Doctoral Thesis

Development of ultrahigh strength austenitic stainless steels alloyed with nitrogen

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DEVELOPMENT OF ULTRAHIGH STRENGTH AUSTENITIC STAINLESS STEELS ALLOYED WITH NITROGEN

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
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presented by

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ABSTRACT

It is well established that nitrogen in austenitic stainless steels causes a remarkable high strengthening by solid solution as well as an increasing in corrosion resistance. For these reasons nitrogen as an alloying element has been successfully used to develop a number of commercial steels in which it stabilizes the austenitic phase (High Nitrogen Austenitic stainless Steels - HNASS). Presently these steels are manufactured by ingot metallurgy carried out under high nitrogen partial pressure in order to achieve sufficient high nitrogen solubility, or by powder metallurgy. Both production routes are “expensive” and quite “exotic”, and this explains why in spite of a good knowledge on favourable effects by nitrogen alloying in austenitic stainless steels, high nitrogen austenitic stainless steels have not been extensively used and adopted in large quantities yet.

This thesis describes the development of new Ultrahigh Strength High Nitrogen Austenitic Stainless Steels with very low nickel content, designed to be made by “ingot metallurgy without overpressure”, i.e. using conventional steel making facilities. These new steels are interesting candidates for structural application in car industry, building industry and ocean engineering, due to high mechanical strength, high resistance to corrosion and low cost of production.

By means of laboratory experiments combined with thermodynamic calculations suitable alloy compositions were designed in order to increase the nitrogen solubility at atmospheric pressure in the liquid and solid phase, avoiding porosity formation into cast ingots during solidification. On these new alloys the effect of:

- solid solution hardening;
- grain boundary hardening;
- dislocation hardening (during cold working);
- dislocation hardening (during hot working);
- precipitation hardening (strain ageing);

on yield strength, ultimate tensile strength and elongation to fracture were investigated in a systematic way.

A high level of strength was achieved combining different strengthening mechanisms following the rule: nitrogen in solid solution as high as possible, grain size as small as possible and cold deformation as high as possible. Solid solution hardening was optimised choosing “the right” amount of carbon and nitrogen taking in account that high nitrogen austenitic stainless steel undergoes to a ductile to brittle transition at room temperature as the sum of nitrogen and carbon content in solid solution approaches one weight percent.

The dependence of the ductile to brittle transition upon alloying elements and grain size was explored.

The introduction of strong nitride former elements, mainly vanadium and niobium, able to form nitrides more stable than those based on chromium and molybdenum, was investigated in order to achieve small grains in bulk materials.

The role of nitrogen on dynamic recrystallization and dislocation hardening during hot rolling was investigated. Nitrogen in solid solution was found to have profound influence on the temperature of dynamic recrystallization and hence on the thermo-mechanical processes such as hot rolling, where an improved hot workability of the austenite becomes the first target to achieved.
RIASSUNTO

L’aggiunta di azoto in acciai inossidabili austenitici provoca uno straordinario aumento della resistenza meccanica, grazie al notevole rafforzamento per soluzione solida, e della resistenza alla corrosione.

Per queste ragioni sempre più spesso nella produzione dei moderni acciai inossidabili austenitici viene impiegato azoto.

Recentemente è stata sviluppata anche una nuova classe di acciai in cui l’azoto agisce principalmente come elemento austenitizzante, consentendo una riduzione del tenore di nickel (Acciai Inossidabili Austenitici all’Azoto: High Nitrogen Austenitic Stainless Steels).

Attualmente questi acciai sono prodotti per mezzo della metallurgia fusoria del lingotto conducendo la fusione in presenza di una elevata pressione parziale di azoto o per mezzo dei metodi della metallurgia delle polveri. Tali vie di produzione sono piuttosto costose, richiedendo equipaggiamenti particolari e complessi; questo è un motivo per il quale gli acciai ad alto tenore di azoto non hanno ancora trovato ampie applicazioni, a dispetto di una buona conoscenza degli effetti favorevoli che l’alligazione con azoto comporta in una matrice austenitica.

Questa Tesi di Dottorato vuole descrivere lo sviluppo di nuovi acciai inossidabili austenitici ad alto tenore di azoto dotati di una elevata resistenza meccanica, contenenti poco nickel, progettati per essere prodotti ricorrendo alla fusione fusoria del lingotto senza bisogno di sovrapressione, usando cioè equipaggiamenti fusori tradizionali.

Questi nuovi acciai sono potenziali candidati per applicazioni strutturali nell’ambito dell’industria automobilistica, delle costruzioni civili e marine, per via della loro elevata resistenza meccanica, elevata resistenza alla corrosione e basso costo di produzione.

Per mezzo di esperimenti condotti in laboratorio affiancati da simulazioni termodinamiche al calcolatore, sono state sviluppate composizioni chimiche capaci di aumentare la solubilità dell’azoto a pressione atmosferica sia in fase liquida che solida; acciai austenitici con elevato tenore di azoto sono stati così ottenuti senza formazione di porosità nei longotti durante la fase di solidificazione.

Con queste nuove leghe è stato successivamente valutato l’effetto dell’azoto sui meccanismi di rafforzamento:

- per soluzione solida;
- per affinamento del grano;
- per incrudimento (durante lavorazioni plastiche a freddo e a caldo);
- per precipitazione ed invecchiamento.

L’effetto di questi meccanismi di rafforzamento è stato valutato in termini delle seguenti proprietà dell’acciaio: resistenza allo snervamento, sforzo a rottura, duttilità e tenacità.

Una resistenza meccanica estremamente elevata è stata ottenuta combinando differenti meccanismi di rafforzamento seguendo la seguente strategia: tenore di azoto in soluzione solida più elevato possibile, dimensioni dei grani più piccole possibili e incrudimento più elevato possibile.

Il rafforzamento per soluzione solida è stato ottimizzato scegliendo la quantità “giusta” di azoto e carbonio tenendo presente che gli acciai inossidabili austenitici ad alto tenore di azoto vanno soggetti al fenomeno della transizione dutile-fragile a temperatura ambiente quando la somma tra il tenore di carbonio e di azoto raggiunge la soglia dell’un per cento.

La dipendenza della temperatura a cui si manifesta la transizione dutile-fragile da altri fattori, quali il tenore degli altri elementi di lega e la dimensione del grano, è stata anche investigata.
L’introduzione di elementi affinanti, principalmente vanadio e niobio, in grado di formare nitruri più stabili di quelli basati sul cromo e molibdeno, è stata investigata allo scopo di ottenere un affinamento del grano austenitico in pezzi di notevoli dimensioni. L’influenza dell’azoto sul fenomeno della ricristallizzazione dinamica e “incrudimento” che ha luogo durante la laminazione a caldo è stato investigato. L’azoto in soluzione solida ha una profonda influenza sulla temperatura di ricristallizzazione dinamica e quindi sui processi termomeccanici come la laminazione a caldo, per la quale la lavorabilità a caldo dell’austenite diventa un parametro importante.
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1. INTRODUCTION

1.1 STAINLESS STEELS

Stainless steels were invented at the beginning of the last century in Germany (Strauss and Maurer 1912) and in England (Brearly 1913) as a surprise result of investigations about the influence of chromium on steels. Brearly’s new alloy contained about 13wt% chromium and 0.25wt% carbon. It had a martensitic structure and was used to manufacture cutlery. The work of Strauss and Maurer culminated in the development of the first austenitic stainless steel, a precursor of 18/8 Cr-Ni steel (AISI 304). Since that time the development in the field of corrosion resistant iron based materials has been extensive. Stainless steels have been developed and investigated with a wide variety of chemical compositions and processing techniques resulting in a wide range of properties (e.g. tensile strengths range from 200 MPa up to 2000 MPa). Although a great array of property combinations have been achieved, the single most important characteristic of all stainless steel remains their corrosion resistance.

Today the only common characteristic of all stainless steels is a chromium content above 10 weight percent, necessary to prevent rust formation when exposed in air (hence the designation stainless) through the formation of an invisible and adherent chromium rich oxide surface film. Beyond these restrictions many alloy combinations are possible; depending upon their microstructure, stainless steels can be divided into four groups:

- martensitic
- austenitic
- ferritic
- duplex

1.2 AUSTENITIC STAINLESS STEELS

Austenitic stainless steels contain several alloying elements combined with an iron base to achieve the desired microstructure and properties. The first austenitic stainless steels used nickel and carbon to stabilise the austenitic structure with 0.25-weight percent carbon for the one stage steel making practice used at that time (melting, metal refining, reducing and alloying were done in the same crucible). High carbon contents in early austenite steels caused problems during service; in these CrNi-type steels, a short exposure in the temperature range 500 to 900°C results in Cr$_3$C$_6$ precipitation along the grain boundaries, leading to material embrittlement and reduced corrosion resistance because of chromium depletion in the matrix surrounding carbides. The high affinity of carbon to chromium made these new steels susceptible to intergranular corrosion.

It was only through the introduction of new steel making methods in the 1960s, Vacuum Oxygen Decarburisation (VOD process) and Argon Oxygen Decarburisation (AOD process), that carbon content was drastically reduced to avoid chromium rich carbides precipitation; in
the meanwhile other elements, such as nickel, manganese and nitrogen were used to stabilize the austenite. Today the majority of the commercial austenitic stainless steels have carbon content as low as 0.005 to 0.015 weight percent and are produced by AOD (for economic reasons), even though VOD production allows higher quality steel. Some well-known examples are the austenitic grades: AISI 304 and 316, their extra-low carbon version 304L and 316L and their nitrogen alloyed version 304LN and 316LN. Other elements, such as Mo, V, Ti and Nb may be added to enhance specific properties for certain applications.

Tab. 1-1 summarises the principal elements found in modern stainless steels and their respective influence on steel properties.

<table>
<thead>
<tr>
<th>Element</th>
<th>Dominant influence on the Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>ferritising</td>
</tr>
<tr>
<td>Manganese</td>
<td>austenitising / ferritising</td>
</tr>
<tr>
<td>Nickel</td>
<td>austenitising</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>ferritising</td>
</tr>
<tr>
<td>Copper</td>
<td>ferritising</td>
</tr>
<tr>
<td>Vanadium</td>
<td>ferritising</td>
</tr>
<tr>
<td>Niobium</td>
<td>ferritising</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>austenitising</td>
</tr>
<tr>
<td>Carbon</td>
<td>austenitising</td>
</tr>
<tr>
<td>Titanium</td>
<td>ferritising</td>
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<tbody>
<tr>
<td>chromium</td>
<td>ferritising</td>
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<td>manganese</td>
<td>austenitising / ferritising</td>
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<td>nickel</td>
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<td>molybdenum</td>
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<td>copper</td>
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<td>vanadium</td>
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<td>niobium</td>
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<tr>
<td>nitrogen</td>
<td>austenitising</td>
</tr>
<tr>
<td>carbon</td>
<td>austenitising</td>
</tr>
<tr>
<td>titanium</td>
<td>ferritising</td>
</tr>
</tbody>
</table>

Tab.1-1: alloying element of modern austenitic steels.

Unlike any other class of steels, austenitic stainless steels are used over a wide range of service conditions, varying in temperature from −196°C to above 800°C, and in a wide range of corrosive media. In addition to these severe operating conditions, stainless steels are expected to be readily weldable and are required to maintain their strength and corrosion resistance in the welded condition. Further, certain applications call for a high degree of cold formability, hot forming and adequate machinability. The demands that are imposed on stainless steels are therefore wide ranging and the versatility of this class of material is particularly outstanding.

Austenitic stainless steels are characterized by rather low yield strengths of the order of 200–300 MPa in annealed condition at room temperature, with excellent ductility and toughness. Aiming to further improve the strength and corrosion resistance of austenitic stainless steels, alternative alloy compositions and production technologies were investigated. The traditional metallurgical strengthening mechanism (solid solution hardening, grain boundary hardening, dislocation hardening, precipitation hardening and strain ageing) were applied and adapted. Among all these researches, nitrogen was found to improve both mechanical strength and corrosion resistance in an outstanding way.
1.3 HIGH NITROGEN AUSTENITIC STAINLESS STEELS

Nitrogen may exist in three forms in steels:

a. as gas molecule;
b. in interstitial solid solution;
c. precipitated as nitrides.

While gas pores are deleterious in steels as well as some nitrides, nitrogen in solid solution is beneficial for austenitic stainless steels and it causes extraordinary improvements in corrosion resistance and mechanical properties resulting in an unusual combination of strength and fracture toughness.

The first reports about nitrogen alloying at atmospheric pressure were published long ago, in the 1938 by A.M. Samarin in the ex-URSS [Sama38] and F. Rapatz [Rapa41] and R. Scherer [Scher42] in Germany, during investigations related to replace a certain amount of nickel in the chromium-nickel stainless steels by manganese and nitrogen.

Later during the nickel shortage period (50s) alloys with nickel contents as low as 1wt%, manganese contents from 4 to 17wt% and nitrogen contents up to 0.25wt% were developed, culminating in alloy series AISI 200.

Although it was soon realized that nitrogen alloying has a strong influence on mechanical and chemical properties of austenitic stainless steels, it was not possible to get the best performances because of the low nitrogen solubility in the system Fe-Cr-Ni at atmospheric condition. Only recently has been possible to increase the nitrogen solubility in steels beyond the limit at atmospheric pressure, when different manufacturing routes (metallurgy under pressure, centrifugal casting, powder metallurgy) were developed in different countries in order to increase the nitrogen solubility [Feich91].

It is in this framework that high nitrogen stainless steels (HNS) were invented. Even if the original definition of "high nitrogen steels" was reserved to steels produced under gas pressure (pressure metallurgy), today a steel to be considered "high nitrogen" has to contain a minimum of 0.08wt% nitrogen in solid solution with a ferritic matrix and a minimum of 0.4wt% nitrogen with an austenitic matrix [Speid90].

HNS have been developed to such extent that this group of steels now includes the materials which exhibit the highest combination of strength and fracture toughness among all the structural materials [Speid87].

