

Corrosion Resistance of High Nitrogen Steels

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1. Introduction

1.1 Some basics about High Nitrogen Steels (HNS)

1.1.1 Nitrogen in steel

Nitrogen as an alloying element has been known and used in technical applications since the 1940s, initially under the premise for nickel substitution in stainless grades.

Nitrogen in low alloy steels is undesirable due to the formation of brittle nitrides. However, the use of nitrogen in high alloy steels has an array of advantages that makes it appear interesting as an alloying element. In references one find this sufficiently researched, so that in this situation only the most important points need to be summarized [Dailly & Hendry, 1998], [Energietechnik-Essen [ETE], 2011], [Allianz Industrie Forschung [AIF], 2003]:

- significant increase of strength without restricting ductility
- Improvement of corrosion resistance
- Increasing the high temperature tensile strength
- Extended / stabilized austenite form
- no formation of tension induced martensite with high cold working rates
- Inhibits the discharge of inter-metallic phases

These as HNS-Alloy (High Nitrogen Steels) specific material group are characterised through an interesting material profile, i.e. a combination of strength and corrosion resistance.

A state-of-the-art production routine is P-ESR melting (pressurised electro slag remelting) which will be covered within the following section. Austenitic steels as well as martensitic steels can be manufactured and are suitable for forging and hot rolling. Some basic knowledge about the material characteristics is mandatory to avoid any potential issues at plastic deformation, heat treatment and to maintain the excellent corrosion resistance.

1.2 About this book chapter

This chapter will not cover the fundamentals of corrosion – we assume that the reader will have a basic knowledge about the principles of corrosion. This paper will provide an overview about the role of nitrogen related to corrosion of stainless steels. Since a lot of

results have been published to date, common knowledge will be summarized and topped up with own data and experimental results.

Finally, some typical HNS grades will be discussed with regards to their industrial application.

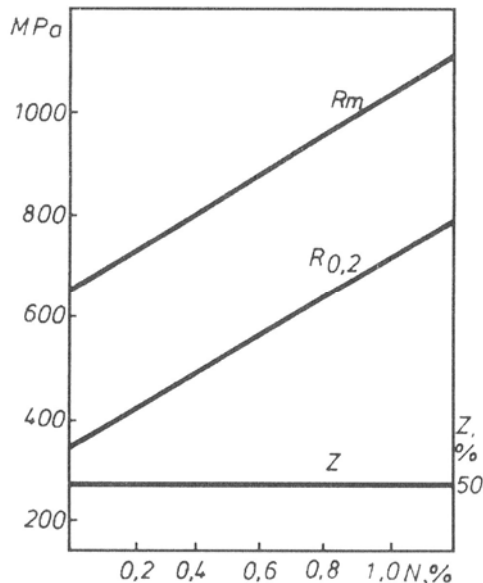


Fig. 1. Mechanical properties in dependency of different nitrogen concentrations after quenching at 1150°C, 2h in water. [Rashev et al.,2003]

2. Melting of HNS alloys

Melting of HNS alloys requires special process techniques as the nitrogen content is above the solubility limit at atmospheric pressure. The equipment development has started in the 1960's with pressurized induction furnaces (lab scale) and has finally led to the first PESR unit in 1980. Today, PESR is state of the art due to its high process capability, good productivity, large ingot sizes and a safe H&S environment [Holzgruber, 1988].

2.1 The PESR-process

Today's biggest PESR unit is located at Energietechnik Essen GmbH, Germany. Its operating pressure is max. 40 bars and can achieve ingot weights up to 20 tons and 1030 mm diameter. The functional principle is shown schematically in fig.2.

Basically, the PESR process is a conventional remelting facility that works in a pressure tank. The process is designed to meet both, an ESR refining and nitrogen pick up. The metallurgical approach is similar to a standard ESR-process, i.e. refining, low segregation, no porosity or shrinkage, defined microstructure and solidification.

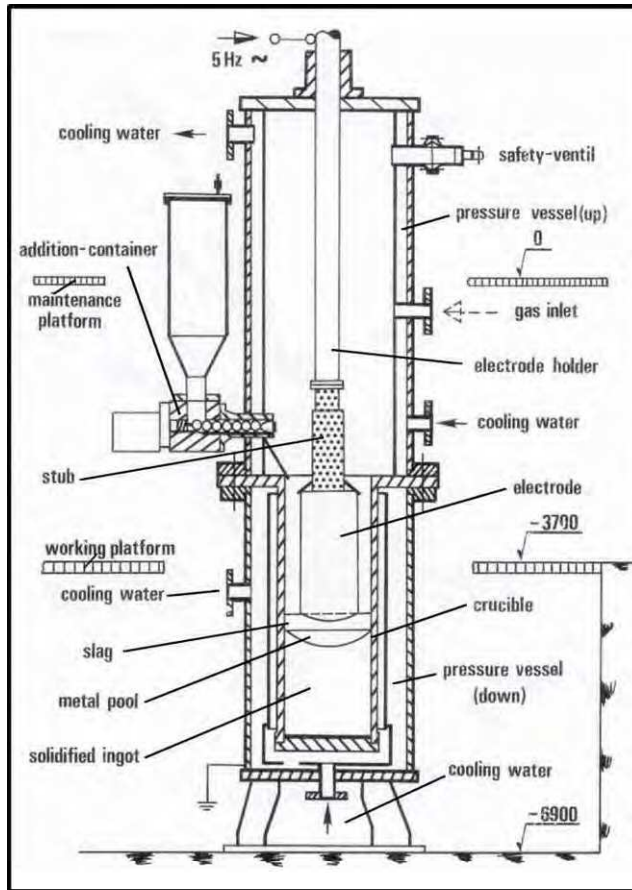


Fig. 2. Schematic design of a pressure electro slag remelting furnace (PESR).

The physical fundamentals of nitrogen pick up are specified over the Sievert square root law, accordingly that the nitrogen solubility is a function of pressure and temperature:

$$[\%N] = k \cdot \sqrt{p_{N_2}} \quad (1)$$

With p_{N_2} : Nitrogen partial pressure over melt in bar, k : Material constant (temperature and alloy dependent)

In real systems, the actual solubility is additionally codetermined through the alloy composition. Thermodynamic activities are used to describe the effect of the individual elements.

$$[\%N]_{Fe-X} = \frac{[\%N]_{Fe}}{f_N^X} \cdot \sqrt{p_{N_2}} \quad (2)$$

With $[\%N]_{\text{Fe-X}}$: Nitrogen solubility in multi-component systems, $[\%N]_{\text{Fe}} = 0,044\%$ (equilibrium constant in pure Fe at 1600 °C and 1 bar)

The activity coefficient f is thereby defined as

$$\log f_N^X = e_N^X[\%X] \quad (3)$$

With e_N^X : interaction coefficient, $[\%X]$: Concentration of the elements X in %



Fig. 3. View of the industrialized PESR -process at Energietechnik Essen GmbH for ingot weight up to 20 t und $\varnothing 1030$ mm.

