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# High Nitrogen Austenitic Stainless Steel

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## Abstract

**Austenitic stainless steel is generally consisting of 16-25 %wt Cr, 0.1%wt C and not less than 7.5% wt Ni, which is necessary to obtain austenitic structure. The interstitial alloying elements (like C and N) have a stronger impact on the constitutions and mechanical properties of steels than that of the substitutionals elements such as Ni, Mo. Carbon has always been used as alloying element in austenitic stainless steels because it is the remainder of the reduction process. The introduction of nitrogen in austenitic stainless steels good progress during the last few decades. The development of high nitrogen austenitic stainless steel is based on a superior combination of properties such as improved mechanical properties in the bulk and enhanced chemical properties at the surface and applications such as corrosion resistant materials and biomaterials. In this paper the needs, manufacturing and applications of high nitrogen austenitic stainless steels will be discussed. From literature survey, it has been observed that the solubility of N is more as compared to C in austenite. Due to high nitrogen content, the mechanical properties, corrosion resistance as well as compatibility with the human body have been improved.**

### Keywords

Austenite, high nitrogen steel, corrosion, body friendly, carbide.

## Introduction

Austenitic stainless steel is generally consisting of 16-25 %wt Cr, 0.1%wt C and not less than 7.5% wt Ni, which is necessary to obtain austenitic structure [1]. From the literature available, it has been observed that the interstitial alloying elements (like C and N) have a stronger impact on the constitutions and mechanical properties of steels than that of the substitutionals elements such as Ni, Mo. Carbon has always been used as alloying element in austenitic stainless steels because it is the remainder of the reduction process. The introduction of nitrogen in austenitic stainless steels started much later and made good progress during the last few decades [2]. The development of high nitrogen austenitic stainless steel is based on a superior combination of properties such as improved mechanical properties in the bulk and enhanced chemical properties at the surface and applications such as corrosion resistant materials and biomaterials [2, 3]. In this paper the needs, manufacturing and applications of high nitrogen austenitic stainless steels will be addressed.

## Need of High Nitrogen Austenitic Stainless Steels

After detailed literature review, it is observed that the motives behind the development of high nitrogen austenitic stainless steels are as follows:

### From corrosion point of view

Corrosion is a uniform metal loss from the surface that produces a uniform thinning of the cross section. With stainless steels it usually occurs in strong, warm acids. Pitting crevice corrosion occurs in a localized area on the surface of a metal. Such types of corrosion generally occur, when the passive film disrupted locally.

While austenitic stainless steels are single phase alloys, they always contain other minor phases that are the normal result of steelmaking. The phase present include oxide and sulfide inclusions from the steel refining practice in the melt shop, ferrite resulting from phase separation during solidification and carbide, chi and sigma phases that can form during annealing and welding. These phases represent discontinuities on the steel surface and they can facilitate pitting or crevice corrosion because they disrupt the passive film [4]. In contrast to C, dissolved N suppressed localized corrosion. The combination of strength, toughness and corrosion resistance of high nitrogen steel distinctly surpasses that of respective carbon grades and is the reason for the development and growing application of high nitrogen steel [2]. In austenitic stainless steels, besides the same effect on passivation, it has been reported a positive influence of N on the surface capability for regenerating the passive layer after pitting [5]. On the other hand, the actual influence of nitrogen on the general corrosion resistance of stainless steels has not been clearly established so far. There are reasons to believe in a positive effect of nitrogen when in solid solution, especially if the enhancement in the metallic character of the atomic bonds due to the presence of this element is considered [6]. Ren at al [7] have been investigated a high nitrogen austenitic stainless steel (BIOSS4) as an alternative to austenitic stainless steel 316L for medical applications. They performed corrosion test of both the steels in 0.9% NaCl solution and artificial blood plasma. They found that BIOSS4 steel shows better corrosion resistance and its pitting potential is higher than that of 316L both in 0.9% NaCl solution and artificial blood plasma.