The origins of these outstanding results were found in the peculiar interactions between nitrogen and lattice defects and atoms of other alloying elements, different from the ones expected from the more traditional interstitial element like carbon. For these reasons high nitrogen steels are principally new materials.
2. PROPERTIES OF HIGH NITROGEN AUSTENITIC STAINLESS STEELS

High nitrogen austenitic stainless steels combine a large number of advantages over the traditional low nitrogen or nitrogen free austenitic stainless steels. These advantages include:

- nitrogen as a potential low cost alloying element;
- nitrogen as an austenite stabilizer;
- nitrogen as a solid solution hardening element;
- nitrogen improving fine grain hardening;
- nitrogen improving the coefficient of work hardening;
- nitrogen improving the pitting corrosion resistance;
- nitrogen improving the crevice corrosion resistance;
- nitrogen improving the intergranular corrosion;
- nitrogen as an essential element for the development of high strength, stress corrosion cracking resistant stainless steels.

It is the combination of these advantages, which constitutes the basis of the industrial applicability of high nitrogen austenitic stainless steels.

2.1 AUSTENITE STABILITY

In order to achieve the above mentioned advantages a fully austenitic microstructure is requested, hence it is of prime importance to know the metallurgical limits of the austenite single phase region in the multicomponent alloys. The modified Schaeffler diagram introduced by Speidel and Uggowitzer for high chromium steels [Speid87], describes the influence of predominant alloying elements on microstructure dividing them into two groups:

- **austenite promoter elements** their effects are described in terms of the Ni equivalent:

  \[ \text{Ni}_{\text{equiv}} = \text{Ni} + \text{Co} + 0.1\text{Mn} - 0.01\text{Mn}^2 + 18\text{N} + 30\text{C} \]  \[1\]

- **ferrite promoter elements** their effects are described in terms of the Cr equivalent:

  \[ \text{Cr}_{\text{equiv}} = \text{Cr} + 1.5\text{Mo} + 1.5\text{W} + 0.48\text{Si} + 2.3\text{V} + 1.75\text{Nb} + 2.5\text{Al} \]  \[2\]

The diagram in Fig. 2-1 shows that austenitic steels need a minimum \( \text{Ni}_{\text{equiv}} \) of about 10, this gives a metallurgical limit for austenitic iron based materials.

Formula [1] shows the very powerful austenite stabilizer effect of nitrogen:

1 weight percent of nitrogen in solid solution is as effective as 18 weight percent nickel!

Therefore nitrogen can replace the more expensive alloying element nickel in order to stabilize the austenite giving the possibility to develop a new class of Ni-free austenitic
stainless steels [Uggo96], as well as duplex Ni-free stainless steels [Wang98], cheaper than the traditional ones with nickel.

\[
\text{Cr}_{\text{eqv}} = \text{Cr} + 1.5\text{Mo} + 1.5\text{W} + 0.48\text{Si} + 2.3\text{V} + 1.75\text{Nb} + 2.5\text{Al}
\]

Fig. 2-1: modified Schaeffler diagram introduced by Speidel and Uggowitzer

High nitrogen austenitic stainless steels need not only a carefully balanced chemical composition but also appropriate heat treatments to assure a fully austenitic microstructure. In fact, the presence of many different alloying elements has the disadvantage of a potential microstructure instability. Already during the solidification and afterwards during thermo mechanical processing and high temperature service a significant number of secondary phases can form in the austenitic matrix. In majority of cases formations of such phases are undesirable, due to their adverse effect on corrosion resistance and toughness, hence careful processing is needed to avoid or to minimize them.

Phase diagrams are important to predict the phases present the austenitic stainless steels. Nevertheless they have limitations due to complexity of multicomponent thermodynamic calculation and transformation kinetics that may prevent the attainment of the equilibrium phases.

The availability of software on the market, able to predict the phase diagrams of complex multicomponent system, based on thermodynamic databases provides a widely appreciated tool for various applications in materials research and alloying development.

A complete list of common precipitates, which may form in modern austenitic stainless steels, is reported in Appendix 1.

Fig. 2-2 shows an example of phase diagram for alloy Fe-23Cr-N in which the range of thermodynamic stability of the austenitic is shaded and marked by gamma [Speid01]. This diagram also shows that the high nitrogen austenite may decompose by precipitating...
chromium nitrides when annealed in the “forbidden temperature range” between 500°C and 1050°C. In order to preserve the austenitic microstructure and to prevent the precipitation of chromium nitrides, rapid cooling or, in general, water quenching from about 1050°C is necessary. If other alloying elements are present, other forms of precipitation can take place such as intermetallic phases or carbides (see Appendix 1 for more details).

Precipitation of chromium nitrides (and/or carbides and intermetallic phases) which occurs on slow cooling, annealing in the “forbidden temperature range” or long time exposure at low temperature during service results in a strong deterioration of both corrosion resistance and mechanical properties as illustrated in Fig. 2-3 [Speid01]. Such precipitation occurs primarily at grain boundaries which then become brittle and also form a corrosion path. This is the main reason to estimate in 400-500°C the upper service temperature limit for high nitrogen austenitic stainless. Often, the stability of the standard austenitic stainless steel microstructure is also considered limited because they can transform to martensite upon cold deformation or upon cooling below room temperature. In this sense high nitrogen austenitic stainless steels are fully stable because no amount of cold working or cooling will transform them partially to martensite. Therefore cold worked nitrogen steels stay nonmagnetic. Since certain applications for austenitic stainless steels rely on the absence of ferromagnetism, high nitrogen austenitic steels can be a good selection; one well-known application of this
feature of HNS is in the fabrication of “generator rotor retaining rings” for electric power plants, where high strength, high resistance to stress corrosion cracking and the absence of ferromagnetism are required [Stein99].

2.2 MECHANICAL PROPERTIES

There are many ways to increase the mechanical strength of a metal or alloy:

- solid solution hardening,
- grain boundary hardening,
- dislocation hardening,
- precipitation hardening
- strain ageing.

Nitrogen in austenitic stainless has a strong influence on all these strengthening mechanisms, making them more and more effective as the nitrogen content increases.
In this chapter only solid solution hardening by nitrogen is shown as systematic investigations of nitrogen effect on the other four strengthening mechanism were performed during this PhD work (the results are presented in Chapter 7).

Nitrogen in solid solution up to and beyond one weight percent strongly increases the yield strength and the ultimate tensile strength, as shown in Fig. 2-4 [Speid01].

![Graph showing solid solution hardening by nitrogen]  
**Fig. 2-4**: solid solution hardening by nitrogen: effect on mechanical strength

Although there is a considerable scatter in the experimental data, a square root relationship between strength and nitrogen concentration appears possible; the relations proposed are:

\[
R_{p0.2} = 150 + 500 \cdot \sqrt{N} \quad [3]
\]

\[
R_m = 500 + 500 \cdot \sqrt{N} \quad [4]
\]

The effect on nitrogen alloying on ductility is shown in fig.2-5 [Speid01].

It is remarkable that such a strong increase in mechanical strength with increasing nitrogen content does not result in a decreased ductility. This is in direct contrast to the widespread experience with other strengthening mechanisms where strength increases always at the expense of ductility.
I elongation to fracture of austenitic stainless steels 295K

\[
\begin{array}{c}
\text{nitrogen content, weight-percent} \\
0 & 20 & 40 & 60 & 80 & 100 \\
0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 & 1.2 & 1.4 & 1.6 \\
\end{array}
\]

Fig.2-6: solid solution hardening by nitrogen; effect on ductility

The origin of the scatter among the experimental data shown in Fig.2-5 and 2-6 is due to the not yet controlled grain size.
Yield strength, ultimate tensile strength and ductility of high nitrogen austenitic stainless steels show a strong dependence on grain size: smaller grains are responsible for higher mechanical strength and lower ductility.

2.3 CORROSION RESISTANCE

It has been demonstrated that the general corrosion rate of stainless steels in acids, measured in terms of weight loss per unit surface and unit time, decreases with increasing nitrogen content in solid solution [Speid91]. Moreover nitrogen alloying increases especially the resistance to localized forms of corrosion such as pitting corrosion and crevice corrosion. Other beneficial features of nitrogen alloying are the retarding effect of sensitisation and increased resistance to environment sensitive cracking, such as stress corrosion cracking, corrosion fatigue and hydrogen embrittlement.

The resistance of metallic materials to localized form of corrosion can be measured in many ways; two particularly popular tests are the potentiodynamic determination of the pitting...
potential \((E_{\text{pit}})\) and the measurement of the critical temperature, that is the temperature above which pitting corrosion or crevice corrosion is observed. The critical crevice corrosion \(T_{\text{CCC}}\) is the temperature above which crevice corrosion is observed in a 24-hour immersion test in 6 percent FeCl₃ solution.

To determine the critical pitting corrosion temperature is possible to carry out potentiodynamic tests in 22 weight percent NaCl solution at different temperatures. Results of potentiodynamic tests are schematically shown in Fig. 2-7, where at potentials more positive than a critical value \((E_{\text{pit}})\) the current density rises abruptly by orders of magnitude. Metallographic observation reveals that this rise is coincident with the formation of corrosion pits on the surface of the steel.

\[
\begin{align*}
\text{potentiodynamic electrochemical polarization curve} \\
\text{current density - potential curve} \\
\text{passivation current density} \\
pitting potential \(E_p\) \\
\text{transpassive potential}
\end{align*}
\]

Fig.2-7: potentiodynamic determination of the pitting potential \((E_{\text{pit}})\)

When such tests are repeated at different temperatures, the critical pitting potential changes as shown in Fig. 2-8 [Speid01]. The pitting potential of each particular alloy drops below the transpassive line at a critical temperature, that is the pitting critical temperature, \(T_{\text{PCT}}\). Both tests reveal that nitrogen in solid solution is highly effective in improving the resistance of stainless steels to pitting and crevice corrosion. This is illustrated in Fig. 2-9 [Speid02], where the two critical temperature are plotted against MARC (Measure of Alloying for Resistance to Corrosion, an empirical parameter dependent on alloy composition) for a large number of different austenitic stainless steels:

\[
\text{MARC} = \text{Cr} + 3.3\text{Mo} + 20\text{C} + 20\text{N} - 0.5\text{Mn} - 0.25\text{Ni} \quad [5]
\]
Fig. 2-8: determination of the critical pitting potential temperature ($T_{PCT}$)

The good fit of experimental points in Fig. 2-9 shows that the MARC correlation describes both pitting corrosion resistance and crevice corrosion resistance of austenitic stainless steels reasonably well.

This also implies that nitrogen in solid solution is twenty times more effective that chromium in increasing the resistance to these particular kinds of localized corrosion, whereas manganese and nickel are slightly negative in this respect.

MARC appears to be very useful for at least two tasks:

- to position a given steel with respect to its corrosion resistance in comparison with other steels;
- to give guidance in the development of austenitic stainless steels with optimum corrosion resistance.

The following relationships were proposed to calculate the critical crevice corrosion temperature $T_{CCC}$ and critical pitting corrosion temperature $T_{PCT}$ starting from MARC:

\[
T_{CCC} = 3.5 \cdot \text{MARC} - 65 \quad \text{in } ^\circ \text{C} \quad [6]
\]

\[
T_{PCT} = 3.5 \cdot \text{MARC} - 112 \quad \text{in } ^\circ \text{C} \quad [7]
\]

Stress corrosion cracking is a common form of failure for high strength steels (with yield strength above 1400 MPa), which were found susceptible to this attack even in water at ambient temperature. This included quenched and tempered steels, austenitic cold worked steels as well as maraging steels and precipitation hardening stainless steels [Speid91].
Certain cold worked austenitic stainless steels with nitrogen up to 1 weight percent shown no stress corrosion susceptibility in water at ambient temperature (and up to 80°C). For this reason they are used for generator-rotor retaining rings in electric power stations [Stein99]. Nitrogen in solid solution increases the resistance to stress corrosion cracking in austenitic stainless steels also in chloride solution, even in cold worked condition [Speid91]. It is well known that in hot concentrated chlorine solutions, standard austenitic and other stainless steels may fail due to transgranular and intergranular stress corrosion cracking. This has resulted in a huge number of service failures with these steels and it continues to be a problem.

In Fig.2-10 the growth rates of stress corrosion cracks in austenitic stainless steel 304 and 316 are shown for environments consisting of aerated water with 22 weight percent sodium chloride, maintained at 105°C [Speid02]. This environment is about as aggressive as that which would be expected in a seawater cooling system in dry-out conditions. Quite generally, austenitic stainless steels crack in this environment with crack growth rates of about 100 mm per year.

In contrast, austenitic stainless steels with 23 weight percent chromium and 0.75 weight percent nitrogen exhibit no such stress corrosion cracking, neither in the solution annealed condition (700 MPA yield strength) nor in the cold worked condition (1400 MPA yield strength).
Fig. 2-10: SCC of HNS in 22%NaCl solution aerated at 105°C.
3. THEORETICAL ASPECTS OF HIGH NITROGEN AUSTENITIC STAINLESS STEELS

So far HNS have been developed in such an extend that always more people, working in the field of stainless steels, cannot ignore anymore their outstanding properties that now can be properly measured and described in terms of alloy composition as shown in the previous chapter. In spite of this well known "empirical evidence" convincing theoretical explanations for nitrogen's role on the strengthening mechanisms and corrosion phenomena are still not yet available. HNS under this point of view represent a very good "terrain" for further investigations not only for metallurgists but also for physicists and chemists.

3.1 NITROGEN IN SOLID SOLUTION

Generally, solid solution hardening is due to the solute atoms size misfit, nitrogen and carbon atoms occupy octahedral interstitial sites in the crystal lattice of austenite. Distortions caused by interstitial elements in the fcc lattice act as obstacles to the movement of mobile dislocations.

Although the basic solid solution hardening mechanism by nitrogen in austenitic stainless steels is still in dispute, some concepts are based on the classical Fleischer theory of solid solution hardening in fcc materials [Uggo88, Reed88, Fleisch64, Hannes02], according to which the yield strength depends on the nitrogen concentration as shown by the following equation:

\[ R_0 = 1.77 \cdot G \cdot \sqrt{c} \cdot f_o^{3/2} \]  

[1]

where \( c \) is the concentration of the solute nitrogen atoms (at%) and \( f_o \) is a parameter to describe the interaction between dislocations and solute atoms [Haas76]. Thus \( f_o \) indicates how strong a nitrogen atoms acts as an obstacle to dislocation movements and represents the sum of the effect of lattice distortion \( \delta \) due to the misfit of the solute atoms and the modulus of elasticity change \( \eta \) with solute atom concentration change:

\[ f_o = \sqrt{\delta^2 + \eta^2 \cdot \beta^2} \]  

[2]

\( \delta = \frac{1}{a} \frac{da}{dc} \), representing the lattice distortion

\( \eta = \frac{1}{G} \frac{dG}{dc} \), representing the local modulus deviation

\( a \) lattice parameter;

\( G \) shear modulus (\( G = \frac{E}{2(1+v)} \));

\( \beta = 1/20 \) in fcc alloys;

\( \delta \sim 0.2 \) for nitrogen in solid solution

\( \eta \) depends on temperature (\( \eta \sim -0.8 \) at RT and +0.8 at 4K) [Uggo88].
The factor $\beta\eta$ is negligible small in comparison with $\delta$, thus an interacting force of $f_0=0.2$ appears reasonably correct [Uggo88].