It is obvious as per table 1 that specific elements will increase the nitrogen solubility (e.g. manganese), while others will reduce the solubility (e.g. silicon). This has not only an impact on the nitrogen pick up at remelting but also on the precipitation of inter-metallic phases in the solid state.

Element	Coefficient e_N	
C	+ 0.125	Reduction of N-Solubility
Si	+ 0.065	
Ni	+ 0.01	
W	- 0.0015	Increase of N-Solubility
Mo	- 0.01	
Mn	- 0.02	
Cr	- 0.045	
V	- 0.11	
Nb	- 0.06	
Ti	- 0.053	

Table 1. Activity coefficients of several elements with effect on the nitrogen solubility in steel at 1 bar.

Due to the general alloy composition, the nitrogen solubility is accordingly larger in austenitic as in ferrite or martensitic steels.

The nitrogen pick up can occur through the gas phase and also as well from a solid nitrogen carrier. The choice of a solid body nitrogen pick up medium is down to the following boundary conditions:

- Nitrogen partial pressure: high enough to allow a dissociation at ~ 40 bar
- Characteristics of the slag or flux are not allowed to change (e.g. electrical conductivity, metallurgical properties, etc)

In practice the standard Si_3N_4 is used, in exceptions CrN as well. A transfer of silicium respectively chromium in this case must be taken into consideration. The following table 2 provides a comparison about advantages and disadvantages of Si_3N_4 and gaseous nitrogen.

	Advantage	Disadvantage
Si_3N_4	<ul style="list-style-type: none"> • Nontoxic • Ease of operation and storage • Ease of dissociation 	<ul style="list-style-type: none"> • Very abrasive (joints and gaskets, valves) • Kinetic of dissociation of N^{3-} -ion must be regarded. • Non-continuous allowance on slag • Silicium transfer in melt
N_2 - Gas	<ul style="list-style-type: none"> • Continuous allowance possible • Simple regulation over the pressure • High equal distribution in ingot • Appropriate for Si-critical steel grades 	<ul style="list-style-type: none"> • Slag composition very important • Sievert'sches law at high pressure not ideally achieved. • Diffusions conditions in system slag-metall must be known.

Table 2. Advantages and disadvantages different nitriding mediums.

The selection of the slag takes place after metallurgical consideration and depends on the alloy. Above all, the slag composition has importance for the nitrogen pick up of the steel.

3. Microstructural characteristics of HNS

Nitrogen stabilizes the γ -area in a very clear way. It is undesired in low alloyed steels due to the formation of brittle phases; however it is very beneficial in terms of strengthening and corrosion resistance for high alloyed steels. It is considered to be the most efficient solid solution strengthening element. [Pickering, 1988] has reported that nitrogen is approximately twice as efficient as carbon.

[Bernauer & Speidel, 2003] et al. has published results, whereas nitrogen can improve the γ -stability by adjusting a carbon/nitrogen ratio. The high interstitial steels, i.e. containing carbon and nitrogen show a higher thermodynamic stability compared to common Cr-Mn-N-steels.

[Pickering, 1988] has investigated the influence of nitrogen within various steelbased alloys with regards to their microstructure. Therefore, nitrogen has a higher solubility in the lattice than carbon. Its presence is related with the formation of nitrides (or carbon nitrides). These nitrides tend to precipitate as small particles and – this is particular of interest for any hot forming applications – grow significantly slower than carbides. It is obvious that this will have an impact on recovery, grain growth and heat resistance. The nitrides are thermodynamically more stable than the corresponding carbides, i.e. have a lower solubility.

At first sight, the considered HNS- alloys are not significantly distinguishable than the nitrogen free varieties. The following fig. 4 & 5 show exemplary micrographs of a Mn-austenite with approx 0.65% nitrogen as well martensite with approx. 0.4% nitrogen.

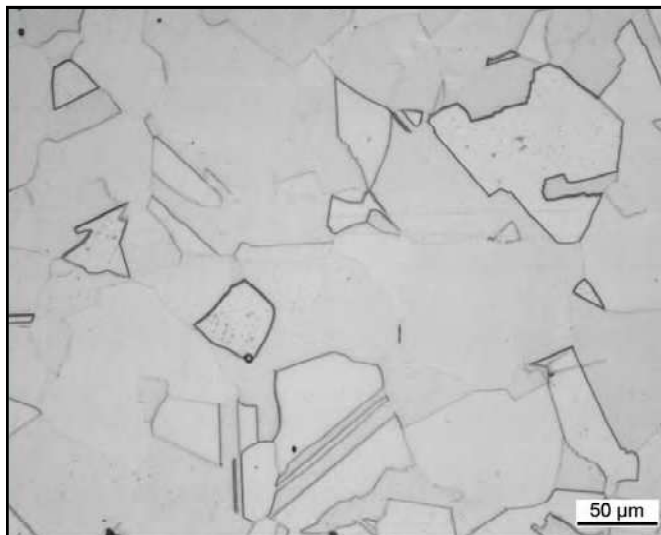


Fig. 4. Microstructure of a unformed and solutions annealed austenite with $\sim 0,6\%$ N.



Fig. 5. Tempered microstructure of a nitrogen alloy martensite (1.4108). (M 1000:1)

However – and this is a difference to the conventional nitrogen free alloy variations – one should consider that HNS-alloys have a specific precipitation behavior. This must be kept in mind so that potential difficulties at hot forming at heat treatment can be avoided. Additionally, any precipitation will affect the corrosion resistance so a good understanding of the alloy is mandatory to maintain the alloy characteristic.

3.1 Atomic structure of nitrogen alloyed steels

Much effort has been put into place to understand the beneficial effect of nitrogen in stainless steels over the past years. A major step was the calculation of the atomic structure within the d-band of Fe-C and Fe-N carried out by [Rawers, 2003], [Gravriljuk & Berns, 1999] and [Mudali & Raj, 2004]. Therefore, nitrogen increases the state density on the Fermi surface whereas carbon leads to a decrease of state density. Consequently, a higher concentration of free electrons can be found in austenitic nitrogen alloyed steels – this result in a metallic character of interatomic bonds. This also explains the high ductility in HNS, even at high strengthening. Contrary, interatomic bonds in carbon austenites show a covalent characteristic. This is due to the localization of electrons at the atomic sites [Rawers, 2003]. The preference for different atoms to be nearest neighbors is defined as short range order and is mainly driven by the degree of metallic character of an intermetallic bond. A metallic interatomic bond supports a homogenous distribution as single interstitials, whereas a covalent bond results in clustering of atoms. These clusters can then potentially precipitate secondary phases such as carbides, nitrides etc. A cluster is to be realized as local accumulation of approx. 100 atoms [Berns, 2000]. The high thermodynamic stability of nitrogen stabilized austenites can also be led back on the hindered clustering of atoms [Rawers, 2003]. In summary, the electron configuration is therefore the main driver for an increased corrosion resistance. Due to nitrogen, the allocation of Cr-atoms within the lattice is homogenous so that Cr- clustering and formation of $M_{23}C_6$ -carbides is reduced. Since

nitrogen delays the precipitation of carbides as seen in fig. 6 & 7 , the likeliness of a local Cr depletion is limited.

