario, Alberta and a few other provinces.

Grades used include: 2304, 2205, 316LN, and some lower alloyed grades (304, XM-28, 2101).

Newer Applications – Rebar for Bridges, etc.

Champlain Bridge in Montreal Quebec will use about 18,000T of 2304 rebar, planned to last 125 years.

Future Applications – Advanced Ultra Supercritical Steam

Increased efficiency in power generation by increasing steam temperatures to 700°C or higher on coal-fired power plants.
Requires new materials to replace the Cr-Mo steels in tubes, e.g. with a high strength austenitic grade.
Alloys being examined include a modified 304H with Cu, N, Nb, and B.
Nickel alloys are needed for the turbines, also grades with higher strength than existing nickel alloys.
E.g. Alloy 617B, Alloy C-263.

Experimental operating stations in Japan and China, as well as Europe.

Technology can also be applied to Nuclear Power Plants.

Grosskraftwerk Mannheim

Energy Production

Stainless steels and nickel alloys also needed for alternative energy production.

- long lasting nuclear power plants

- carbon sequestration

- concentrating solar power

- geothermal

- fusion

Nickel Alloys

Quiz question #10

What did I learn this evening?

Sell my shares in SS & nickel alloy producers?

Maybe I will specify plastics next time?

→ **Stainless steels and nickel alloys have a great future.**

Nickel INSTITUTE

Information on materials for various industries can be found in the *Nickel Use in Society* on our website at:

http://www.nickelinstitute.org

If later you have any questions about nickel-containing materials, go to:

https://inquiries.nickelinstitute.org/

QUESTIONS?