With this magnitude the obstacle force of nitrogen atoms is about ten times higher than typical values for substitution atoms, thus showing quantitatively that nitrogen atoms are very powerful hardeners.

Nitrogen atoms have smaller atomic radius compared to carbon (0.074nm and 0.077nm respectively) but in spite of this they cause a higher dilatation in the fcc crystal lattice giving a higher strengthening effect, that cannot be completely explained only in terms of elastic distortion of the lattice.

Such behaviour originates from the peculiarities of electrons exchange in austenitic nitrogen and carbon steels [Gav96].

The crystal lattice of metals is formed by ionic cores (atomic nuclei and closed electronic shells around them) and free electrons. Interactions between atoms constituting the crystal are caused by free electrons (conduction electrons which are delocalised in the interatomic space) and the overlapping unfilled electrons shells (localised external d-electrons). Roughly, the first ones are responsible for the metallic component on interatomic bonding (characterized by high ductility and high toughness) and the second for covalent bond (responsible for the brittleness).

It was speculated that nitrogen atoms in austenite increase the concentration of free electrons, i.e. enhance the metallic component of atomic interactions; on the contrary carbon atoms contribute to the localised electron, i.e. to enhance covalent bonds [Gav96]. Higher lattice dilatation of nitrogen austenite as compared to the carbon one is expected if a weaker covalent component of interatomic bonding is present.

Another hardening concept is based on the assumption that short range ordering occurs between chromium and nitrogen atoms [Byrn87, Gav96].

Nitrogen affects the distribution of alloying elements in austenitic steels through the interstitial-substitution interactions. The distribution of solute atoms is far away from that typical for ideal solid solutions where solute atoms do not interact with each other. The distribution of solute atoms is determined by their interactions with the host atoms and other solutes. These interactions affect the homogeneity of solid solution, solubility of nitrogen and, in particular, control the temperature and sequence of precipitation from the solid solution. It is known, for example, that Ni atoms prefer to have the iron ones as nearest neighbour in iron-based austenite as Fe-Ni bonds are preferred in comparison to Fe-Fe and Ni-Ni ones, a situation described as short range atomic ordering (SRO) [Gav99].

Instead, Fe-Cr alloys are prone to short-range decomposition of solid solution, i.e. clustering of Cr atoms, as Cr-Cr bond is stronger than Fe-Cr. Even Mn and Mo in iron-based alloys are prone of clustering.

In absence of interstitials, austenitic CrNi and CrNiMn steels are prone to short range decomposition, i.e. clustering. Alloying with nitrogen diminishes this tendency whereas carbon enhances it, because the metallic bonds enhance the short range ordering and covalent bonds cause the clustering.

Nitrogen atoms in austenitic steels prefer to be neighbours of solute atoms belonging to element located left in the iron in the periodical table to form substitution-interstitial atomic complexes, such as Mo-N, Cr-N, Mn-N-Cr. The solid solution strengthening by N in austenitic steel is determined by the symmetry of these complexes and the strength of distortions induced by them in the fcc crystal lattice. Short-range ordering increases the flow stress due to the disruption of the local ordered structure; because the short range ordering is
related to the nitrogen concentration, the yield stress increases with increasing nitrogen content [Owen90].

As pointed out in section 2.2.1 a distinctive feature of nitrogen austenite is an excellent combination between strength and ductility and toughness. It has been speculated that this unusual effect of nitrogen on strength/ductility/toughness is the result of the increased concentration of free electrons with increasing nitrogen content thus enhancing the metallic component of the interatomic bonding [Gav96, Gav99]. The nitrogen-assisted metallic character of the atomic interaction in austenitic steels withstands the embrittling influence of nitrogen expected for interstitial impurities. Some authors assume that the opposite situation occurs for carbon in steels where both the carbon-induced elastic distortion and the enhanced covalent component of atomic interaction act as embrittling factors [Gav99]. However above a certain amount on nitrogen in solid solution, another phenomenon appears: the ductile to brittle transition causing brittleness of austenitic steels even at room temperature. This phenomenon is explained in more details in section 3.5, as it fixes the maximum content of nitrogen in solid solution that can be tolerated in order to achieve high toughness at room temperature.

3.2 NITROGEN AND PLASTIC DEFORMATION

The interaction of nitrogen atoms with dislocations plays an important role in the strengthening of austenitic steels. It has been reported that nitrogen atoms lock dislocations more effectively than carbon; the binding energy between nitrogen atoms and dislocations increases with increasing the nitrogen content in austenite, whereas such trend supposedly is not found for carbon [Gav99]. This results in a stronger obstacle for the dislocation slip. The main contribution to the interaction between dislocations and impurity atoms is provided by elastic distortion of the lattice. The stress fields created by edge and screw dislocations results in the formation of interstitial clouds in the vicinity of the nuclei of such dislocation (Cottrel clouds). In nitrogen austenitic steels the formation of Cottrell clouds, obeying the exponential temperature dependence (as reported by many authors [Gav99, Uggo91, Uggo88]) is the controlling mechanism for interstitials-dislocation interaction. A further contribution is the chemical interaction, i.e. the formation of Suzuki’s clouds at stacking faults. Even if nitrogen atoms induce higher distortion in the fcc austenite than the carbon ones, the elastic contribution to the interaction of interstitial atoms with dislocations in austenitic steels is not a unique factor determining the pinning of dislocations. Additional dislocation pinning is caused by electrostatic interaction between interstitial atoms and dislocations. It has been speculated that nitrogen atoms in austenite are negatively charged and carbon atoms carry a positive electric charge [Gav99], whereas dislocation nuclei are positively charged. Therefore an electrostatic attraction between nitrogen atoms and dislocations has to exist in addition to the elastic one, whereas in the carbon austenite, the elastic attraction, as compared to nitrogen, has to be counterbalanced by the electrostatic repulsion. These small additions of opposite sign to the prevailing elastic interaction can possibly explain the observed higher pinning of dislocation in austenitic steels by nitrogen atoms as compared to carbon ones.
Nitrogen in solid solution produces also remarkable change in dislocation structure during plastic deformation [Müll93]. While nitrogen free austenite exhibits a homogeneous cellular dislocation structure during plastic deformation, nitrogen assists planar dislocation and deformation twinning; both factors resulting in higher work hardening rate and response to ageing. According to some scientists, this change in the slip behaviour can be explained by the effect of nitrogen on the stacking fault energy (SFE) [Gav88,Gav99,Schr75]. Dislocations in austenitic steels are usually split, i.e. they consist of stacking faults limited by two partial dislocations. Stacking faults are errors in a normal sequence of atomic planes (ABCABC... of the fcc or ABAB.... of the hcp lattice). The SFE depends strongly on the chemical composition of austenitic steels, although no quantitative relationship has been proposed until now. Lower stacking fault energy leads to wider partial dislocation separation, reduced cross-slip and climbing, making planar slip the most common way of deformation. Low SFE also leads to a pronounced twinning during deformation, making this deformation mechanism possible even for low strain applied. After heavy deformations, many very fine deformation twins are observed. Twins within twins are generated, in a process described as "second order twinning" activated by the stress field of primary twins [Müll94b]. Both primary and secondary twins are effective obstacles for moving dislocations and further twinning, and therefore contribute effectively to cold work hardening.

Planar slip is attributed not only to low stacking fault energy but also to short-range atomic order in austenitic nitrogen steels. Short range ordering in the alloys assists planar slip because each successive dislocation needs a lower stress to pass over the slip plane as compared to the first one which passes through the ordered crystal and consumes an additional energy to shift the atoms from the low energy sites. Thus, in spite of the real mechanism involved, planar slip and twinning appear to be the two main features of deformed high nitrogen austenite responsible for high flow stresses and high work hardening rates observed in high nitrogen deformed alloys.

3.3 NITROGEN AND GRAIN BOUNDARY

The yield strength of high nitrogen austenitic stainless steels in function of grain size is usually expresses by the Hall-Petch equation:

\[ R_{0.2} = R_o + k_y \cdot \frac{1}{\sqrt{d}} \]  

where \( R_o \) is the friction stress for dislocation movement inside the grains, \( k_y \) is a coefficient describing the effectiveness of grain boundary hardening and \( d \) is the average grain size. The nitrogen contents and the temperature markedly affect \( k_y \) [Hannes02]. With higher nitrogen contents the grain size hardening becomes stronger; at low temperatures the grain size hardening of nitrogen is more effective. At high temperature the effect of nitrogen is small and disappears at about 550°C when recovery takes place [Uggo88].
Many theories were proposed to explain the Hall-Petch equation; they can be divided in three main groups based on the critical role of:

1. planar dislocation arrays,
2. work hardening,
3. grain boundary sources.

1. Planar dislocation arrays theories
Grain boundaries are obstacles to dislocation movement. Slip in one grain of a polycrystalline material does not spread into a neighbouring grain by simply forcing a dislocation through the boundary. Hall (1951) and Petch (1953) postulated the formation of dislocation pile-ups at the grain boundaries causing a stress concentration \( \tau^* = n \tau \) at the head of the dislocation pile-ups, where \( n \) is the number of dislocations in the pile-up and \( \tau \) is the shear stress applied. If \( \tau_i \) is the friction stress inside the grains the stress concentration becomes \( \tau^* = n (\tau - \tau_i) \).

Plastic deformation will occur in the next grain if \( \tau^* > m \tau_0 \) where \( \tau_0 \) is the critical shear stress necessary to unlock the dislocation source in the adjacent grain and \( m \) is an orientation factor (Cottrel 1958).

The number \( n \) of dislocation in the pile-up of length \( L \) can be calculated by:

\[
    n = \frac{\pi \cdot L}{b \cdot G} \left( \frac{\tau - \tau_i}{\tau} \right)
\]

where \( b \) is the Burgers vector and \( G \) is the shear modulus.

If \( L \) is proportional to the average grain size \( d \) then the Hall-Petch relationship is found:

\[
    \tau^* = n (\tau - \tau_i) \geq m \cdot \tau_0
\]

\[
    \tau_f = \tau_i + \left( \frac{G \cdot b \cdot m \cdot \tau_0}{\pi} \right)^{1/2} \frac{1}{\sqrt{d}}
\]

where \( \tau_f \) is the flow shear stress.

Multiplying equation [5] with the average orientation factor of fcc polycrystalline materials, the Taylor factor 3.06, the relation [5] is equal to [3] with:

\[
    R_{p02} = 3.06 \cdot \tau_f
\]

\[
    R_o = 3.06 \cdot \tau_i
\]

\[
    k_y = 3.06 \left( \frac{G \cdot b \cdot \tau_0}{\pi} \right)^{1/2}
\]

2. Work hardening theories
In the cold work hardening model one postulates a stress independent \( \sigma_0 \), a parabolic stress-strain relation \( \sigma \sim \sqrt{\varepsilon} \) and a linear relation between the Hall-Petch slope \( k_y \) and the square root of strain, \( k_y \sim \sqrt{\varepsilon} \). A linear relation between the yield stress and the square root of the dislocation density is accepted as an experimental fact [Honey81]. According to the work hardening model, the dislocation density is increased with decreasing grain size according
which leads to the Hall-Petch relation and therefore the term $k_y \cdot d^{1/2}$ is attributed to work hardening.

This model was supported by the theory proposed by Ashby [Ashby70], in which a higher dislocation density at the grain boundaries as compared to the grain core can explain strengthening by a barrier effect of these grain boundary layers of increases dislocation density leading to a grain size dependent contribution to the work hardening of polycrystalline materials.

3. Grain boundary sources

In the grain boundary source theory the Hall-Petch relation is determined by the capacity of grain boundaries to emit dislocation under loading [Li70]. This approach does not require a stress concentration created by pile-ups and in contrast to the work hardening model the hall-Petch slope $k_y$ does not depend on the strain.

Most modern attempts to understand the effect of nitrogen and temperature on the Hall-Petch coefficient $k_y$ are based on the pile-up of dislocation on grain boundaries theories.

In high nitrogen austenite the slip behaviour of the dislocations becomes more planar with increasing nitrogen content, planar slip is expected to increase the grain boundary efficiency to look the dislocations because preventing cross-slip and others dynamic recovery processes the grain boundary becomes a more difficult obstacle to be overcome. The grain boundary hardening contribution to the yield strength of high nitrogen austenitic steels can be calculated in this way [Uggo88, Uggo92b]:

$$\Delta R_{p02} = \left( 8 + 75 \left[ 1 - \left( \frac{T}{823} \right)^{3/2} \right] C_N \right) \frac{1}{\sqrt{d}} = k_y \cdot \frac{1}{\sqrt{d}}$$  \[6\]

$C_N$ nitrogen concentration in weight percent and $d$ average grain size in mm.

Recently, taking into account that nitrogen atoms in austenite reveal a strong interaction with dislocations (more than carbon), a new theory based on the Cottrell's model was proposed [Gav99]. According this new model the contribution of nitrogen to grain boundary strengthening is provided by a strong interaction of nitrogen atoms with dislocations. Such interaction can be strong enough to lock dislocation sources, which have to be initiated in adjacent grains for the transfer of plastic deformation from one grain to others, a process that requires an increased applied stress.

3.4 STRAIN AGEING HARDENING

A low temperature heat treatment on cold worked high nitrogen austenitic stainless steels, in the range 300-600°C, results in a significant increase in strength. Depending on nitrogen content and amount of cold deformation a strength improvement up to 500 MPa can be achieved [Uggo91]. This strengthening is caused by "strain ageing" as a results of a chemical interaction between nitrogen atoms and dislocations.
The chemical interaction is determined by the enhanced nitrogen solubility in the stacking fault. The binding energy is influenced by the width of dislocation separation. Assuming that nitrogen reduces the stacking fault energy, a stronger interaction at higher nitrogen contents is expected. The segregated nitrogen atoms in the stacking fault again reduce the stacking fault energy, leading to a wider separation of the partial dislocations and therefore to reduced energy of the whole dislocation arrangement. Thus, the nitrogen segregation ("Suzuki atmosphere") will pin the dislocations.