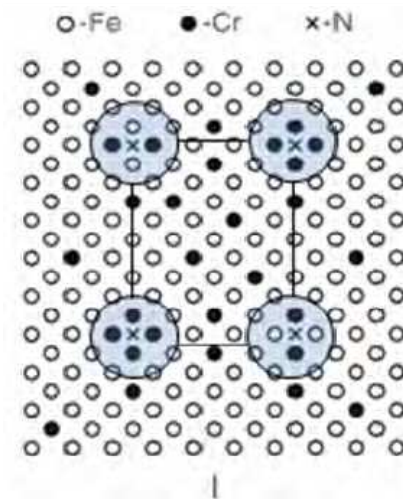


Fig. 6. Schematic of a short range order. Nitrogen increases the concentration on free electrons. Thereby forming a non-directional bonding and an equal distribution of the atom in crystal lattice. [Berns, 2000]

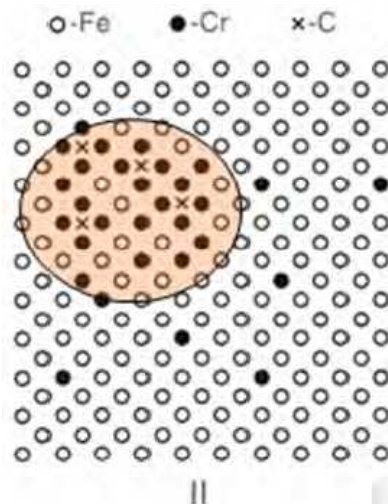


Fig. 7. Schematic of a cluster formation. Carbon decreases the concentration of free electrons. Thereby forming a directional bonding of non equal distribution of the atom in crystal lattice. [Berns, 2000]

3.2 Carbides

In dependency to the carbon content and the tempering time, austenitic steels tend to precipitate $M_{23}C_6$ -Carbides at the grain boundaries. Through this the ductility and corrosion resistance of the material significantly declines. However, the strength properties have no mentionable change. The susceptibility for intercrystalline corrosion clearly increases.

The precipitation behavior of this carbide can only be prevented through a quick quench in the critical temperature range. Fig.8 shows the location of the precipitation with relation to the alloy composition. Fine carbides are beneficial with regards to the corrosion resistance as the local chrome depletion is less in comparison to coarser carbides. The Cr depletion can be balanced out through an extended homogenisation (i.e. holding time) within the precipitation area.

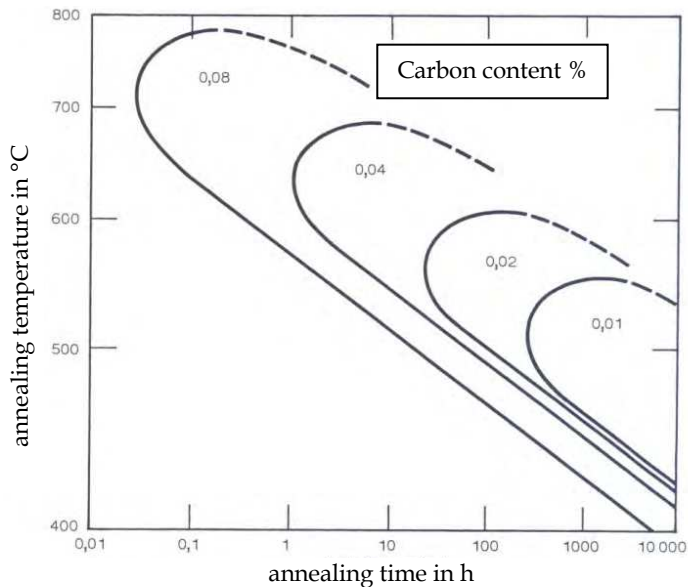


Fig. 8. Influence of the carbon content in location of grain decay in unstable austenitic steels with circa 18 % Cr und 8 % Ni. Examination in Strauß-Test. [Thyssen, 1989]

For 12% Cr-steels, containing nitrogen it has been observed by [Pickering, 1988] that nitrogen lowers the martensite start temperature M_S ; 1% nitrogen lowers M_S by 450 °C.

[Pickering, 1988] has investigated the influence of nitrogen on the carbide morphologies. The main type is as previously described the $M_{23}C_6$ type. In Nb-containing alloys, M_4X_3 have been observed where nitrogen can occupy interstitial dislocations. It also can be solutioned within M_6C .

HNS martensitic steels are also characterised with good high temperature strength and show an according hot forming behavior. Under circumstances these steels are found in thermo mechanical forging and rolling applications. The last forming step will effectively increase the dislocation density so that adequate nucleation for a desired precipitation exists. For example, the precipitation of carbides, nitrides as well as carbon nitride could be finely distributed. This

could be of interest to the high temperature strength. The previously mentioned effects of fine carbides concerning the dissolution and corrosion resistance are also valid here.

3.3 Nitride and nitrogen perlite

In the case of the austenitic steels it should be considered, that in the temperature range of approx. 500- 900 °C and in connection with the alloy composition a precipitation of nitrides (Type Cr_2N) occurs. This nitrogen perlite identified microstructure raises significantly the susceptibility to cracking of the steel but can also support intergranular cracking. Depending on the alloy composition, the precipitation window for nitrogen perlite or other nitrides are adjusted to higher or lower temperatures. The figures 9 & 10 show exemplary an austenitic structure with beginning and advance nitrogen perlite precipitation. Clear to recognize at what speed that the precipitation occurs.

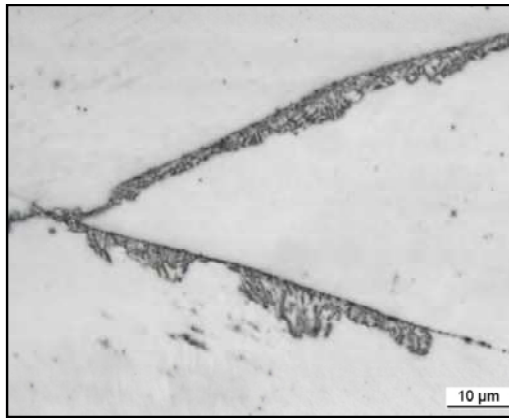


Fig. 9. Beginning of precipitation of nitrogen perlite cold worked austenitic structure 1.3816. 800 °C/15 min.

