HOW NICKEL IMPROVES FERRITIC & MARTENSITIC STAINLESS STEELS

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PRESENTATION OUTLINE

1. What nickel does for Ferritic SS
2. What nickel does for Martensitic SS
3. What nickel does for Precipitation Hardenable (PH) SS

While nickel has an important role to play in these families, most of the grades discussed are specialty alloys with niche applications rather than high volume alloys.

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NICKEL IN FERRITIC SS

1. Some Nickel-containing Ferritic SS
2. Effect on Mechanical Properties
3. Effect on Corrosion Resistance

Ferritic stainless steels are a family of non-hardenable stainless alloys which have a corrosion resistance from low (will corrode slightly even in pure water) to very high (as good as the 6%Mo austenitic SS grades)

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NICKEL IN FERRITIC SS

Some nickel-containing ferritic SS

UNS / EN	Common Name	Cr	Ni	Mo	Other
S44660	Sea-cure	25.0-28.0	1.0-3.5	3.0-4.0	Nb, Ti
S44800	29-4-2	28.0-30.0	2.0-2.5	3.5-4.2	
S44635	Monit	24.5-26.0	3.5-4.5	3.5-4.5	Nb, Ti
1.4575	2803Mo	26.0-30.0	1.8-2.5	3.0-4.5	Nb
S40975	409Ni	10.5-11.75	0.5-1.0	-	
S41003	3CR12	10.5-12.5	1.5 max.	-	

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In all of these alloys, nickel is added intentionally to give specific properties to the alloy

NICKEL IN FERRITIC SS

Effect on Mechanical Properties

- Major beneficial effect of nickel is to increase the toughness of ferritic SS
- Ferritic stainless steels have a very distinct ductile-to-brittle transition temperature (DBTT)
- The DBTT is affected by many factors
  - interstitial content, mostly C & N
  - heat treatment
  - grain size
  - nickel content

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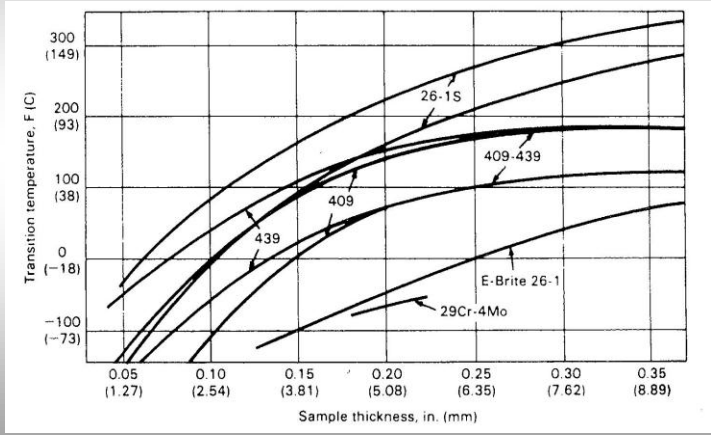
NICKEL IN FERRITIC SS

Ferritic SS - Toughness

DBTT for various ferritic SS grades by thickness



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NICKEL IN FERRITIC SS

Ferritic SS - Toughness

- 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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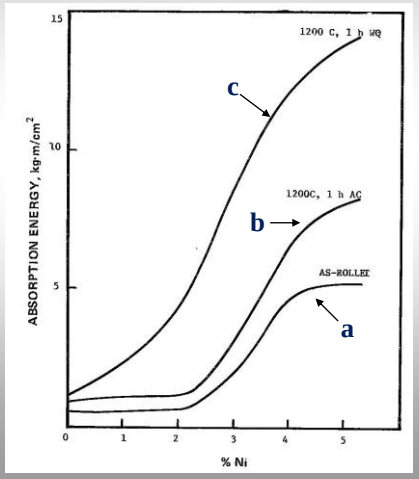
NICKEL IN FERRITIC SS

Effect of Nickel on Toughness

Effect of % of nickel on the toughness of a 25Cr-3Mo-0.7Nb ferritic SS at 25°C
a) as-rolled
b) annealed 1200°C / air quench
c) annealed 1200°C / water quenched



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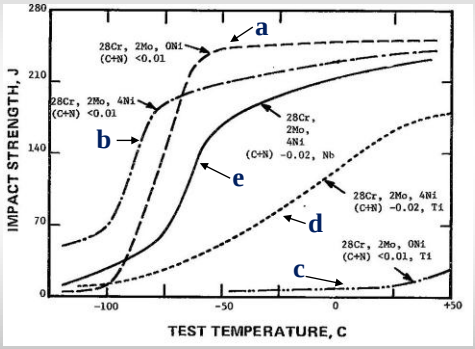
NICKEL IN FERRITIC SS