At room temperature the nitrogen atoms are more or less immobile. Dislocations generated during cold deformation are not pinned and dislocations are still mobile. After ageing at low temperature Suzuki atmosphere are formed, yielding strong dislocation pinning. These pinned dislocations will acts as a barrier against subsequent deformation. This results in an increase in strength.

At temperature above 600°C nitrides precipitate, resulting in a decrease in dislocation pinning and a corresponding decrease in strength; whereas below a certain temperature, approximately 300°C, diffusion of nitrogen atoms practically ceases to occur within any useful time frame. Therefore, in order to maximize the strength, a proper combination of time and temperature has to be found [Uggo91].

3.5 TOUGHNESS AND DUCTILE TO BRITTLE TRANSITION

Up to 0.8 weight percent nitrogen in solid solution the fracture toughness of solution annealed austenitic steels remains very high (>200 MPa·m^{1/2}) when measured at ambient temperature [Speid91]. However at cryogenic temperatures, a ductile to brittle transition is observed resulting in cleavage cracking of the face centred cubic crystals. The transition from ductile to brittle fracture, usually well known only for ferritic materials, is a peculiarity of high nitrogen austenite [Uggo92, Müll94, Vogt94].

The temperature at which this transition occurs (ductile to brittle transition temperature T_{DBTT}) is strongly affected by nitrogen and carbon concentration in solid solution, as shown in Fig. 3-1, and the following empirical expression, see Fig. 3-2, was proposed by M.O. Speidel [Speid02]:

\[
T_{DBTT} = 300 \cdot N + 100 \cdot C
\]

In order to avoid the transition near room temperature the sum of nitrogen and carbon content must be restricted to about 1 weight percent fixing a practical limit for nitrogen alloying in austenitic HNS. Grain size is reported to have an insignificant effect on ductile to brittle behaviour [Tomo90, Uggo92], which is quite different from the behaviour of bcc materials where conventional cleavage is observed, in which grain refining is always accompanied by increasing in toughness. In HNS cleavage fracture is observed along the crystallographic planes (111), i.e. along the slip planes, that is why it is described as a "slip band cleavage-like cracking", pure cleavage would results in (001) fracture planes. The appearance of ductile to brittle fracture depends on what limit is first reached: the flow stress \( \sigma_f \) or the cleavage fracture stress \( \sigma_T \) [Honey81].
ductile to brittle transition phenomena in HNS

Fig.3-1: ductile to brittle transition temperature on N and C content [Speid02]
The fracture mechanism in high nitrogen austenite is considered as slip band and/or twin boundary cracking, caused by two peculiarities these steels:

- a strong planarity of the dislocation structure (dislocations are concentrated on distinct slip planes) and a high density of deformation twins, loading to a high level of internal stresses and therefore to an apparent decreases of the (111) fracture stress \( \sigma_f \);
- a strong temperature dependence of the yield stress, hence flow stress \( \sigma_y \) [Uggo88, Uggo92] (for normal low nitrogen austenite the cleavage fracture stress is rather high and slightly depending on the temperature, whereas the flow stress changes weakly with the temperature, thus cleavage fracture usually does not occur).

In high nitrogen austenitic steels formation and growth of cleavage fracture is strongly connected to locally concentrated plastic deformation. A cleavage crack could be formed because of the intersection between slip bands and deformation twins with grain boundaries, slip bands and twin boundaries.

The cleavage fracture stress can be calculated by means of this relation:

\[
\sigma_f = A \frac{G \cdot \gamma}{k_y \cdot \sqrt{d}}
\]

\( K_y \) Hall-Petch slope coefficient, \( G \) shear modulus, \( \gamma \) surface energy, \( d \) grain size, \( A \) constant.

Accordingly, the cleavage fracture stress will be low with low surface energy \( \gamma \), high \( K_y \) and coarse grain.

Assuming a slip plane fracture as a fracture mode, the following mechanism was proposed [Uggo92].

In a favourably oriented grain a slip band is formed. The slip band is the more pronounced the higher the nitrogen content. Since cross slip is restrained, the plastic deformation is restricted to this peculiar area of structure; i.e. the density of piled up dislocations increases rapidly. As a consequence of this high density of lattice defects, high internal stresses may occur. A remarkably high stress concentration results at intersections of slip bands and twins. In addition to the applied tensile force component, these deformation induced internal stresses cause a final cleavage separation in the tensile mode.

This implies that the plastic deformation necessary for crack forming is lower in steels with distinct planar slip; because of the slip (and stress) concentration i.e. a macroscopically smaller deformation may lead to crack formation in high nitrogen steels. Since the work done in deformation has to be taken into account for the calculation of the specific “surface energy \( \gamma' \)”, \( \gamma \) is expected to be smaller with high nitrogen content. Furthermore, a temperature dependence of \( \gamma \) is expected, because it is assumed that low temperatures increase the concentration of slip on distinct planes. Applied to high nitrogen steels, this means that the fracture stress \( \sigma_f \) decreases with increasing nitrogen content and decreasing temperature, if the grain size \( d \) remains constant.

On the base of these mechanisms, the effect of nitrogen and grain size on the ductile to brittle transition can be understood comparing the flow stress \( \sigma_y \) and the cleavage fracture stress \( \sigma_f \).

Low nitrogen content leads to a low flow stress with weak temperature dependence and the fracture strength is high. High nitrogen content, on the other hand, results in high flow stress...
and a low fracture stress. Leaving the grain size constant, this causes a shift of the $T_{DBTT}$ to higher values according to Fig. 3-3a.

A change in grain size, leaving the nitrogen content constant, has no strong effect on the transition temperature. Finer grain affects the flow stress and the cleavage fracture stress in the same way; it shifts both curves to higher values. The intersection of the two curves, and accordingly the ductile to brittle transition temperature, remains approximately at the same level of temperature (Fig. 3-3b).

![Fig. 3-3: schematic effect of nitrogen content (a) and grain size (b) on the ductile to brittle transition temperature $T_{DBTT}$ (stress state and loading rate effects not included)](image)

### 3.6 CHEMICAL PROPERTIES

Passivity is the origin of good corrosion resistance of stainless steels and it is based on thin surface film formation acting as diffusion barrier and having specific electrical properties exerting, thus, a profound influence on the corrosion rates of metals and alloys. Passive properties of the film are related to its chemical composition, thickness, crystal and defect structure, electrical properties and mechanical properties.

Four existing hypothesis interpreting the corrosion behaviour of nitrogen steels were summarised by Speidel [Speid91]:

- nitrogen segregates to the metal surface as other metal elements dissolve preferentially, leaving a nitrogen enrichment at the surface improving the passivity;
- nitrogen is incorporated into the passive oxide film to form a dense protective oxynitrided layer;
- nitrogen in the steels dissolves to form nitrides or nitrates which act as local inhibitors;
- nitrogen dissolves during corrosion reaction to form ammonia, which increases pH and renders the electrolytes at the pit sites, inside the crevices and cracks less acid.

Corrosion resistance of stainless steels is based on their chromium content, which after certain heat treatments can locally decrease on the grain boundaries due to carbide/nitride precipitation (sensitization) leading to intergranular corrosion attack. The high resistance to sensitization of high nitrogen austenite is related to [Hänn99, Gav99]:

$$\sigma_y \text{N}_{\text{low}} \quad \sigma_f \text{N}_{\text{low}} \quad \Delta T_{\text{DBTT}}$$

$$\sigma_y \text{N}_{\text{high}} \quad \sigma_f \text{N}_{\text{high}}$$

$$\sigma_y \text{D}_{\text{high}} \quad \sigma_f \text{D}_{\text{small}} \quad \Delta T_{\text{DBTT}}$$

$$\sigma_y \text{D}_{\text{small}}$$
• weak tendency of nitrogen to form grain boundary segregations in steels as compare to carbon;
• retardation of nucleation and/or growth of Cr-rich carbides (a more homogenous solid solution alloying with nitrogen is achieved by short range ordering);
• changes in the activity of Cr in equilibrium with the carbide;
• nitrogen enhanced passivation, i.e. more Cr-depletion is required to failure;
• prevention of $\alpha'$ martensite formation along the grain boundaries due to the austenite stabilizing effect of N.

The beneficial effect of N on carbide sensitization is only possible if the solubility limit of N is not exceeded, since Cr$_2$N precipitation may lead to localize depletion in Cr and a reduction in corrosion resistance. Therefore, in general this retarding effect is only observed up to a certain content of N.

In high nitrogen steels, N has been observed to retard the precipitation of intermetallic phases, which are also very detrimental for corrosion properties due to local Mo and Cr depletion in the matrix immediately surrounding the intermetallic phases.

Pitting type of corrosion precedes SCC of austenitic stainless steels in hot chloride solutions and therefore the elements that suppress pitting corrosion such as Mo and N should also reduce the susceptibility to SCC in these environments. Also the increased austenite stability due to alloying with nitrogen, which does not transform into martensite upon severe plastic deformation, may explain the increased resistance to stress corrosion cracking of cold worked nitrogen austenite.
4. PRODUCTION ROUTES OF HIGH NITROGEN STAINLESS STEELS

Melting practice for High Nitrogen Steels, since the beginning of their invention has two problems:

1. how to introduce high nitrogen contents into the melt;
2. how to keep nitrogen in solid solution during the process of solidification thus avoiding porosities in cast ingots.

To overcome these problems, nitrogen solubility evaluation models in the liquid state and solid state as well as different manufacturing routes were developed.

Nitrogen can be added in many ways. It may come from molecular or ionised gas atmosphere at normal or elevated pressure, it may be offered by nitride ferro-alloys (FeCrN, FeMnN, FeVN, CrN, MnN) or highly concentrated ceramic nitrides (S13N4). Introduction may be directly into the melt or indirectly through the slag [Feich99].

Independently of the nitrogen source used, the dissolution of nitrogen in iron-based alloys can be described by the reaction:

\[
\frac{1}{2} N_{2(g)} \leftrightarrow [N]_{(s)} \quad [1]
\]

where the equilibrium constant \( K_N \) for reaction [1] can be written as

\[
K_N = \frac{a_N}{P_{N_2}} = \frac{f_N \cdot [\%N]}{\sqrt{P_{N_2}}} \quad [2]
\]

\( a_N \) activity of N dissolved in alloy;
\( P_{N_2} \) nitrogen partial pressure;
\( f_N \) nitrogen activity coefficient;
[\%wt] nitrogen solubility in weight percent.

Nitrogen solubility for pure iron is very small (~0.045wt% @ 1550°C 1bar) but may be significantly improved through the addition of the alloying elements which decrease the nitrogen activity \( f_N \) such as chromium and manganese.

Detailed evaluations related to study the influence of different alloy elements on the nitrogen solubility in pure iron [Schü67] as well as in multicomponent iron base materials were carried out [Zhen91, Kunz94, Kow00], investigating the basic behaviour of the alloys. Zheng [Zhen91] quantified the influence of the alloying elements in the solid phases. Equations [3] and [4] give the mathematical description of the thermodynamic influence of the alloying elements, the temperature and the partial pressure as given by Zheng:

\[
\log f_N = \sum e_N X_i \cdot [\%X_i] + \sum r_N X_i \cdot [\%X_i]^2 + \sum r_{N,j} X_i \cdot [\%X_i] \cdot [\%Y_j] \quad [3]
\]
The interaction parameters $e_N$ and $r_N$ for different alloy combination were determined by Zheng and may be found in Appendix 2.

Based on these theories and investigations, it was possible to evaluate the nitrogen solubility in the alloys of interest.

Nowadays all this information is available in software packages like ThermoCalc, based on databank of experimentally obtained data in which, the accuracy of the results is directly connected to the accuracy and exhaustiveness of the databank used.

At atmospheric pressure the solubility of nitrogen is function of alloy composition and temperature. During cooling nitrogen solubility increases with decreasing temperature, but abruptly decreases just below the solidus due to formation of bcc $\delta$ ferrite (see Fig. 4-1).

\[
\log[\%N] = \log K_N - \log f_N + \frac{1}{2} \log P_{N_2} \quad [4]
\]

The sudden decrease of nitrogen solubility (solubility gap) may result in pore formation and loss of nitrogen. This problem during solidification has long been a major obstacle in the manufacturing of HNS.

To overcome the "solubility gap problem", the nitrogen content of molten iron alloys can be increased beyond the solubility limit at atmospheric pressure by raising the nitrogen partial pressure melting under pressure (pressure metallurgy).

Among different pressure metallurgy production routes developed in different countries, the more popular are:

- pressurized electroslag remelting furnaces (PESR);
- pressurized induction furnaces (counter pressure casting);
- plasma arc remelting furnaces (PAR);
- arc slag remelting furnaces (ASR).
The first two are routinely used among HNS producers around the world, whereas the last two have found limited applications.

Another way to overcome the “solubility gap” is to use the powder metallurgy route, as the nitrogen solubility in HNS is always higher in the solid phase than in the liquid state, see Fig.4-1.

Therefore, instead of adding nitrogen in the liquid state it may be introduced into a steel powder thermally by diffusion or mechanically by milling; subsequently powder is compacted to give a pre-shape or a near-net shape products with a wide range of nitrogen content.

While all these manufacturing routes sounds quite “exotic” and “expensive”; this can explain why in spite of a good knowledge, accumulated since the end of the 60s, on favourable effects by nitrogen alloying in austenitic stainless steels, HNS have been not extensively used and adopted in large quantities yet.

This situation is expected to change in the near future if HNS could be made using conventional equipments, increasing the nitrogen solubility at atmospheric pressure and avoiding the “solubility gap” during solidification.

This can be done with a carefully chemical composition, adding elements with a negative interaction parameter and avoiding those of positive sign; in this way nitrogen activity is lowered resulting in an increased solubility by more than two orders of magnitude. Fig.4.2 shows the effect of different alloying elements on nitrogen solubility.

![Fig.4-2: suitable elements for HNS metallurgy arranged in the periodic system [Feich99]](image)

The strongest nitrogen solubility promoter’s elements: titanium, zirconium, vanadium and niobium (see Fig.4.2), can hardly be used, because of low solubility of their respective nitrides in the solid state, which may lead to indissoluble embrittling precipitates (coarse primary nitrides form directly into the liquid).