### From austenite formation and stabilization point of view

A sufficiently high content of austenite forming elements such as Ni, N, C and Cu are required in the steel to allow the desired austenite structure to form at annealing temperatures and to persist to room temperature [8]. It is also well known that minimum 7.5-8% Ni along with 0.1% C and 16-25% Cr is sufficient for austenitic structure [1]. The expressions giving the Cr and Ni equivalents for annealing at 1075 oC are as follows [9]:

$$Cr\ eq = (Cr) + 2(Si) + 1.5(Mo) + 5(V) + 1.75(Nb) + 0.75(W)$$

$$Ni\ eq = (Ni) + (Co) + 0.5(Mn) + 0.3(Cu) + 25(N) + 30(C)$$

Where alloy contents are in mass percentage.

Therefore, the austenite forming elements can be grouped in to two categories: interstitial alloying elements and substitutionals alloying elements. The interstitial alloying element C assists the formation of austenite but impairs the toughness and corrosion resistance because of covalent bonding and intermetallic precipitations such as carbides. Another interstitial element N can also act as austenite stabilizer but its solubility is less than that of C. however, the solubility of N can be increased by increasing Cr and Mo contents. Gaveriljuk and Bern [2] have reported that high CrMo content stabilize ferrite and intermetallic precipitations, but in presence of N stability of ferrite and intermetallic precipitation is reduced. Therefore for stable austenitic structure low C and high N must be preferred.

The substitutionals elements like Ni and Mn stabilize austenitic structure. Ni in steel enhances the metallic bond as a result there is increase in toughness and corrosion resistance, but it lowers the N solubility. The N solubility can be increased by adding another substitutionals element Mn by replacing some of the Ni content. Mn is strengthening embrittling covalent bond but lowers the corrosion resistance. Pistorius and Toit [8] have reported that the Mn is a week austenite forming element because the Ni cotent required for austenite formation changes little if Mn is added. Therefore, high nitrogen austenitic stainless steel should contain high Cr, Mn and N, lower contents of Ni and C. In standard austenitic stainless steel about 0.15 mass% N are added to improve strengths and corrosion resistance. Replacing Ni by Mn and N yields low cost CrMnN steels of moderate corrosion resistance.

## From mechanical properties point of view

Ren et al [3] studied the mechanical properties of austenitic stainless steels with and without N. The mechanical properties are shown in Table 1:

Table 1: Comparison of material properties of different materials [3]

| Materials | Conditions | Yield strength (MPa) | Ultimate strength (MPa) | Elongation (%) | Reduction of area (%) | Hardness HV10 |
|---|---|---|---|---|---|---|
| **316 stainless steel** | Solution | 225±2.7 | 555±3.2 | 64+3.6 | 72±3.9 | 164±3.6 |
| **Co-28Cr-6Mo alloy** | Solution | 492±4.1 | 1013±5.3 | 19±3.1 | 24±3.5 | 308±4.4 |
| **High nitrogen steel** | Solution | 546±8.9 | 941±9.2 | 52±4.5 | 64±3.8 | 284±3.4 |
| **High nitrogen steel** | 30% cold deformation | 1205±21.3 | 1245±27.6 | 24±4.1 | 58±5.7 | 390±8.9 |

From the Table 1 [3], it is seen that both yield strength and ultimate tensile strength of high nitrogen steel are much higher than those of those of conventional austenitic stainless (316L) steel. Compared with Co-28Cr-6Mo alloy, the high nitrogen steel has similar high strength and hardness but more than twice the plasticity and toughness. Even after 30% cold deformation, the ultimate strength of the high N steel was increased about 50%, the yield strength was double increased, the elongation was decreased considerably and was still higher than that of Co-28Cr-6Mo alloy and the reduction in area still kept its initial level. Re et al [3] reported that, the excellent mechanical properties of the high N steel should be mainly due to high nitrogen content in the steel. Nitrogen dissolved in the austenitic stainless steels usually enhances their strength, hardness, work hardening rate, wear resistance etc.