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 SS

Effect on Mechanical Properties

- **The presence of interstitials reduces toughness**
- **The presence of stabilizing elements (Nb or Ti), especially Ti, reduces toughness**
- **Nickel increases toughness in all cases**

Heat exchanger tubes in UNS S44660 for a seawater condenser. Courtesy Plymouth Tube

NICKEL IN FERRITIC SS

Effect on Mechanical Properties

409Ni (S40975) with 0.5-1.0% Ni

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°C)

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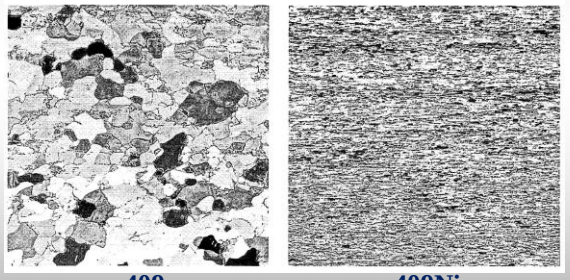
NICKEL IN FERRITIC SS

Effect on Mechanical Properties

409Ni (S40975) with 0.5-1.0% Ni



409
coarse grain

409Ni
fine grain

24X magnification of grain structure for hot rolled and annealed 7.9 mm thick plate of 409 and 409Ni

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NICKEL IN FERRITIC SS

Effect on Mechanical Properties

S41003 with max. 1.5% Ni

Similar role for nickel in other weldable 12%Cr ferritic alloys such as S41003, which also form some martensite.

Railway Car for Coal built in S41003. Note some minor discolouration on the outside. Courtesy SASSDA.

NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

- **Chloride Stress Corrosion Cracking Resistance**
- **General Corrosion Resistance**
- **Pitting / Crevice Corrosion Resistance**

NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

Chloride Stress Corrosion Cracking (SCC)

- **In boiling $MgCl_2$, even a small amount of nickel (0.25%) can have a major detrimental effect on chloride SCC**
- **In other boiling chloride solutions (NaCl or $CaCl_2$), there is no major effect of up to 4 or 5% Ni; may have a detrimental effect in extreme conditions, i.e. if very highly stressed or heavily cold worked (~75%)**

SCC behaviour of an alloy in a boiling magnesium chloride test doesn't correlate well with chemical industry experience in other chloride environments

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NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

Stress Corrosion Cracking Tests on a 28%Cr-2%Mo stainless steel

%Ni	Time to Failure (h) 42% $MgCl_2$ @ 144°C	Time to Failure (h) 60%$CaCl_2$ + 0.1% $HgCl_2$ @ 100°C
0	>600	>1430
2	50	>1430
4	45	>1430

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NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

Chloride Stress Corrosion Cracking (SCC)

- Even in seawater, which contains some $MgCl_2$, the nickel-containing superferritic grades have shown excellent chloride SCC properties in practice

NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

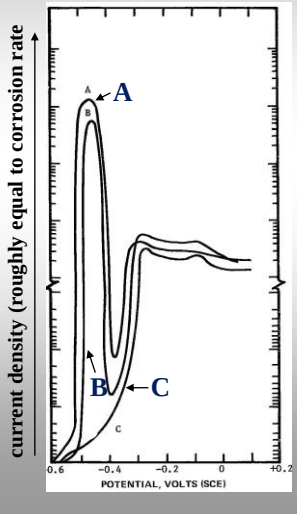
General Corrosion Resistance

- While the higher chromium ferritic grades can show excellent resistance in oxidizing acids, they can show poor resistance in reducing acids such as dilute sulphuric and hydrochloric acids
- Nickel lowers the active corrosion rate in reducing solutions

NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

Polarization curve for a 25Cr-3.5Mo ferritic SS in 5% H_2SO_4 solution at 30°C
A) 0% Ni
B) 1% Ni
C) 3.5% Ni
The C) alloy has no active corrosion peak



Example: In boiling 10% H_2SO_4, a 29Cr-4Mo had a corrosion rate of > 1000 mm/yr. The same alloy with 2% Ni had a corrosion rate of 0.2 mm/yr.