Chromium, manganese and molybdenum are the only elements that increase the nitrogen solubility with a moderate tendency to form nitrides (compare the others ones). Among them Cr and Mn are the most effective.

In order to increase the nitrogen solubility up to 0.5 weight percent, chromium contents higher than 25 weight percent are necessary, but it is not possible to add so much chromium alone because of intermetallic phases precipitation.

The situation for high chromium contents does not improve adding molybdenum, because also this element stabilizing the bcc structure increases the risk of pore formation.
The solution is to use Cr and Mn together, as manganese is the only alloying element in austenitic steels that increases the nitrogen solubility and can stabilize the austenitic phase within certain composition limits [Speid87], reducing the risk of pores formation.

The modified Schaeffler diagram, introduced by Speidel and Uggowitzer for high chromium steels [Speid87] shown in Fig. 2-1, is the tool to design high nitrogen austenitic stainless steels produced without overpressure, with Cr, Mn, C and N content adjusted in order to assure a fully austenitic structure.

Small carbon additions were found beneficial to extend austenitic phase field towards lower temperature, increasing the phase stability, at least until when \(\text{M}_2\text{C}_6\) carbides precipitation does not take place [Coba02, Shan02].

Small addition of molybdenum (1–2 wt%) can be tolerated, in same circumstances, with the aim to improve the corrosion resistance.

Nitrogen up to 0.8 weight percent in solid solution, without pore formation during solidification, was successfully achieved in the system Fe-Cr-Mn-C-N. For nitrogen content higher than 0.8 weight percent, porosity during solidification becomes again a problem, and only small addition of nickels (< 4 wt%) prevented their formation.

Fig. 3 summarizes schematically alloy design for high nitrogen austenitic stainless steel produced without overpressure; an austenite free of porosities is achieved when the CrMnNi and eventually Mo contents are correctly balanced.

For these reasons ultrahigh strength austenitic stainless steel with high nitrogen amounts belong to the multicomponent system Fe-Cr-Mn-Ni-C-N, and they can be made with these facilities:

- Electroslag Remelting Furnace (ESR);
- Induction or Electric Arc Furnaces, blowing \(\text{N}_2\) instead of \(\text{Ar}\) during the refining process in the Argon Oxygen Decarburisation (AOD) converter.

Fig. 4-3: schematic effect of main alloying elements used for high nitrogen austenitic stainless steels on austenite stability, pore formations and nitrogen solubility.
5. AIM OF THIS PhD PROJECT

One target of this ph.D. project was to show how new ultrahigh nitrogen austenitic stainless steels, containing up to 1.4 weight percent nitrogen in solid solution, can be designed to be made by "ingot metallurgy" without overpressure, using conventional equipment, with appropriate amounts of chromium and manganese and small addition of nickel (to avoid pores formation at the higher nitrogen content during solidifications), the basis being iron.

The starting point for these researches was the high nitrogen austenitic stainless steel with composition Fe23Cr16Mn0.17C0.72N, developed at the ETH Institute of Metallurgy by Prof. Markus O. Speidel.

High strength austenite can be achieved superimposing different strengthening mechanism, such as solids solution hardening, grain boundary hardening, dislocation hardening and static strain ageing.

With the aim to optimise each mechanism a number of questions arise which need to be elucidated.

Taking into account that a minimum carbon content is necessary to extend the austenitic single phase region at low temperature, is it possible to decrease the carbon content and increasing nitrogen in solid solution avoiding the ductile to brittle transition near room temperature, getting the best from solid solution hardening by nitrogen?

Is it possible to obtain small grains adding niobium and vanadium without adverse effects on toughness and corrosion resistance?

Which are the minimum grain sizes that can be achieved by means of static recrystallization heat treatment in bulk materials and in small samples?

Does a "practical limit" for grain boundary hardening exists beyond which this strengthening mechanism cannot be used due to adverse effects on some mechanical properties like ductility? toughness?

Is the ductile to brittle transition temperature really independent on grain size?

Which is the highest mechanical strength in high nitrogen austenitic stainless steels that can be achieved superimposing all four strengthening mechanism (solid solution hardening, grain boundary hardening, dislocation hardening, precipitation hardening)?

Which is the behaviour of high nitrogen steels during hot rolling?

Is it possible to improve furthermore the mechanical strength by dislocation hardening using this processing route for wrought products?

Answers to these questions can be found in what follows.
6. HIGH NITROGEN AUSTENITIC STAINLESS STEELS MICROALLOYED WITH NIOBIUM AND VANADIUM

6.1 SCOPE

In this chapter results of investigations related to increase the mechanical strength, without adverse effect on toughness, in high nitrogen austenitic stainless steels with fix nitrogen content in solid solution by grain boundary hardening are described. In order to obtain small austenitic grains the primary grain refining mechanism is the recrystallization of austenite during hot deformation. However, in austenite devoid of second phase particles, the high temperature involved in hot rolling or hot forging leads to marked grain growth with the result that grain refining during subsequent working is limited. The situation is greatly improved if fine particles (such as carbides, nitrides or carbonitrides) are introduced into the austenitic matrix.

The theory of grain boundary pinning by particles defines the critical size of particles below which pinning is effective. The control of grain size at high austenitizing temperatures requires as fine precipitates as possible on the grain boundaries [Honey81].

The best grain refining elements are strong carbide and nitride formers, such as niobium and vanadium. As both carbon and nitrogen are present in high nitrogen austenitic stainless steels, the most effective grain refining compounds are the respective carbonitrides.

More stable nitride former elements, such as titanium and aluminium, were not considered in this work because all alloys were produced by ingot metallurgy at atmospheric pressure and by this route it is not possible to avoid formation of TiN and AlN in the liquid phase. These nitrides, due to a different specific weight in comparison with the rest of the melt, float on the liquid and thus are not homogeneously distributed in the austenite after the solidification. Indeed after casting they are coarse and cannot be dissolved by a subsequent heat treatment, resulting in poor mechanical and chemical properties.

Vanadium and niobium react less harmfully than titanium and aluminium in this respect. If niobium and vanadium carbonitrides are useful to control the grain growth, their precipitation into the austenitic matrix results in a toughness reduction, which can be tolerated only if it is not severe. To achieve this goal the degree of solubility that such stable compounds have in austenite is important and it was investigated.

In carbon-containing high nitrogen austenitic steel, carbon is used to extend the austenite single phase region, but high carbon contents may result in M23C6 carbides precipitation at low temperature, with adverse effect on toughness. A compromise between these two carbon effects was analysed in order to still have high toughness values.

6.2 MATERIALS AND METHODS

On high nitrogen low nickel austenitic stainless steels with 0.75wt% nitrogen in solid solution, the effect of different carbon contents (0.08 - 0.2wt%), niobium contents (0.02 - 0.3wt%) and vanadium contents (0.3 - 1wt%) on strength, toughness, ductile to brittle transition and corrosion resistance was investigated.

The thermal stability of the austenite against precipitation of Cr2N and/or M23C6 on the grain boundaries was investigated by means of thermodynamic simulation using the software
package ThermoCalc (the new “TCFE Thermocalc Alloy Database for Steel 2000” was used) and experimental tests.

The chemical composition of alloys investigated is reported in Tab. 6-1 (Appendix 4).

In alloys containing vanadium the nitrogen content was chosen in order to have 0.75wt% nitrogen in solid solution and the rest in compound state as vanadium carbonitrides; depending on vanadium content this amount of nitrogen was chosen in stoichometric way.

All the alloys were cast into 3 Kg ingots, homogenized at 1250 °C for 6 hours and water quenched, then hot forged to plates with a thickness of 16 mm. Sections were cut from the hot forged plates and solution annealed at different temperatures for one hour and water quenched. After each heat treatment, specimens for tensile test, impact energy test and metallographic investigation was machined.

In order to study the influence on the mechanical strength of grain size, heat treatments of static recrystallization on cold worked round bars with a diameter of 10 mm were carried out. Cold deformation was performed using a swage forging machine starting from 15 mm diameter bars, machined from the initial hot forged plates, for a final degree of cold working of 56%. The holding time used during SRX heat treatment was in the range of twenty minutes to four hours.

6.3 RESULTS

6.3.1 NITROGEN AND CARBON IN SOLID SOLUTION

6.3.1.1 TOUGHNESS

The results of impact energy tests performed on alloys with different carbon content are shown in Fig. 6-1.

Curves in Fig. 6-1 show a same typical trend: for annealing temperature higher than a critical value the toughness, measured as impact energy, is high and tend to remain more or less stable with increasing the annealing temperature. As the annealing temperature decreases below a critical values a suddenly drop in impact toughness toward very low levels is observed.

Metallographic observations and thermodynamic simulations by Thermocalc have shown that such behaviour at low temperatures is due to precipitation of M23C6 carbides or Cr2N nitrides along the grain boundary, with typical morphology shown in Fig.6-2a/2b. Chromium nitrides were found to precipitate in cellular form (a morphology called “false perlite”) in agreement with the literature of precipitation phenomena in HNS (see Appendix1).

The highest toughness levels are typical of a fully austenitic microstructure.

The curves in Fig. 6-1 show little difference in toughness above 1000°C for different carbon content, whereas big difference appears at lower annealing temperatures.

These results can be understood analysing the carbon effect on the single-phase γ region in phase diagram for the system Fe-Cr-Mn-C-N calculated by ThermoCalc.

Phase diagrams in Fig. 6-3 show how carbon extends the single-phase austenite field. As a drawback the line for M23C6 carbides precipitation shifts towards high temperature with increasing carbon content (compare Fig. 6-3a/b/c/d). For carbon content near to 0.1wt% (Fig.6-3c) such line is tangent at the deepest point of the austenitic field (point A). Under this condition the highest thermodynamic stability of the austenite is achieved, being limited at low temperature only by Cr2N precipitation function of the nitrogen content.
Fig. 6-1: Effect of different carbon contents on the toughness of steels annealed at different temperatures ($T_{\text{ann}}/1^h/\text{H}_2\text{O}$).

Fig. 6-2: Examples of precipitation phenomena to avoid in HNS:
- a) $M_{23}C_6$ carbides along grain boundaries in Fe$_{23}$Cr$_{16}$Mn$_{0.17}$C$_{0.72}$N$_{0.1}$ at $950^\circ\text{C}/1^h/\text{H}_2\text{O}$;
- b) Cr$_2$N nitrides (false perlite) in Fe$_{23}$Cr$_{16}$Mn$_{0.17}$C$_{0.72}$N$_{0.1}$V$_{0.6}$ at $950^\circ\text{C}/1^h/\text{H}_2\text{O}$.

For carbon content higher than 0.1 wt%, Fig. 6-3d, the $M_{23}C_6$ precipitation line penetrates into the austenitic field, and a single-phase austenite exist only at higher temperature.
Fig. 6-3 (below): phase diagrams of alloys Fe 23Cr 16Mn xC yN calculated by ThermoCalc.

(a) C = 0%

(b) C = 0.05%
c) $C = 0.10\%$

d) $C = 0.20\%$
6.3.1.2 YIELD STRENGTH AND ULTIMATE TENSILE STRENGTH

The yield strength and the ultimate tensile strength as function of the grain size are shown in a Hall-Petch type diagram in Fig. 6-4.

![Hall-Petch diagram](image)

Fig.6-4: effect of different carbon contents and grain sizes on tensile properties (continuous lines and dotted lines are the Hall-Petch type correlation for alloys with 0.20C and 0.10C 2Ni respectively).

With different cold working facilities and static recrystallization heat treatments, grain sizes in the range 10–200 μm were achieved.

The elongation to fracture for all the alloys investigated was in the range 45–60%.

Fig. 6-4 shows a difference in the level of strength between the alloy with lowest and highest carbon content; this reduction in mechanical strength was most likely due to a reduction of the solid solution hardening effect by carbon, as the nitrogen content was kept constant.

6.3.1.3 DUCTILE TO BRITTLE TRANSITION

Nitrogen and carbon are known to have a strong influence on the ductile to brittle transition temperature ($T_{DBT}$) in high nitrogen austenitic stainless steels [Müll94,Uggo92,Vogt94].

For $C + N > 1$wt% in solid solution the transition occurs at room temperature or above [Uggo96].

Impact energy tests at different temperature, from -198°C to RT (25°C), were performed on samples cut from the hot forged plates and annealed at 1050°C/1h in order to achieve fully austenitic microstructure.

The results are shown in Fig. 6-5, where the shape of the curves shows the typical “ductile to brittle transition” behaviour of HNS, with a rapid decreasing in impact energy from high to low values with decreasing the testing temperature.
The temperature at which this transition occurs ($T_{DBTT}$) is reported in Fig. 6-6. $T_{DBTT}$ decreases with decreasing carbon content and in particular, with 0.1 wt% carbon the transition appears only at $-100^\circ$C.

As a carbon content nearly 0.1 wt% is requested in order to have a good stable austenite, the reduction on tensile strength, shown in Fig. 6-4, can be counterbalanced adding more nitrogen in solid solution. In fact, starting from such a low ductile to brittle transition temperature, it is still possible to increase the nitrogen content up to 0.8-0.9 wt%, balancing the other alloying elements Cr, Mn and Ni to avoid porosities in the cast ingots, with positive effect on the strength, keeping the $T_{DBTT}$ still below room temperature and getting the best from solid solution hardening by nitrogen.

---

**Fig. 6-5:** carbon effect on ductile to brittle transition phenomena.

**Fig. 6-6:** ductile to brittle transition temperature ($T_{DBTT}$) in function of carbon content with 0.75 wt% nitrogen.
6.3.2 GRAIN REFINING BY NIOBIUM

6.3.2.1 TOUGHNESS

The results of impact energy tests performed on alloys with different niobium and carbon content are shown in Fig.6-7.

![Impact energy test results](image)

Fig. 6.7: effect of different niobium contents on the toughness of steels annealed at different temperatures ($T_{\text{ann}}/\text{H}_2\text{O}$)

Curves in Fig.6-7 show a general trend similar to the one described for Fig.6-1: for annealing temperature below a threshold values the impact energy drop suddenly to very low levels due to precipitation of chromium nitrides and/or M23C6 carbides along the grain boundary; for higher temperature the toughness is higher due to absence of such deleterious forms of precipitation.