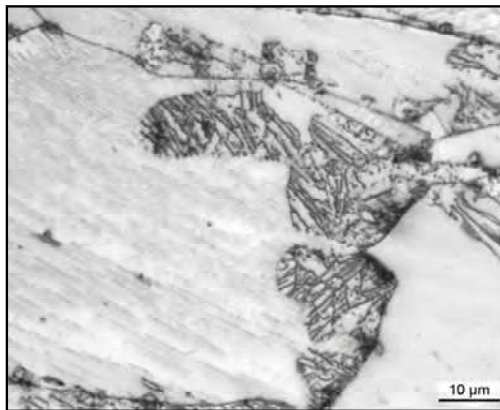


Fig. 10. Advanced precipitation of nitrogen perlite cold worked austenitic structure 1.3816. 800 °C/30 min.

For prevention of such brittle phases the precipitation area of the hot forming must be followed through fairly quick. The nitrogen level has obviously an impact on the precipitation kinetics of Cr_2N , see figure 11 for details. Best corrosion resistance can be achieved if all nitrogen is in solid solution, i.e. no nitrides are precipitated.

As seen in fig. 11 the precipitation depends on both, the alloy composition and holding time. The Cr_2N -formation has been reported by [Pickering, 1988] to be a major issue to high Cr and/or high Ni-alloys

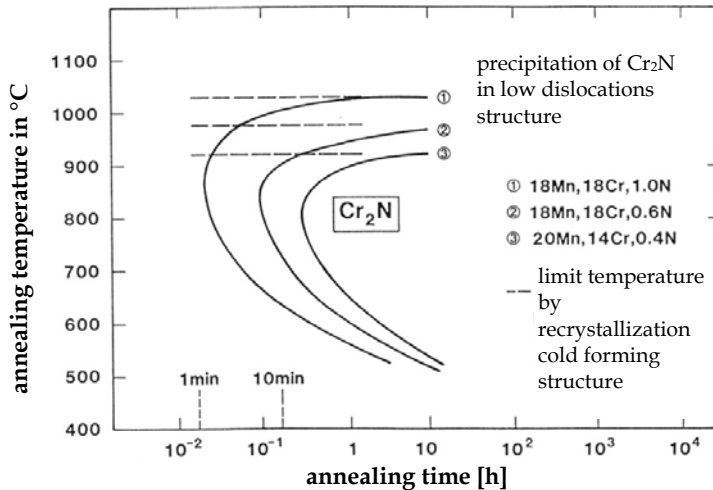


Fig. 11. Precipitation of Cr_2N in 18Mn18Cr at various nitrogen levels. [Uggowitzer, 1991]

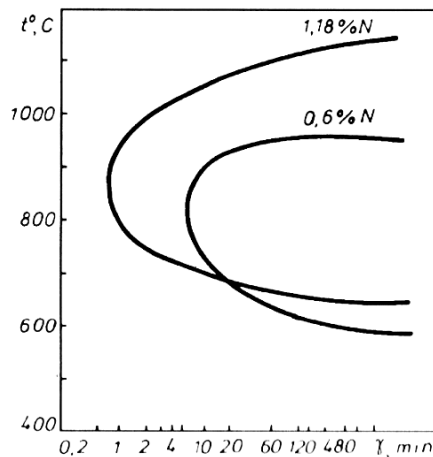


Fig. 12. TTT-diagram for the beginning of Cr_2N -precipitation at different nitrogen contents. Curve is based on X5CrMnN18-12. [Rashev et al., 2003]

Other intermetallic phases, such as Laves-phase, Z-phase and χ -phase have been investigated with regards to nitrogen alloying within literature. Generally, nitrogen seems to delay the formation of intermetallic phases. The underlying mechanism has been discussed controversially; the enhanced solubility of Chromium and Molybdenum due to nitrogen or its influence on Gibbs free energy for phase formation [Mudali & Rai, 2004]. The following table will provide an overview about the influence of nitrogen on some intermetallic phases [Mudali & Rai, 2004], [Heino et al., 1998].

Description	Influence of nitrogen...	Remark
σ	Suppresses formation of σ	
χ	Shifted to longer times Narrows temperature range for precipitation	M ₆ C appears instead of χ
M ₂₃ C ₆	Suppresses formation of M ₂₃ C ₆	Can be replaced by M ₆ C with increasing nitrogen contents
Laves	Precipitation is shifted to higher temperature but accelerated	
R		See Laves

Table 3. Overview about the role of nitrogen alloying on the precipitation behavior of some intermetallic phases. [Mudali & Raj, 2004], [Heino et al., 1998]

4. Corrosion resistance of HNS

The role of nitrogen in stainless steel with regards to the corrosion resistance has been previously reported within literature [Pleva, 1991], [Truman, 1988], [Pedrazzoli & Speidel, 1991], [Dong et al., 2003], [Mudali & Rai, 2004]. This chapter will review today's knowledge and present own data; corrosion fatigue and high temperature corrosion will not be covered.

4.1 General

It is well known that nitrogen in high alloyed steels improves the corrosion resistance; this is especially true for pitting and crevice corrosion. Additionally, nitrogen helps to prevent the alloy from stress corrosion cracking, though in an oblique way. Generally, the beneficial effect of nitrogen can be led back to an enrichment of nitrogen at the oxide/metal-interface and its influence on passivation. It has been reported that the enrichment increases with increasing potentials. However, these mechanisms have been discussed controversially [Mudali & Rai, 2004]:

- a formation of nitrides or mixed nitride layer, e.g. Ni₂Mo₃N
- enrichment of negatively charged N-ions, i.e. N^{δ-}. These ions will lower the potential gradient of the passivation film and reject Cl⁻ ions
- formation of Cr₂N. A high local Cr-concentration should improve the corrosion resistance. However, this approach is unlikely as nitrogen does not change the matrix composition underneath the passivation film. No Cr depletion whatsoever has been reported.

Nitrogen does not show any influence on the thickness of the oxide layer, investigations of various alloys with different nitrogen contents have confirmed an average thickness of 12-22 Å [Mudali & Rai, 2004] within all varieties.

A synergism of nitrogen and molybdenum is suggested by many authors [Mudali & Rai, 2004], [Pickering, 1988], [Pedrazzoli & Speidel, 1991]. Molybdenum shifts the metal dissolution to higher potentials which will consequently lead to an increased enrichment of nitrogen at the metal/oxide-interface. In this case, nitrogen can lower the current density below the critical value for pitting corrosion [Mudali & Rai, 2004].