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NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

<u>Pitting / Crevice Corrosion Resistance</u>

- **Nickel seems to have no major effect on the resistance to <u>initiation</u> to pitting or crevice corrosion (some tests show a small benefit, some tests show a small detrimental effect)**
- **Nickel seems to have a significant effect on the lowering the <u>propagation</u> rate of pitting and crevice corrosion, which is similar to active corrosion in a reducing environment**

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NICKEL IN FERRITIC SS

Effect of Nickel on Corrosion Resistance

Summary

- In most practical chloride SCC environments, a small nickel addition may have a negative effect in only extreme conditions (high stress or cold work), or in $MgCl_2$
- Nickel gives increased corrosion resistance in reducing environments, including the propagation of pits and crevices

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NICKEL IN MARTENSITIC SS

1. Some Nickel-containing Martensitic SS
2. Effect on Mechanical Properties and Corrosion Resistance

Martensitic stainless steels are hardenable by heat treatment, in some cases up to Rockwell C 60 or BHN 650. They have very high strength, but relatively low ductility and toughness. Generally they have lower corrosion resistance than 304, but are useful as dental and surgical tools, knives, fasteners, etc.

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NICKEL IN MARTENSITIC SS

Some nickel-containing martensitic SS

UNS / EN	Common Name	C max.	Cr	Ni	Other
S41400	414	0.15	11.5-13.5	1.25-2.5	
S41500	410NiMo	0.05	11.5-14.0	3.5-5.5	Mo
S42200	422	0.20-0.25	11.5-13.5	0.5-1.0	Mo, V, W
S43100	431	0.20	15.0-17.0	1.25-2.5	
S41425	AF913	0.050	12.0-15.0	4.5-6.5	Mo, N
S41426	SM	0.03	11.5-13.5	4.5-6.0	Mo, Ti, V
1.4418	16-5-1	0.06	15.0-17.0	4.0-6.0	Mo, N

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NICKEL IN MARTENSITIC SS

3 Stage Heat Treatment

1. **Forming and machining are normally done in the annealed condition, where the metal is soft**
2. **Hardening heat treatment followed by a rapid quench (oil or water normally)**
3. **Tempering heat treatment to soften slightly and give more ductility. The tempering temperature primarily determines the final strength, hardness and ductility.**

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NICKEL IN MARTENSITIC SS

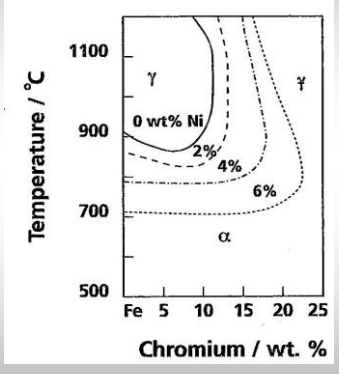
Effect on Microstructure

1. **Nickel (as well as other elements) makes many small changes to the metallurgical structure, cannot cover all changes here**
2. **Key role - in order to form martensite in SS, austenite is needed at elevated temperature; the higher the Cr content, the more austenitizers (Ni, C, N) are required**

NICKEL IN MARTENSITIC SS

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



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

NICKEL IN MARTENSITIC SS

Effect on Mechanical Properties

Many factors determine the yield strength and ductility of martensitic SS, with Nickel content being one factor that enhances these properties slightly.

Martensitic stainless steel beater bars in a manure spreader

NICKEL IN MARTENSITIC SS

Applications

Grade	Typical Applications
414	Fasteners, beater bars, springs, mining equipment, scissors, scraper knives, shafts, valve seats,
422	Turbine blades and highly stressed sections in gas turbines, furnace parts, burners operating above 650°C, valve parts, fasteners, oil refinery equipment, mining equipment, screens, files, rifle barrels
431	Aircraft fittings, fasteners, beater bars, valve and pump parts, marine hardware

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NICKEL IN MARTENSITIC SS

Improved Weldability Martensitic SS

Martensitic grades are generally very difficult to weld, and especially to obtain equivalent properties in the weldment (weld metal and Heat Affected Zone). This is partly because of their low ductility, and partly because of the effect of heat from welding on the microstructure. Typically high carbon contents have also resulted in poorer corrosion resistance in the weldment.