The threshold temperature is found strongly depending upon carbon content and decreases with decreasing the carbon content, as can be seen comparing the position of curves belong to alloys with different carbon content and same amount of niobium.

However, a new feature appears: the reduction of the upper shelf energy at the higher annealing temperature with increasing niobium in alloys with fixed carbon content. This reduction in toughness is related to precipitation of niobium carbonitrides Nb(C,N) within the austenitic matrix responsible on grain refining effect.

Precipitation of niobium carbonitrides, as well as vanadium carbonitrides (see section 6.3.3), may occur in the liquid phase (primary carbonitrides) or in solid phase (secondary carbonitrides) as results of solid-state transformation within the austenite.

Primary carbonitrides are usually coarse, difficult to dissolve even at temperature above their temperature of formation and grow at the expense of smaller precipitates. They result in a severe reduction in toughness as well as corrosion resistance [Cott98,Yong01].
Secondary carbonitrides are usually very fine, homogeneously distributed within the austenitic matrix from which they form and are responsible for grain refining with still relatively high values in toughness. In alloys with concentrations of carbon and niobium, large amounts of nitrogen in the melt encourage the formation of primary carbonitrides during solidification (as show in the phase diagrams in Fig. 6-9a/b). Such precipitates were found along the grain boundary and within the grains, as shown in Fig. 6-8b, and they were responsible for low upper shelf impact energy in these alloys (see Fig. 6-7). In alloys with low carbon and niobium concentration high values in upper shelf impact energy were due to precipitation of secondary niobium carbonitrides. Indeed metallographic observation by mean of optical microscope did not show any forms of precipitation and only a homogeneous austenitic microstructure with fine grains was observed, as shown in Fig. 6-8d. Therefore, even if the niobium carbonitrides were too small to be detected by optical microscope their grain refining effect coupled with still relatively high level of toughness, due to their small size, was clearly evident.

Fig.6-8: grain refining by niobium (CW = cold worked):
(a) Fe 23Cr 16Mn 0.17C 0.75N @1100°C/1h/H2O
(b) Fe 23Cr 16Mn 0.17C 0.75N 0.30Nb @1100°C/1h/H2O
(c) Fe 23Cr 16Mn 1Ni 0.12C 0.75N @1000°C/30min/H2O after 33% CW
(d) Fe 23Cr 16Mn 1Ni 0.12C 0.75N 0.05Nb @1000°C/30min/H2O after 33% CW
Fig. 6-9 (below): phase diagrams in alloys Fe23Cr16Mn xC yN zNb calculated by ThermoCalc

\[ \text{Primary carbonitrides formation} \]

\[ \text{Nb(C,N)} = \text{NbCN} \]

\[ \gamma + \text{Cr}_{2}N + \text{NbCN} \]

\[ \gamma + \text{M}_{23}C_{6} + \text{NbCN} \]

\[ \text{Liq.} + \gamma \]

\[ \alpha + \gamma + \text{NbCN} \]

\[ \alpha + \gamma + \text{M}_{23}C_{6} + \text{NbCN} \]

\[ a) C = 0.17\% \text{ Nb} = 0.30\% \]

\[ b) C = 0.17\% \text{ Nb} = 0.15\% \]
Fig. 6-10 shown as in alloys containing niobium, grain refining was achieved during solution annealing of samples directly cut from hot forged plates in comparison with alloys without niobium.

Fig. 6.10: grain size in hot forged and annealed alloys with/without niobium ($T_{\text{anneal}}/1^\circ/\text{H}_2\text{O}$).
In alloys containing niobium, the grain size as a function of the annealing temperature, remains more or less constant until the temperature for Nb(C,N) dissolution is reached. Above this temperature fast grain growth, accelerated by the high temperature involved, takes place resulting in bigger grain size.

On the contrary, the grain size of alloys without niobium were always found to increase with increasing annealing temperature, as no obstacles for grain growth were present into the austenitic matrix.

The temperature above which Nb(C,N) dissolution takes place were found to increase with increasing Nb content (with same carbon content); in the alloy with less than 0.15wt% Nb such a temperature was found between 1100+1200°C, whereas for 0.30wt% Nb it was above 1250°C, as small grains were still found at such a high temperature (60 μm).

A comparison among curves in Fig. 6-1 and 6-7 belong to alloys with same carbon content, show as niobium addition has the drawback to decrease the toughness at all the annealing temperatures investigated in comparison with the same alloys without niobium. The decreasing in toughness was severe for alloys with high carbon and high niobium contents due to formation of primary carbonitrides, but moderate, hence tolerable, in alloy with low niobium and low carbon where precipitation in the solid state of niobium carbonitrides occurred.

6.3.2.2 YIELD STRENGTH AND ULTIMATE TENSILE STRENGTH

The yield strength and the ultimate tensile in function of the grain size are shown in a Hall-Petch type diagram in Fig. 6-11.

![Fig. 6-11: effect of different niobium contents and grain sizes on tensile properties (continuous lines and dotted lines are the Hall-Petch type correlation for alloy with 0.17C 0.30Nb and 0.12C 0.05Nb respectively; * = 0.83wt% N, ** = 0.87wt% N).](image-url)
In spite of the big difference in toughness for alloys with different carbon and niobium contents shown in Fig. 6-7, the grain size was in the range of 3+100 μm and does not show a big difference for various niobium content. The difference in yield strength and tensile strength in the alloys with 0.30wt% Nb, compare with the one with 0.05wt% Nb, is most likely due to higher carbon content in the former one, although a significant contribution by precipitation hardening from massive precipitation of primary carbonitrides might be expected. However, in the alloy with 0.05wt % Nb a yield strength and a tensile strength near 1 GPa and 1.2 GPa respectively have been achieved with a grain size of ~3μm, after SRX at 900°C/15\text{min} made possible by the increased thermal stability of this alloy (see Fig. 6-12).

Fig. 6-12: alloy Fe 23Cr 16Mn 1Ni 0.75N 0.12C 0.05Nb after 33\% cold working and SRX at 900°C/15\text{min} (a), 930°C/15\text{min} (b), 950°C/15\text{min} (c) and 970°C/15\text{min} (d).

Grain sizes smaller than 3 μm were expected after SRX heat treatment below 900°C on the two most stable alloys (0.02wt% Nb and 0.08wt% C, see Fig. 6-7), instead it was not possible to achieve grain sizes smaller than 6-7 μm (at 870°C/15\text{min}): the amount of Nb(C,N) precipitates was not enough to prevent excessive grain growth resulting in bigger grain size. These investigations shown how in order to achieve a good combination of grain refining, hence mechanical strength, and toughness low carbon and low niobium content, around 0.1wt% and 0.05wt% respectively, are necessary.
6.3.2.3 DUCTILE TO BRITTLE TRANSITION

Impact energy tests at different temperature, from -198 to +100°C, were performed on samples cut from the hot forged plates and annealed at 1050°C/1h in order to avoid precipitation of deleterious phases (M23C6 and Cr2N). The results are shown in Fig. 6-13.

Fig.6-13: niobium effect on ductile to brittle transition phenomena.

The shape of the curves reported in Fig. 6-13 shown the typical “ductile to brittle transition” of HNS, with a rapid decreasing in impact energy from high to low values with decreasing the testing temperature.

The temperature at which this transition occurs (TD_BTT) is reported in Fig. 6-14.

Fig. 6-14: ductile to brittle transition temperature (TD_BTT) in function of niobium content.
Niobium addition was found to increase the ductile to brittle transition temperature at the same carbon and nitrogen content. Therefore a low niobium content is necessary to avoid further increasing in the ductile to brittle transition temperature when the nitrogen content in solid solution is increased above 0.75wt% in order to optimise the solid solution hardening by nitrogen.

6.3.3 GRAIN REFINING BY VANADIUM

6.3.3.1 TOUGHNESS

The results of impact energy tests performed on alloys with different vanadium and carbon content are shown in Fig. 6-15.

vanadium addition (0.3-1wt%) in alloys containing different carbon content (0.08-0.17wt%), was found to have a detrimental effect on toughness after annealing at temperature below 1150°C; whereas some differences were found at higher annealing temperature depending on carbon and vanadium content.

The low toughness was always due to massive precipitation of very coarse vanadium carbonitrides in the austenitic matrix as illustrated in Fig. 6-16a/b/c.

High amount of vanadium and carbon shift the solubility curve for V(C,N) precipitation above 1200°C, as indicated on phase diagrams in Fig.6-17a/b; hence, it was not possible to dissolve such coarse precipitates even after annealing at 1150°C for one hour resulting in very low toughness.

On the contrary, in the alloy with 0.12wt% C it was possible to dissolve completely in the austenite the coarse V(C,N) at temperature higher than 1150°C achieving a toughness over 200J but losing the grain refining effect by vanadium carbonitrides, Fig. 6-17d.
The phase diagram of these alloys, Fig. 6-18c, shows that the solubility line for V(C,N) precipitation is shifted towards low temperatures by less carbon content. Therefore a carbon content lower than 0.12% together with a vanadium content lower than 0.5% should give arise to precipitation of very fine vanadium carbonitrides, instead of coarse ones, with not so detrimental effect on toughness.

![Microstructure images](a) Fe 23Cr 16Mn 0.17C 0.5V 0.95N @1150°C/17H2O; (b) Fe 23Cr 16Mn 0.17C 1V 1.06N @1150°C/17H2O; (c) Fe 23Cr 16Mn 0.12C 0.6V 0.88N 1Ni @ 1110°C/15min/H2O; (d) Fe 23Cr 16Mn 0.12C 0.6V 0.88N 1Ni @ 1160°C/15min/H2O.

6.3.3.2 YIELD STRENGTH AND ULTIMATE TENSILE STRENGTH

The dependence of the yield strength and ultimate tensile strength on the grain size is shown in a Hall-Petch type diagram in Fig. 6-18.
Fig. 6-17 (below): phase diagrams of alloys Fe 23Cr 16Mn xC yN zV calculated by ThermoCalc.

**Diagram 1:**
- **a)** $C = 0.17\%$ $V = 1\%$
- **Diagram 2:**
- **b)** $C = 0.17\%$ $V = 0.5\%$

Legend:
- $V(C,N)$: primary carbonitrides formation
- $V(C,N) = VCN$
- $\alpha + \gamma + VCN + M_{23}C_6$
Primary carbonitrides formation

\[ V(C,N) = VCN \]

\[ \gamma + VCN + Cr_N \]

\[ \gamma + Cr_N \]

**Fig. 6-18**: effect of different vanadium contents and grain sizes on tensile properties (continuous lines and doted lines are the Hall-Petch type correlation for alloy with 1V and 0.5V respectively).

With 1wt% V it was possible to achieve grain size of ~2μm but the final microstructure was very brittle, due to the massive precipitation of carbonitrides which took place, shown in Fig. 6-16b. The different slope of the hall-Petch line for the two alloys with 0.5 and 1wt% V,
cannot be explained only by nitrogen effect but due to the high amount of precipitation that took place in these alloys further strengthening by precipitation hardening was likely occurred.

6.3.3.3 DUCTILE TO BRITTLE TRANSITION

Impact energy tests at different temperature, from −198 to +200°C, were performed on samples cut from the hot forged plates and annealed at 1150°C/h; the results are shown in Fig. 6-19. Vanadium addition seems to increase the ductile to brittle transition temperature, but for all the alloys such ductile to brittle transition is likely due to the higher content of nitrogen in solid solution in the austenite due to partial dissolution of vanadium carbonitrides during solution annealing treatment at 1150°C.

![Graph showing vanadium effect on ductile to brittle transition phenomena.](image)

Fig.6-19: vanadium effect on ductile to brittle transition phenomena.

6.3.4 GRAIN REFINING BY VANADIUM PLUS NIOBIUM

6.3.4.1 TOUGHNESS

Grain refining by simultaneous addition of niobium and vanadium was investigated in alloys containing 0.17C 0.1Nb 0.6V 0.75N and 0.08C 0.02Nb 0.3V 0.88N. The results of impact energy tests performed on these alloys annealed at different temperature are shown in Fig.6-15. As expected, due to higher content of C, Nb and V the former was very brittle after annealing in a range of 950-1200°C (the highest impact energy measured was ~ 150J after annealing at
1200°C for one hour), whereas the second alloy shown higher toughness levels in the same range of temperature (above 200 J for annealing temperatures above 1050°C). Phase diagrams of these alloys, Fig.6-20a/b, show the presence of mixed carbonitrides of vanadium and niobium (Nb,V)(C,N); such complex carbonitrides precipitate in a wide range of temperature and chemical composition. The formation of such complex carbonitrides is explained by similarities in the crystal lattice structure of V(C,N) and Nb(C,N) (see Appendix 2 for more details) allowing Nb to partially replace V as C does with N [Cott98].

6.3.4.2 YIELD STRENGTH AND ULTIMATE TENSILE STRENGTH

The dependence of the yield strength and ultimate tensile strength on the grain size is shown in a Hall-Petch type diagram in Fig. 6-18. It was not possible to achieve grain size smaller than 6-7 µm and tensile properties higher than the ones obtained in the alloy with only 0.05wt%Nb and same grain size (that also shown better toughness!). As described in the previous section, vanadium and niobium form mixed carbonitrides, which are stable up to very high temperatures (depending on vanadium content). The formation of such complex carbonitrides at high temperature explains why it was always found coarse in size, leading to deleterious effect on toughness and not efficient grain refining.

Fig. 6-20 (below): phase diagrams of alloys Fe 23Cr 16Mn xC yN zV tNb calculated by ThermoCalc
6.4 DISCUSSION

The effect of carbon content on the thermal stability of high nitrogen low nickel austenite was investigated in austenitic stainless steel with ~23wt% Cr, ~16wt% Mn and ~0.75wt% N. A carbon content near 0.1% was found to be beneficial to obtain a very good stable austenite against unfavourable precipitation of secondary phases such as Cr$_2$N and M$_{23}$C$_6$ at 950°C.

A low carbon content makes it possible to increase the nitrogen content in solid solution up to 0.8-0.9wt%, with positive effects on the mechanical strength with a ductile to brittle transition temperature still below room temperature.

The effect of niobium as austenite grain refining element in reducing the austenite grain size below ~3μm after recrystallization at low temperature was shown. However, a negative effect on toughness and ductile to brittle transition temperature was measured. Niobium contents lower than 0.05wt% seem to be not enough to prevent excessive grain growth resulting in austenitic grain size of 6-7μm.