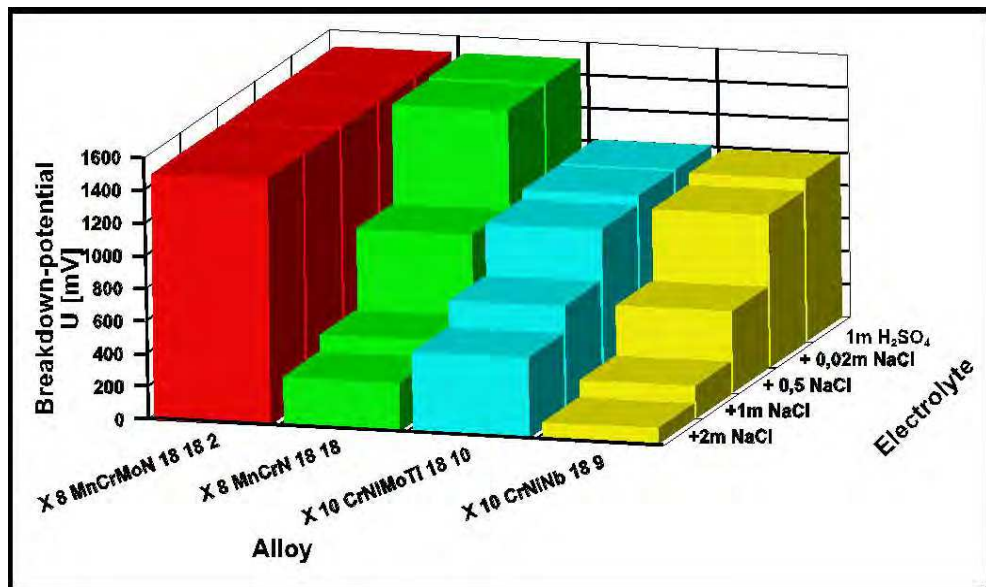


Fig. 13. Breakdown potential of HNS and commercial stainless steels in various electrolytes. [ETE-11]

It has been suggested that Molybdenum and nitrogen support the formation of highly mobile ions that interact with the passivation film. Additionally, nitrogen seems to have a buffer effect by reacting as follows in oxidizing corrosive media:



The formation of NH_4^+ - ions helps to increase the pH value which results in an improved repassivation and reconditioning of the base material [Mudali & Rai, 2004]. It also has impact on the deprotonation, which might explain the good performance in acids and halide containing liquids such as Cl^- , Br^- and I^- [Truman, 1988].

4.2 The role of nitrogen on pitting and crevice corrosion

Pitting corrosion is a very serious and harmful type of corrosion and is classified as local corrosion, characterized by small holes or pits. Usually, a repassivation cannot be achieved so that these pits can initiate cracks. This is the main reason why pitting often comes along with stress corrosion cracking. Pitting can be determined either by current-density-curves or a critical pitting temperature. It has been reported that nitrogen lowers the passivity in the current-density diagram. In austenitic steels, 1 % nitrogen improves the pitting potential by 600 mV [Pedrazzoli & Speidel, 1991]. Crevice corrosion follows generally the same principles; however the conditions are significantly tougher due to the geometric impact (electrolyte concentration in crevice). This will be covered at a later stage.

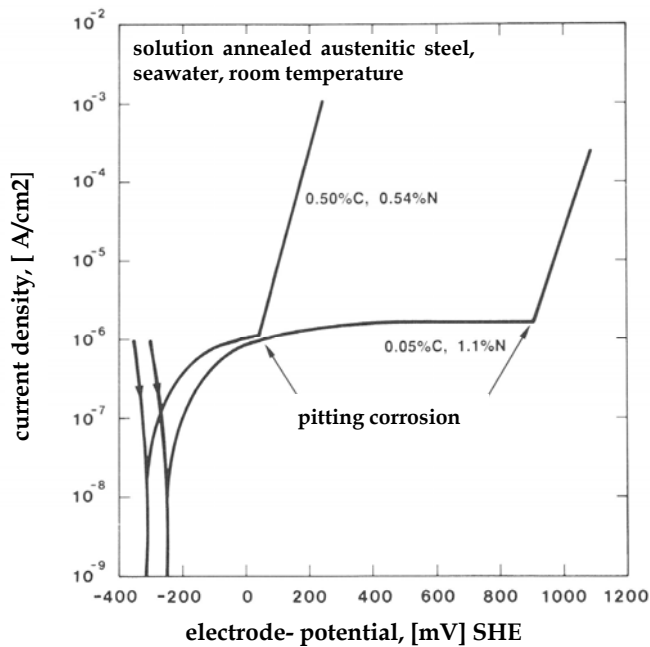


Fig. 14. Influence of nitrogen on Current-density depending of a given alloy. [Pedrazzoli & Speidel, 1991]

Pitting corrosion is a well-known corrosion problem for stainless steels. It can come along with sensitization, i.e. a local Cr depletion can support pitting corrosion. Therefore, any segregation, welding joint, heat treatment etc. can have an impact on pitting corrosion.

The critical pitting temperature (CPT) is defined at what temperature pitting occurs. A common range for stainless steels is 10-100 °C and obviously depends on the alloy composition. [Pedrazzoli & Speidel, 1991] has reported that the critical temperature for crevice corrosion (CCT) is approx. 20 ° lower compared to pitting, see fig.16 & 17 for details.

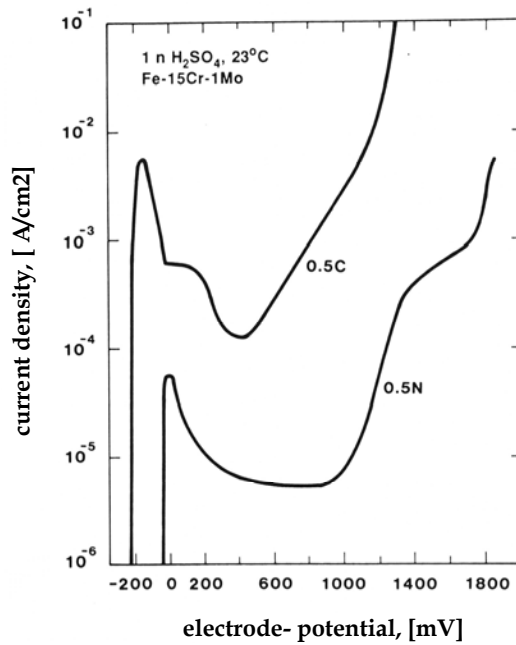


Fig. 15. Comparison of nitrogen and carbon on Current-density depending of a given alloy. [Pedrazzoli & Speidel, 1991]

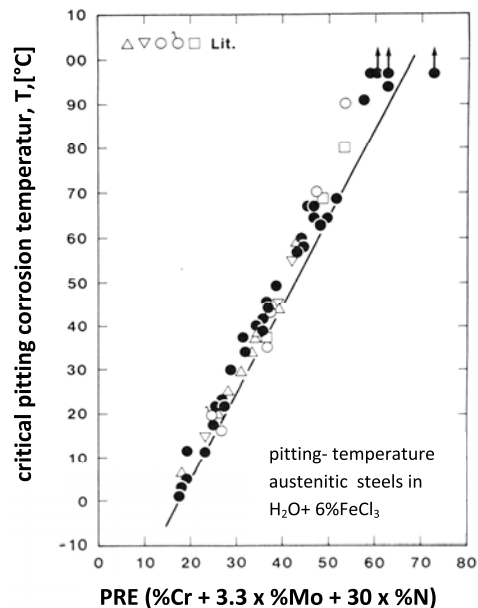


Fig. 16. Critical Pitting Temperature (CPT) as a function of PRE. [Pedrazzoli & Speidel, 1991]