### Cost and compatibility of Ni and N

Pistorius and Toit [7] reported that the fluctuations in the Ni price continue to drive the search for alternatives to Ni in austenitic stainless steels. Stainless steels producers are significant consumers of ferroalloys, including ferrochromium, ferromanganese, ferrotitanium, ferronickel and nickel. Pistorius and Toit [7] mentioned that stainless steel production uses two thirds of primary Ni and it is a major contributor to the price and price volatility of austenitic stainless steels. Due to high and volatile price of Nickel, there is a long history of searching for alternatives to Ni in stainless steels. The most successful development has been the 200 series steels. The Cr-Mn-Ni-N stainless steels can have similar corrosion resistance to type 304 in many environments, typically containing 4% Ni.

Ren et al [3] has reported that most commercialized coronary stents are made of 316L stainless steels due to its good combinations of mechanical properties. However, the presence of high content of Ni, which is known to trigger the toxic and allergic responses, has caused many concerns. Such concerns motivated the researchers for developing Ni free austenitic stainless steel.

## Manufacturing of High Nitrogen Austenitic Stainless Steel

Compared to C the solubility of nitrogen is lower in the melt but higher in the austenite which entails differences in manufacturing between HNS and respective carbon grades. The high solubility of N in austenite provides the basis of HNS. Austenite is used in its stable form or as a parent phase of martensite which emerges during cooling or cold working. The volatility of N requires special measures to achieve a sufficient solubility in the melt. The most common one is alloying, especially by Cr, leading. stainless steel grades. The N content of approximately (mass%) ≤ 0.2 in martensitic HNS, and ≤ 1 in austenitic CrMn HNS. A further rise in N calls for pressure or powder metallurgy which add to the costs. This holds true for subsequent costs by impaired workability and weldability. Pre-shaping by casting under pressure is excluded for costs as well. Pressurized electroslag remelting is e.g. applied to martensitic HNS for stainless steel bearings, tools and valves to gain a high hardenability and also to austenitic HNS for high strength and body friendly applications. Powder metallurgy may e.g. provide wear resistant stainless grades with upto about 3 mass % of N. As always, only a convincing performance justifies higher costs. Therefore the major part of HNS is produced by melting under normal pressure employing N2 blowing or nitride ferrochromium to induce nitrogen [2].

## Applications of High Nitrogen Austenitic Stainless Steel

High nitrogen austenitic stainless steel can be used in varieties of applications:

As biomaterials: Ren et al [3] have developed a Fe-Cr-Mn-Mo-N type high nitrogen austenitic stainless steels, which has better mechanical properties, corrosion resistance and having the blood compatibility.Another high nitrogen austenitic stainless steel developed by Ren et al [7] is BIOSS4, as biomaterials to remove Ni as allergic materials.

Corrosion resistant: Steels with up to 0.5 mass% N are commercially melted under normal pressure and pressure melted steels of up to 0.9 mass% N have been developed. N suppresses localized corrosion, assisted by < 7 mass% of Mo. The high CrMo is only feasible with the help of N procuring the necessary stability of austenite to the formation of ferrite and to deteriorating intermetallic phases. These superaustenitic HNS are meeting new demands in chemical and process engineering [2].

Austenitic HNS for service at elevated temperatures contain up to about 0.25 mass% N in solid solution. In addition up to 0.7 mass% N precipitated as nitrides in pressure melted steels. The short time creep resistance is raised by dissolved N [2].

## Conclusions

1. The solubility of N in austenite is higher than that C which jointly improves strength and toughness.
2. Nitrogen stabilizes the austenite without being as close to embrittling precipitations as carbon grades. This again promotes toughness, especially in thicker cross section [2].
3. After aging or tempering carbides tend to decorate grain boundaries, while nitrides are more evenly distribute and smaller. As a result the mechanical and chemical properties of high nitrogen austenitic stainless steel are enhanced.
4. Corrosion generally occurs, when the passive film disrupted locally by the presence of intermetallic compounds.
5. N is the better alternative for Ni austenitic stainless steel as for as mechanical properties, stability of austenite, cost and allergic phenomenon is concerned.

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