The effect of vanadium as grain refining and precipitation hardening element was investigated. Vanadium contents higher than 0.5wt% and carbon contents higher than 0.12wt% must be avoided, due to unfavourable dispersions of precipitates that cause deterioration of the toughness and corrosion resistance.

A positive grain refining effect coupled with still a relative good toughness was observed alloying with low vanadium (0.3wt%) and low niobium (0.02wt%) content; but a comparison between the grain size and mechanical properties achieved using only niobium as grain refining elements, shows niobium as the most promising microalloying element able to give grain refining (at least until ~3μm) with still good level of toughness in high nitrogen low nickel austenitic stainless steels. Based on these preliminary conclusions, the next steps towards the development of ultrahigh strength austenitic stainless steels, were to develop new alloys belonging to the system Fe-Cr-Mn-Ni-N-C-Nb containing C~0.1wt%, N~0.9wt% and Nb~0.05wt%, taking advantages by solid solution hardening by nitrogen and grain refining by niobium without adverse effect on toughness.
7. STRENGTHENING MECHANISMS IN HIGH NITROGEN AUSTENITIC STAINLESS STEELS

7.1 SCOPE

This chapter presents results concerning the role played by nitrogen on yield strength, ultimate tensile strength and ductility in steels strengthened by grain boundary hardening, dislocation hardening and precipitation hardening. Different strengthening mechanisms were analysed singly and combined with the aim to achieve an ultrahigh strength austenite containing nitrogen in solid solution as high as possible, regardless of the adverse effect on the ductile to brittle transition.

Answers to the following questions were also searched:

- Does there exist a practical limit for grain boundary hardening beyond which this strengthening mechanism ceases to be applicable due to adverse effect on ductility in steels?
- How does this limit change with nitrogen?
- How can this limit be overcome in order to achieve a higher strength austenite?
- Does grain refining have some influence on the ductile to brittle transition?

7.2 MATERIALS AND METHODS

By means of ThermoCalc, alloys were developed with nitrogen content up to 1.34wt% in solid solution. The content of Cr, Mn and Ni was balanced in order to increase the nitrogen solubility avoiding porosity during solidification in the ingots. Some alloys contain small amount of niobium as further help to obtain small grains.

The chemical composition of the alloys investigated is found in Tab.7-1 in Appendix 2. All the alloys were cast into 3 Kg ingots, homogenized at 1240 °C for 8 hours and water quenched, then hot forged at a temperature between 1100 and 1200°C to plates with a thickness of 17 mm.

All alloys underwent a heat treatment at 1100°C/30min/H2O before any further investigation in order to bring back into solution eventual precipitates formed during the hot forging process thus assuring a fully austenitic structure.

In order to achieve very small grains (smaller than 2-3 μm), static recrystallization heat treatments were carried out on small samples heavily cold worked for short times, in the range of one minute to fifteen minutes.

Cold deformation was performed by swaging round bars with an initial diameter of 15 mm and a final one of 5 mm, for a degree of cold work of 89%.
Fig. 7-1: Phased diagram (by ThermoCalc) of alloys:
  a) Fe25Cr16Mn2Ni0.10C0.90N
  b) Fe25Cr16Mn2Ni0.10C0.90N0.10Nb
7.3 RESULTS

7.3.1 GRAIN BOUNDARY HARDENING

7.3.1.1 STATIC RECRYSTALLIZATION EXPERIMENTS

During static recrystallization heat treatments the final grain size depends on: degree of cold work, previous grain sizes, temperature and time [Honey81]. When the first and second parameter are fixed, as in this case, the final grain size is a function of temperature and time. The holding time is the most critical parameter to control, because for relative big samples (for the purposes of this research samples were considered “big” with minimum sizes of 11 x 11 x 70 mm) at least fifteen to twenty minutes are necessary to reach a uniform temperature distribution.

To assure slow grain growth for such a relative long time, a low temperature is necessary but this solution can be apply only if the austenite is stable at such a low temperatures, without precipitation of Cr-nitrides or carbides.

Fig. 7-2 shows the yield strength, ultimate tensile strength and grain size after recrystallization at 1000°C for different holding time, in two alloys containing 0.9wt% nitrogen in solid solution: one without niobium and the others with 0.1 wt% niobium. Nb containing alloys show smaller grain size compare the one without niobium for holding times longer than 2-3 min. Grain growth was inhibited by precipitation of niobium carbonitrides, whereas in the alloy without niobium the grains were always found to increase with increasing the holding time.

There was no big difference in grain size alloying with different niobium content; in fact, as explained in the previous chapter, only a minimum niobium content is requested to obtain an effective grain refining effect.

For holding time shorter than 3 min there was no appreciable difference in grain size in all alloys investigated; hence to obtain grain size smaller than 1-2 μm shorter holding time are more important than microalloying with niobium, see Fig.7-3 and Fig.7-4 (this also explain why small samples were used, as a lower limit for the holding time is dictated by sample’s size in order to achieve an homogenous distribution of temperature in the whole sample).

This result can be explained by different kinetics involved in niobium nitrides precipitation and recrystallization.

In heavily cold work samples the nucleation of new grains is an extremely fast process due to the high amount of lattice defects present, with the new grains growing until their grain boundary does not come into collision to obstacles, such as other grain boundaries or small precipitates. When niobium is present in HNS, precipitation of niobium carbonitrides takes some time to occur, during which grain boundaries are free to expand into the deformed matrix without excessive drag; grain refining by niobium is therefore achieved only after extended time.

In Fig.7-5 the yield strength, ultimate tensile strength and grain size after one hour of recrystallization heat treatment at different temperatures are shown.

In alloys containing niobium the grains remain small in size until the temperature for niobium carbonitrides dissolution is not exceeded.

Such temperature was found in the range 1150–1200°C for 0.1wt% Nb as shown from the extremely rapid increase in grain size in Fig.7-6, probably due to “secondary grain growth”, a process according which in grains heavily pinned by particles a rapid increasing in grain size suddenly may occur (the driving force of this process is the surface energy which tends to
decreases as the grains becomes bigger). This could also explain the higher slope of the grain size growth line for 0.1 wt% N above 1150°C compared with the steel without Nb.

Fig. 7.2: Effect of the holding time and niobium content on grain size during SRX at 1000°C

Fig. 7-3: Fe25Cr16Mn2Ni0.1C 0.9N SRX @ 1000°C/1 min, TEM 200kV (D ~ 0.7μm)

Fig. 7-4: Fe25Cr16Mn2Ni0.1C 0.9N 0.1Nb SRX @ 1000°C/1 min, TEM 200kV (D ~ 0.6μm)
A temperature for Nb(C,N) dissolution around 1150°C was also in agreement with the phase diagram in Fig. 7-1b. The different trend in grain size with holding time or SRX temperature gives an explanation for the yield strength and ultimate tensile strength levels illustrated in Fig. 7-2 and 7-5 respectively, in which higher strength are correlated to smaller grain sizes. From these experiments it is clear that niobium is effective to prevent excessive grain growth after long holding times. This is necessary when dealing with big samples, and at high temperature as long as the temperature for niobium carbonitrides dissolution into austenite is not exceed.

7.3.1.2 EFFECT OF NITROGEN

The yield strength, the ultimate tensile strength and the ductility, measured as elongation to fracture, in function of the grain size are shown in Fig. 7-6 for the low interstitial austenitic stainless steel AISI 316. This material was chosen as reference to make a comparison between low nitrogen and high nitrogen austenite, due to its wide industrial application.

The numerical values for the two parameters of the Hall-Petch equation:

\[ R_{p02} = R_o + k_y \frac{1}{\sqrt{d}} \quad [1] \]

the slope of the Hall-petch line \( k_y \) and the intercept for infinite grain size \( (d^{1/2} \to 0) R_o \), are also reported, as well as the ones for \( R_u \), \( K_u \), \( A_o \) and \( K_d \), the meaning of which will be subsequently explained.
Fig. 7-6 shows as the yield strength and ultimate tensile strength increase with decreasing the grain size whereas the ductility decreases.

Yield strength in the neighbourhood of 1000 MPa was achieved by means of extreme grain refining down to 0.25\(\mu\)m in size, after \(~\sim\)92\% cold working followed by SRX at 800\(^\circ\)C/4\(\text{min}\).

Nitrogen in solid solution makes grain-hardening mechanism more effective, and Fig.7-7 shows as ten times bigger grains results in similar yield strength for austenitic steel with 0.9wt\% nitrogen.

In the same steel the minimum grain size achieved was 0.6\(\mu\)m for yield strength of 1200 MPa, achieved after heavy cold work \(~\sim\)89\% and SRX at 1000\(^\circ\)C/1\(\text{min}\).

The numerical values for the two parameters of the Hall-Petch equation, \(R_0\) and \(K_y\), are also reported, as well as the ones for \(R_u\), \(K_u\), \(A_0\) and \(K_A\), the meaning of which will be subsequently explained.
Tensile properties even higher were achieved alloying with 1.2wt% nitrogen in solid solution, as shown in Fig.7-8, in which grain refining down to 0.6μm gave yield strength above 2000 MPa. The following sequence of mechanical and heat treatments (HT) was carried out in order to obtain such a small grain size:

Hot forging, HT at 1050°C/30min/H2O, cold rolling for 44% degree of cold work, SRX at 1060°C/20min/H2O, cold rolling for 21% degree of cold work, SRX at 1060°C/20min/H2O, swage forging for 89% cold deformation and final SRX at 1050°C/2min/H2O.

The numerical values for the two parameters of the Hall-Petch equation, $R_0$ and $K_y$, are also reported, as well as the ones for $R_u$, $K_u$, $A_o$ and $K_A$, the meaning of which will be subsequently explained.

From the analysis of the dependence of the yield strength versus grain size for different nitrogen content, reported in Fig.7-9, two features appear:

- The well known Hall-Petch relation between yield strength $R_{po.2}$ and grain size $d$, $R_{po.2} = R_0 + K_y \cdot d^{1/2}$, was found valid for high nitrogen austenitic stainless steels down to sub-micrometric scale (at least until 600nm) and for AISI 316 down to 250nm;
The effect of nitrogen on the grain boundary hardening is to increase the slope of the Hall–Petch, $K_y$; whereas the increasing of $R_0$ with $N$ is due to solid solution hardening.

![Graph showing tensile properties in function of grain size in HNS with 1.2wt% N](Speid03)

These test results confirm the known positive effect of nitrogen on grain boundary hardening. Many theories were proposed to explain this dependence (see section 3.3).

The validity of the Hall-Petch law for grain size below one micron is in agreement with other recent researches; according to it was found valid until 100 nm [Schi02] and 50 nm [Taka01] grain sizes.
From the analysis of Fig. 7-6, 7-7, and 7-8, a relation similar to the Hall-Petch equation was found to exist between ultimate tensile strength $R_m$ and grain sizes as well as elongation to fracture $A_s$ and grain size, for all the range of grain size investigated. Such new relations have been established by Speidel [Speid01b, Speid02, Speid03]

$$R_m = R_u + k_u \cdot \frac{1}{\sqrt{d}} \quad [2]$$

$$A_s = A_u + k_d \cdot \frac{1}{\sqrt{d}} \quad [3]$$
The new coefficients are defined in similar manner as the traditional $R_o$ and $K_y$, namely: $K_u$ and $K_d$ are the slope of the line drawn for ultimate tensile strength and ductility respectively, whereas $R_u$ and $A_o$ are the intercept value at infinite grain size for the ultimate strength and ductility line.

The coefficients: $R_u$, $K_u$, $A_o$, and $K_d$, as the traditional $R_o$ and $K_y$, were found depending upon nitrogen concentration and temperature (such dependences were studied extensively in a parallel research work carried out by Hannes J. Speidel [Hannes02]).

The dependence of $K_y$, $R_o$, and $R_u$ upon nitrogen concentration at room temperature is shown in Fig.7-10 and Fig.7-11.

![Graph showing the influence of nitrogen content on $K_y$ at room temperature.](image)

Fig. 7-10: influence of nitrogen content on $K_y$ at room temperature (low nickel HNS)

The following correlation were found to fit quite well the experimental points at room temperature:

$$k_y = 9 + 22 \cdot N$$ [4]

$$R_u = 530 + 400 \cdot N$$ [5]

$$R_o = 150 + 370 \cdot N$$ [6]
The relations [1], [2] and [3], show as yield strength and ultimate tensile strength increase with decreasing the grain size, whereas the ductility, measured as elongation to fracture, decreases.

Therefore, if grain boundary hardening helps to increase the mechanical strength it has as main drawback a decreasing in ductility that can drop to very low values for extreme grain refining coupled with very high nitrogen content, as shown in Fig. 7-8.

This may represent a practical limit for grain boundary hardening, if a certain level of ductility has to be maintained.

At the moment the relationship between grain size and ductility, as well as the one between ultimate tensile strength and grain size, cannot be explained by currently available theories.
about grain boundary hardening in high nitrogen austenitic stainless steel, hence should be "taken" as an experimental fact. Actually, the situation does not become better even when considering the effect of nitrogen on the more traditional Hall-Petch equation, which is described in different ways/models but no general consent has been established to identify the correct theory among the HNS specialists yet!

7.3.2 DISLOCATION HARDENING AND PRECIPITATION HARDENING

High nitrogen austenitic stainless steels, which have already a high yield strength due to solid solution hardening and due to fine grain hardening, can be further strengthened by cold working and subsequent strain ageing. This is illustrated in Fig. 7-12, 7-13, 7-14 and 7-15 where the yield strength, the ultimate tensile strength and the elongation to fracture for alloys with different nitrogen content are plotted in function of degree of cold work. These pictures show that the effect of cold work on increasing both yield strength and ultimate tensile strength is much higher for HNS than for low interstitial austenite such as type 316. Nitrogen increases the strain hardening rate achieving higher level of strength with the same degree of cold work; the reason of such effect is related to profound influence of nitrogen on plastic deformation in austenite, as described in details in section 3.2.

![Graph showing the effects of dislocation hardening on yield strength, ultimate tensile strength and ductility in low interstitial austenitic stainless steels (AISI 316 N<0.01wt%)](image)

Fig. 7-12: effects of dislocation hardening on yield strength, ultimate tensile strength and ductility in low interstitial austenitic stainless steels (AISI 316 N<0.01wt%)
Fig. 7-13: Effects of dislocation hardening on yield strength, ultimate tensile strength and ductility in high nitrogen austenitic stainless steels (N ~ 0.9 wt%).