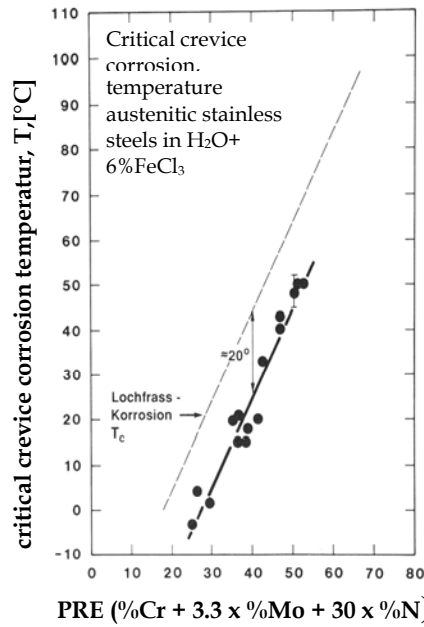


Fig. 17. Critical Crevice Temperature (CCT) as a function of PRE. [Pedrazzoli & Speidel, 1991]

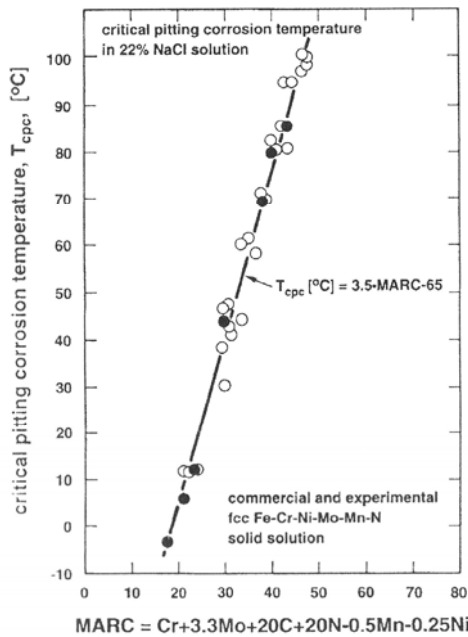


Fig. 18. MARC equation to rank various alloying element in regards to the alloy pitting resistance. [Speidel & Theng-Cui, 2003]

A commonly accepted ranking of alloys in terms of their pitting addiction is the Pitting resistance equivalent (PRE). It is defined as

$$\text{PRE} = \text{Cr} (\%) + 3,3 \text{ Mo} (\%) + x \text{ N} (\%) \text{ whereas } x = 13 \dots 30 \quad (5)$$

It has been suggested by [Pleva, 1991] to use $x = 16$ for steels containing $\text{Mo} < 4,5 \%$ and $x = 30$ for steels containing $\text{Mo} 4,5 - 7,0 \%$.

The PRE does not take any other elements but Cr, Mo and N into account. [Speidel & Theng-Cui, 2003] has suggested a new figure to include also C, Mn and Ni into the equation and has defined MARC (Measure of alloying for resistance to corrosion):

$$\text{MARC} = \text{Cr} (\%) + 3,3 \text{ Mo} (\%) + 20 \text{ C} (\%) + 20 \text{ N} (\%) - 0,5 \text{ Mn} (\%) - 0,25 \text{ Ni} (\%) \quad (6)$$

The MARC-equation is the first formula that considers carbon to be beneficial against pitting. [Bernauer & Speidel, 2003] has suggested a high carbon + nitrogen alloyed steel with improved pitting resistance. This is due to the higher thermodynamic stability of Cr-Mn-N-C systems compared to carbon-free Cr-Mn-N steels. However, both carbon and nitrogen must not form any precipitations but stay into solid solution.

A very global description of the influence of alloying elements on pitting potential was published by [Pedrazzoli & Speidel, 1991]. As seen in fig. 19, nitrogen and molybdenum have a significant impact on the potential shift.

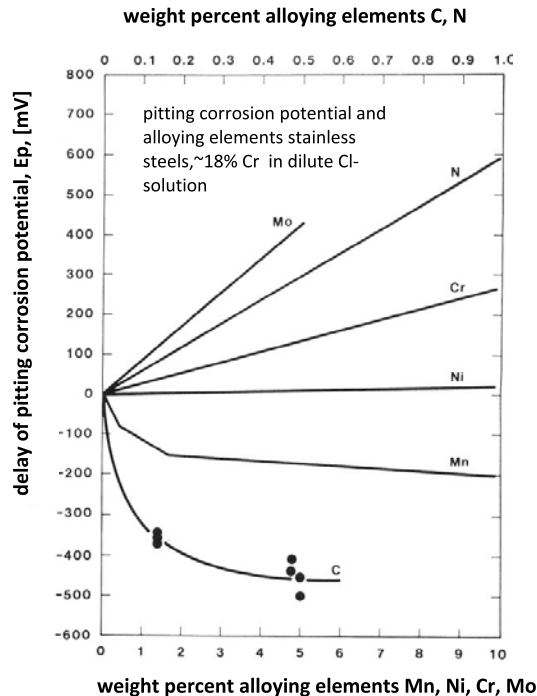


Fig. 19. Influence of various alloying elements on the pitting potential. [Pedrazzoli & Speidel, 1991]

Cold forming is supposed to have an impact on corrosion resistance; however the role of nitrogen in this case is not fully clear. Within Literature, the following has been reported [Mudali & Rai, 2004]:

- cold forming in stainless steels: no significant influence on pitting potential
- cold forming in nitrogen alloyed steels: a cold forming degree up to 20 % improves the critical pitting potential (CPP). A drop in CPP at higher deformation rates has been reported.

The improved pitting potential at low deformation rates i.e. below 20 % is due to the decreased tendency for twin formation. At higher deformation rates, deformation bands will appear which will be influenced by nitrogen (width and dislocation configuration). [Pleva, 1991] reports that the degree of cold working does not show any influence on the pitting corrosion. This has been also confirmed by own data on X8CrMnN 18-18 material, see fig.20 & 21 [ETE-11].

Various investigations have tried to explain the mechanism of nitrogen in terms of pitting. It has been agreed, that nitrogen stabilizes the γ -range in a very clear way. This is important to prevent δ -ferrite, esp. in Mo containing alloys. It also supports a homogenous, single-phase microstructure and avoids carbides to precipitate.

4.3 Ammonium theory

Nitrogen and Molybdenum obviously show a synergism in regards to pitting. Molybdenum seems to support the Cr_2O_3 -formation by acting as an electron acceptor. This also leads of a deprotonation of hydroxides. In addition, nitrogen reacts as follows:



The NH_4^+ - formation will increase the pH-value which support the repassivation. [Mudali & Rai, 2004] reports that NH_4^+ - ions have been confirmed by XPS within the passivation layer.