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NICKEL IN MARTENSITIC SS

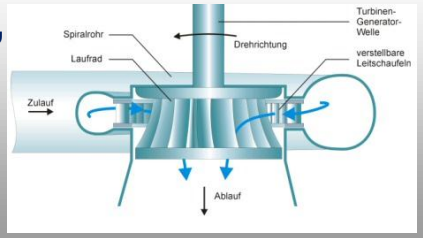
Improved Weldability Martensitic SS

Two types are mentioned here, one which has been used for 60+ years, and a family of super-martensitic grades for the oil and gas industry

NICKEL IN MARTENSITIC SS

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**



NICKEL IN MARTENSITIC SS

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°C)

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NICKEL IN PH GRADE SS

1. Some Nickel-containing PH grades
2. General Description
3. Effect on Corrosion Resistance and Mechanical Properties

PH grades are also hardenable, but involves a different hardening mechanism, that is the formation of intermetallic precipitates. These grades can be hardened to different strength and hardness levels, usually with more ductility and higher corrosion resistance than the pure martensitic grades.

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NICKEL IN PH GRADE SS

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

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

NICKEL IN PH GRADE SS

General Description

1. **I personally consider PH grades to be a much under-utilized family of materials due to lack of knowledge by end users.**
2. **Although their initial cost is higher than standard martensitic grades, the heat treatment performed after machining is simpler (lower temperature and no quench) with therefore less possibility for distortion and an easily calculated change of dimension**
3. **In general, they have higher corrosion resistance than the standard martensitic grades**

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NICKEL IN PH GRADE SS

General Description

2 stage heat treatment

1. **Austenite (formed at elevated temperature) is transformed to martensite on cooling (does not apply to the austenitic PH grades)**
2. **Aging heat treatment at 485-620°C**
   - causes precipitation of intermetallic phases (note that these intermetallic phases are not detrimental to corrosion resistance)
   - also tempers the martensite

The aging heat treatment is sometimes called the hardening heat treatment; however the aging heat treatment may reduce the hardness of the steel!

NICKEL IN PH GRADE SS

General Description

3 families of PH grades

1. **Martensitic type - basically fully martensitic structure after transformation, plus intermetallic phases during aging heat treatment**
2. **Semi-austenitic type - mixed martensitic / austenitic structure after transformation, reasonable soft and formable in this condition; then intermetallic phases form during aging**
3. **Austenitic type - does not form martensite; forms intermetallic compounds during aging**

NICKEL IN PH GRADE SS

General Description

1. For critical parts (e.g. in aircraft), they are usually double vacuum melted or Vacuum Induction Melted (VIM) for increased fracture toughness and stability at elevated temperatures
2. Nickel content has been increased slightly to eliminate or minimize detrimental ferrite content in the hardened structure
3. Over the years, there have been other slight modifications to the chemistry (especially C, P, S, Si, Mn) and the melting practices for critical applications

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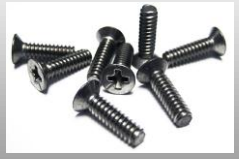
NICKEL IN PH GRADE SS

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 SS

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 900ºF (482ºC) for 1 hour, then air cool**

NICKEL IN PH GRADE SS

Applications

1. **Wide variety of applications in many industries, .e.g. aerospace, power plants, chemical, petrochemical, food, pulp and paper, marine, etc.**
2. **Used as pump shafts, valve stems, balls, mould injection dies, bushings, screws and other fasteners, couplings, wear rings, hydraulic actuators and screws, aircraft parts including landing gears, etc.**

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NICKEL IN FERRITIC, MARTENSITIC & PH SS

Summary

1. **Nickel is necessary in certain of the martensitic and all of the PH grades to obtain the desired metallurgical structure.**
2. **Nickel improves the corrosion resistance in most of these families. In the case of ferritic grades, the chloride SCC properties are reduced in $MgCl_2$ solutions and in other specific cases.**
3. **Nickel improves the mechanical properties, mostly the notch toughness of most of these families.**

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NICKEL IN FERRITIC, MARTENSITIC & PH SS

Summary

Use of Nickel-containing Ferritic, Martensitic and PH SS

Alloy family	Properties	Applications
Superferritic	Corrosion resistance, toughness	Heat exchanger tubes, plate heat exchangers
Low alloyed ferritic	Weldability, toughness, thick plate	Structural applications
Martensitic	Weldability, corrosion resistance in a hardenable alloy	Pump shafts, valve stems, sweet gas, water turbines, wear rings, fasteners
PH grades	Weldability, corrosion resistance in a hardenable alloy	Pump shafts, valve stems, aircraft components, dies, wear rings, fasteners

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