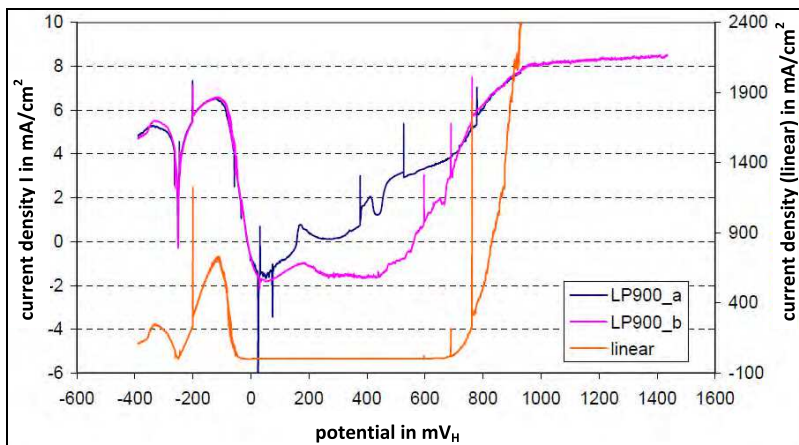


Fig. 20. Influence of cold working on current-density of X8CrMnN 18-18 (0 % cold work). UR: -250 / UL: 722 mV / ΔU : -972 mV / 1m H_2SO_4 + 0,5m NaCl [ETE-11]

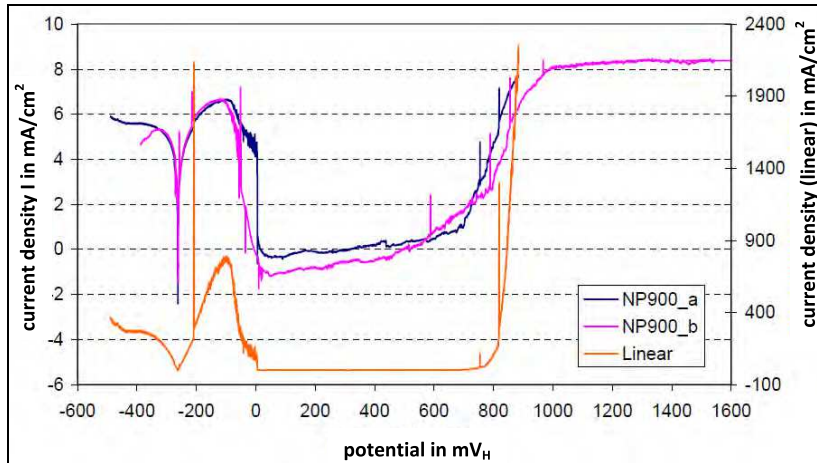


Fig. 21. Influence of cold working on current-density of X8CrMnN 18-18 (37 % cold work).
UR: -250 / UL: 780 mV / ΔU : -1030 mV / 1m H₂SO₄+ 0,5m NaCl [ETE-11]

4.4 Surface enrichment theory

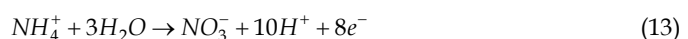
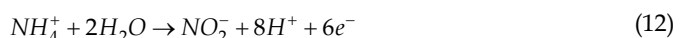
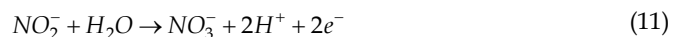
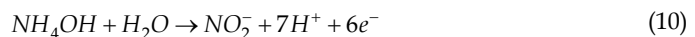
The surface enrichment theory is based on the general idea, that nitrogen is build into the lattice underneath the passive layer in solid solution. This nitrogen rich layer shall avoid dissolution of the substrate. Tentatively, there are chemical reactions with Cr and Mo who might change the local potentials as well. The formation of various N-rich phases has been reported, such as Cr₂N or Ni₂Mo₃N [Mudali & Rai, 2004], [Pickering, 1988]. Negatively charged N-ions, i.e. N^{δ-} are supposed to enrich at the metal/oxide interface. These ions will lower the potential gradient of the passivation film and reject Cl⁻ -ions.

4.5 Inhibitive nitrate formation theory

This theory covers the formation of pit growth inhibiting species. It is basically linked with the ammonia formation theory. The NH₄⁺-formation in the pit tip appears to happen quicker than the OH⁻-formation due to oxide reduction at the pit entrance.



The repassivation by NH₄⁺ can be described as follows:



Crevice corrosion underlies basically the same principles than pitting; due to the geometry of the crevice the corrosion conditions are believed to be more challenging. [Pedrazzoli & Speidel, 1991] has reported that the critical temperature for crevice corrosion is approx. 20 ° lower compared to pitting.

4.6 The role of nitrogen on Intergranular corrosion (IGC)

IGC is mainly driven by the depletion of Cr at the grain boundaries and/or the precipitations of carbides, usually $M_{23}C_6$. Therefore, Carbon is supposed to be the main driver for IGC but also grain size, cold working and heat treatment have a significant influence on IGC.

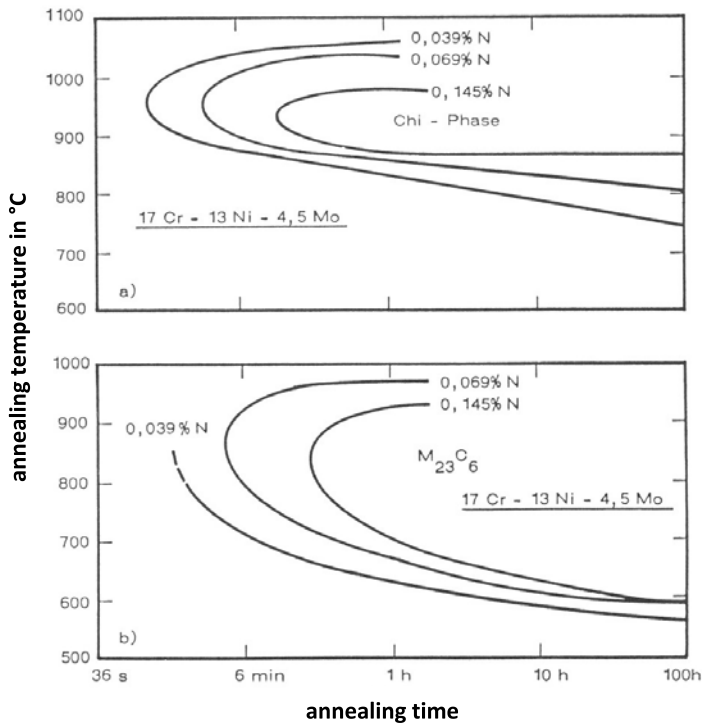


Fig. 22. Precipitation of $M_{23}C_6$ and χ -phase of a given alloy (17Cr-13Ni-4.5Mo) depending on annealing times and temperatures. [Gillesen et al., 1991]

As discussed in the previous chapter (microstructure), nitrogen tends to delay the $M_{23}C_6$ formation as it changes the Cr activity within the carbide. It also increases the passivity (i.e. lowering the current-density) and avoids the formation of α' -martensite at grain boundaries. However, this is only valid as long as nitrogen is in solid solution. It has been reported [Truman, 1988], [Dong et al., 2003] that an excess of nitrogen can lead to Cr_2N precipitations on the grain boundaries which can significantly decrease the intergranular corrosion resistance.

4.7 The role of nitrogen on Stress corrosion cracking (SCC)

It is commonly known that high alloyed steels are generally sensitive to SCC. The role of nitrogen against SCC has been discussed over the years but it appears that the positive effect of nitrogen is to be seen in a more oblique way. As previously discussed, nitrogen delays the carbide precipitation and avoids a local Cr depletion. Additionally, the crack growth velocity does not only depend on the actual Cr content, but also on the C content. The crack growth is much higher with increased C levels. It has been reported that nitrogen doesn't have any influence on crack growth velocity at $C > 0,5\%$. The impact of carbon is therefore higher compared to that of nitrogen. [Pedrazzoli & Speidel, 1991]

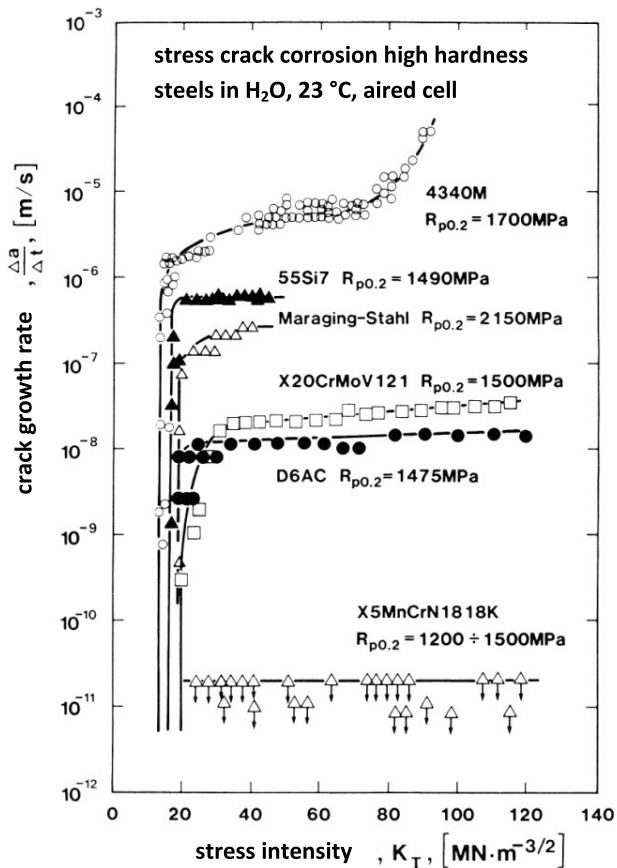


Fig. 23. Crack growth velocity for various alloys as a function of stress intensity. SCC for stainless steels, Water, 23 °C, ventilated. [Pedrazzoli & Speidel, 1991]

[Pickering, 1988] reports that the role of nitrogen is somehow inconsistent. In principle, nitrogen reduces the stacking fault energy which would be diametric to corrosion resistance. Low stacking fault energy in fcc-lattice is undesired in terms of SCC. Elevated nitrogen levels above 0,3 % are reported to be beneficial as the support of passivity is obviously

higher than the influence on stacking fault energy. [Mudali & Raj, 2004] confirms that increased stacking fault energy does improve the SCC resistance. As nitrogen decreases the stacking fault energy it should be detrimental to SCC. Carbon, due to the formation of wavy slip bands, should be theoretically beneficial. However, it appears that the role of nitrogen on SCC is fairly complex and depends on the alloy design and corrosion media.

The benefit of nitrogen alloying appears to be more oblique - the delay in $M_{23}C_6$ precipitation and improved pitting corrosion resistance has been recognized to be beneficial against SCC since pits are likely to initiate SCC.

5. Applications of HNS

High nitrogen steels are characterized through an interesting material profile that has led to a variety of demanding applications. The following will provide an overview about today's use of HNS alloy, please note it reflects only pressurized alloys, i.e. PESR alloys. Any air melted nitrogen alloy steels will not be part of this chapter.

5.1 Martensitic steels

Since its development in the early 1990s, Cronidur 30 (X30CrMo 15-1 plus 0,4 % nitrogen) has been approved as high performance alloy for aerospace applications such as spindles, shafts and bearings. It is used as material for helicopter bearings, flap traps, fuel pumps etc. Its excellent corrosion resistance combined with a high hardenability of 60 HRC makes it unique. The alloy has become an important material to industries as cutlery and knives, general engineering, medicals (since it is free of nickel) and powder metallurgy.



Fig. 24. High precision bearing of Cronidur 30 [ETE-11].



Fig. 25. Extruder screw, Cronidur 30 [ETE-11].

A heat resistant alloy is based on X15CrMoV12-1 and contains 0,2 % nitrogen (trade name HNS 15). It precipitates fine V(C,N) and provides a good creep resistance and heat resistance up to 650 °C. Above this temperature the appearance of Laves-phase restricts its usage.

A Molybdenium-free version is known as HNS 28 and consists of X28Cr13 with 0,5 % nitrogen. Its purpose was the closed-die casting industry where a good polish and corrosion resistance is required.

5.2 Austenitic steels

A main driver for the development of HNS austenitic steel was the power generation in the 1980's. A material for retaining rings was required that could resist the mechanical loads but also stress corrosion cracking. This has finally led to the introduction of X8CrMnN 18-18 also known as P900 or 18-18. This alloy combines superb mechanical properties, e.g. high ductility at elevated strength level with good corrosion resistance.

Further developments have also come up with Mn-stabilized austenites, e.g. X13CrMnMoN 18-14-3 (P2000). This alloy can achieve strength level (σ_s) beyond 2000 MPa, still with good ductility and corrosion resistance. One should consider heat treatment conditions and corresponding part dimensions with regards to the precipitation of Cr₂N.

Another market is powder metallurgy, i.e. thermal spraying and metal injection moulding (M.I.M.). The powders are gas atomized and very homogenous in terms of nitrogen and chemical composition. Main consumers are jewelry and general engineering.



Fig. 26. Generator shaft with retaining rings, X8CrMnN 18-18 [ETE-11].

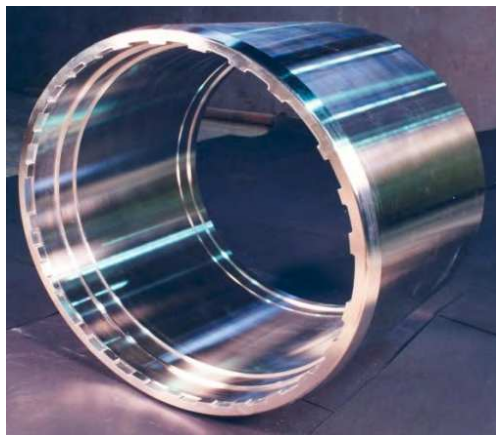


Fig. 27. Retaining ring. X8CrMnN 18-18 [ETE-11].

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