Fig. 7-14: Effects of dislocation hardening on yield strength, ultimate tensile strength and ductility in high nitrogen austenitic stainless steels (N ~ 1.2 wt%).
In this way, by means of dislocation hardening, yield strength levels around 2600 MPa can be reached with 0.9wt% N in solid solution, that is ten times the level of solution annealed austenite type 304 and 316; whereas a yield strength higher than 3000 MPa were measured for alloys with nitrogen content higher than 1.2wt%.

Further strengthening can be obtained in these steels by a low temperature treatment after cold reduction. Subsequent ageing at 500°C for one hour was carried out on the two alloys with the higher nitrogen content, after 89% of cold working. During this treatment, nitrogen tends to diffuse towards dislocations and stacking faults, where it “condenses” to form nitrogen atmospheres. Once formed, they are very effective to pin the dislocation. As a consequence of their reduced mobility the strength increases strongly, as shown in Fig.7-16.

Yield strength of 3200 MPa and 3600 MPa were achieved in alloys containing 1.2wt% and 1.35wt% nitrogen respectively; the elongation to fracture measured in the same condition was very low: 0.1% for the first alloy and <0.1% for the second. Cold working can therefore be applied to HNASS to produce an attractive combination of strength and ductility, although the product form is limited to wire and thin, flat products.

Fig. 7-12/13/14/15 show as dislocation hardening and precipitation hardening are very effective to increase the mechanical strength but with adverse effect on ductility, which decreases with increasing the yield strength and ultimate tensile strength.
The same trend between strength and ductility was also found for grain boundary hardening, as described at the end of the previous section.

![Graph showing ultimate tensile strength as a function of degree of cold working for different materials, including pure iron, AISI 316L, 0.4N 33Cr, 0.8N 25Cr, 1.2N 30Cr, 1.35N 30Cr, 1.2N after ageing, and 1.35N after ageing.](image)

**Fig. 7-16:** ultimate tensile strength as a function of dislocation hardening and precipitation hardening (static strain ageing) in HNS with different nitrogen content

One of the most remarkable developments concerning HNS has always been the attainment of higher and higher yield strengths level by judicious combination of all four basic hardening mechanisms. The result of this strategy is summarized in Fig. 7-17, which shows a sort of "historical trend" in the development of ultrahigh strength high nitrogen austenitic stainless.

In a fully austenitic microstructure free of any kind of precipitates (even martensite) yield strength of 2000 MPa in annealed condition and 3600 MPa in cold work and strain ageing condition were achieved during this Ph.D. work. These values represent so far a new record in strength for HNS! In Fig. 7-17 the former record is also shown, as a point at 3400 MPa of yield strength reached in 1991 [Uggo91].

This level of strength was achieved in wires; heavily cold draw with a final diameter less than 1 mm and the material was HNS produced by pressure metallurgy.

Therefore, another outstanding result is that the new record in strength was achieved in bulk material (sample with a diameter of 5 mm) made without overpressure with traditional ingot metallurgy as results of alloy development strategy.
7.3.3 STRENGTH AND DUCTILITY COMBINED

Strength alone, as resistance to plastic deformation, and ductility can be quite high in separate materials, however for structural materials a balanced combination of both is necessary. Common criteria used by metallurgist for the evaluation of engineering materials is the combination of yield strength and ductility; main objective of alloy development, used for structural materials, is to increase both properties at the same time.

Fig. 7-18 and Fig. 7-19 show yield strength ($R_{p0.2}$) and ultimate tensile strength ($R_m$) versus ductility, measured as elongation to fracture ($A_S$), in alloys with different nitrogen content in solid solution.

For every nitrogen content, the experimental points representative of different combination ($R_{p0.2} - A_S$) or ($R_m - A_S$), obtained using different strengthening mechanisms, were found to fit quite well on a same curve. The curves differ in the strength-ductility plane because of their nitrogen content in solid solution.
Based on this fact, two important conclusions can be inferred.

1. Independently from the strengthening mechanisms used to achieve a certain level of strength the final combination of strength and ductility will be the same.

This is important for practical application of HNS, in which depending on the final products different strengthening mechanisms, singly or combined, can be active. For example, flat products by hot rolling can take advantages from grain refining whereas during cold drawing, for wires or high strength fasteners production, dislocation hardening is active and strain ageing could be also applied.

2. While grain boundary hardening, dislocation hardening and precipitation hardening increase the mechanical strength always at expense of ductility, solid solution hardening by nitrogen is the only way to increase strength and ductility in the same time, as shown from the position of the curves on the plane strength/ductility, shifted toward higher strength and ductility with increasing nitrogen content (Fig. 7-18/19).
The situation according to alloying with nitrogen the mechanical strength increases without a corresponding drop in ductility is the *metallurgist's dream*: a higher strength without loss of ductility!
The reasons why nitrogen in solid solution can make this possible were explained in detail in section 3.1.
Fig. 7-20 shows a schematic summary of effects on strength and ductility of all four strengthening mechanisms for austenitic stainless steels.

7.3.4 DUCTILE TO BRITTLE TRANSITION IN HNS

High nitrogen austenitic stainless steels undergo a ductile to brittle transition fracture behaviour with decreasing the service temperature.
The temperature at which this transition appears, the ductile to brittle transition temperature ($T_{DBTT}$), was found depending on nitrogen and carbon content.
Results described in Chapter 5 show how such a transition temperature was also found to depend on other alloying elements, namely niobium and vanadium.

In order to clarify the role of different alloying element on $T_{DBTT}$ a regression analysis using the last squares method was carried out on many different kind of high nitrogen austenitic stainless steels, some of them developed during this work and other taken from different sources (literature and previous Ph.D works at the Institute of Metallurgy ETZ-Zurich). A collection of results for different alloys is shown in Fig. 7-21, where the real $T_{DBTT}$, as measured by impact energy tests carried out at different testing temperature, is compared with the one calculated by means of the following formulas:

$$T_{DBTT} = 300 \cdot N + 100 \cdot C$$  \hspace{1cm} [11]

$$T_{DBTT} = 300 \cdot N + 100 \cdot C - 20 \cdot (Ni + Cu)$$  \hspace{1cm} [12]
Fig-7-21: experimental and theoretical T_{DBTT} values calculated by [11] and [12] in austenitic stainless steels in the range of composition of:

17±30wt% Cr, 7±26wt% Mn, 0±42wt% Ni, 0±2wt% Cu, 0.6±1.4wt% N, 0±0.3wt% C,
0±3.2wt% Mo, 0±0.30wt% Nb, 0±1tw% V

Even though the relation [12] described the experimental data better (compared with [11]), Fig.7-22 shows that the best correlation was found taking into consideration many more alloying elements using the formula [13]:

\[
T_{DBTT} = 45 \cdot V + 305 \cdot Nb - 19 \cdot Mo + 59 \cdot C + 576 \cdot N + 6 \cdot Cu + 2.2 \cdot Ni - 6.8 \cdot Mn - 18.2 \cdot Cr \tag{13}
\]

However, with this new formula [13] the disagreement between values for T_{DBTT} measured and calculated remain still relatively high, within a scattering band error of ±10%.

May the origin of such big scattering band rely on some "hidden variables"? Does the grain size have any influence on T_{DBTT}?

To answer this questions, a systematic investigation was carried out on alloys with chemical composition listed in tab.7-3 (Appendix 4), with different nitrogen content and with different niobium content.

Different grain sizes, in the range 7±300μm, were achieved following different routes; hot rolling plus SRX and cold working plus SRX.

The results of impact energy test at different temperature, from −198 to +200°C, performed on the two groups of alloys, with and without niobium, are reported in Fig. 7-23 and 7-24 respectively.
Fig. 7-22: DBTT measured and computed according to the relation [13].

Fig. 7-23 (below): Grain size effect on the ductile to brittle transition phenomena in niobium containing alloys with different nitrogen content.
Fig. 7-24 (below): Grain size effect on the ductile to brittle transition phenomena in niobium containing alloys with different nitrogen content.

- **0.08C 1.25N 0.05Nb**
  - Cracks indicated
  - Various grain sizes: 60, 150, 290, 65 μm

- **0.09C 1N 0.05Nb**
  - Various grain sizes: 16, 35, 70 μm

- **0.1C 0.95N 0.05Nb**
  - Various grain sizes: 85, 140, 290, 265 μm
In alloys with grain size smaller than 20μm precipitation of chromium nitrides in the austenite occurred, resulting in lower toughness compared with the same alloys with bigger grain size (doted lines in Fig.7-23/24). Therefore it was not possible to distinguish the grain size effect on the ductile to brittle transition for grain size smaller than 20 μm.

Fig. 7-25 shows the ductile to brittle transition temperature as a function of grain size with a microstructure fully austenitic.

Unlike in ferritic steels, a fine grain structure has no advantageous effect on the ductile to brittle behaviour. The ductile to brittle transition temperature was found rather independent of the grain size in the range 30÷300 μm, a result that confirms results from other authors [Uggo92, Tomo90].

As described in section 3.5 the ductile to brittle transition in HNS is due to a strong temperature influence on yield strength, which can reach very high values for very low temperature.

To prove this, tensile tests at three temperatures: -75 / 25 / 250°C were carried out on two alloys with 0.88 and 1.03 wt% N in solid solution and different grain size; results are reported in fig. 7-26, 7-27 and 7-28.

As expected, with decreasing temperature, the yield strength increases very rapidly and the same trend was found for the coefficient $k_\gamma$. Higher $k_\gamma$ values cause a decreasing in the cleavage fracture stress (according to $\sigma_f = A \frac{G\gamma}{k_\gamma \sqrt{d}}$) and therefore the (111)-cleavage stress can be reached without extensive plastic deformation, culminating in a brittle fracture.
Fig. 7.26: ultimate tensile strength and yield strength in function of the temperature for two alloys with 0.88 and 1.03 wt% nitrogen in solid solution and different grain sizes.
Fig. 7-27: Hall-Petch curves for alloys containing 0.88 and 1.03 wt% nitrogen in solid solution at different temperatures.

Fig. 7-28: Influence of the temperature on the coefficient \( k_y \) and \( R_0 \) in the Hall-Petch equation.
As no grain size effect on DBTT was seen, the origin of the big scatter band in Fig. 7-22 most likely lies in the experimental procedure carried out to determine the DBTT from the impact energy tests: more impact energy tests should be carried out at different temperatures with a narrow gap between each other.

7.4 DISCUSSION

Nitrogen in solid solution was increased up to 1.34 weight percent without overpressure adjusting the other alloying elements: Cr, Mn and Ni in order to increase the nitrogen solubility in the liquid and in the solid phase avoiding porosity in the ingots during solidification.

In small samples grain boundary hardening was extended down to grain size of 0.6 μm in HNS with 1.2wt% N in solid solution (yield stress of ~2000 MPa) and 0.25 μm in AISI 316 (yield stress ~1000 MPa); the Hall-Petch equation was found valid even at such a small grain sizes.

Relations similar to the Hall-Petch law were found to describe the dependence on the grain size of ultimate tensile stress and ductility. In particular with decreasing the grain size, the ultimate tensile strength was found to increase and the ductility to decrease; the ductility can drop to very low values in presence of very high level of nitrogen in solid solution.

With a judicious combination of all four strengthening mechanism a new record in yield strength in HNASS was achieved: 3600 MPa in round bars with 5 mm in diameter.

Grain boundary hardening, dislocation hardening and precipitation hardening by nitrogen strain ageing were found to increase the mechanical strength but with adverse effect on ductility; on the contrary, solid solution hardening by nitrogen increases both strength and ductility at the same time.

A comparison between strength and ductility in samples with different strengthening mechanisms (singly and combined) showed how the same combination of strength and ductility is achieved independent from the strengthening mechanisms applied.

This gives a new idea toward the development of ultrahigh strength austenitic stainless steels in bulk materials. In big samples was shown that grain refining cannot be extended below 6-7μm even by addition of niobium; in bulk materials dislocation hardening can be used to increase furthermore the strength in spite of this limit.

For this reasons, the next task was to study the mechanical properties of HNS during hot rolling, a processing route which allows to add dislocation hardening as further strengthening mechanism if the hot deformation is carried out below the recrystallization temperature regime allowing retention of deformation (warm-hardening).

The ductile to brittle transition temperature (DBTT) was found depending not only on N and C but also on other alloying elements, primarily Nb, Cr, Mn and Ni. In contrast, DBTT was found rather independent from grain size in the range 30÷300 μm.
8. HOT ROLLING OF HIGH NITROGEN AUSTENITIC STAINLESS STEELS.

8.1 SCOPE

Hot rolling is a well-known industrial practice for the production of a wide range of wrought products; thus hot rolling of high nitrogen austenitic stainless steels plays a “key role” toward a wider industrial application of these new steels. Hot rolling experiments at the laboratory scale were performed on alloys with different nitrogen and niobium contents with the final aim to obtain high strength austenite in bulk material by solid solution hardening, grain boundary hardening and dislocation hardening. In this way the difficulty to get very small grain size, even adding niobium as grain-refining elements, in big samples can be overcome and further strengthening comes from dislocation hardening during hot rolling (warm-hardening).

8.2 HOT ROLLING and DYNAMIC RECRYSTALLIZATION (DRX)

During hot rolling a piece of material previously heated up to a particular temperature (hot-rolling temperature $T_{HR}$) is passed through a couple of roles in which a vertical load is applied to deform the material. Because the mechanical deformation takes place at high temperature, if certain conditions are fulfilled, the microstructure recrystallizes immediately (with time scale of the order of seconds or less) by Dynamic Recrystallization (DRX), see Fig.8-1.

![Fig.8-1: hot rolling (schematic)](image)
Hot rolling is usually carried out by means of hot train mills where there are many couples of rolls with different and complicated strain, strain rate and temperature programs optimised to achieve certain values of mechanical properties in the final products depending on the application (Thermo Mechanical Controlled Process-TMCP) [Cho01,Yama85,Tendo01 Yosh96,Karj96].

During multi-pass hot rolling not only dynamic recrystallization (DRX) but also static and meta-dynamic recrystallization (SRX and MDRX respectively) occur.

Metadynamic recrystallization is a very complex phenomenon, not completely understood yet consisting by continued growth of the nuclei formed by dynamic recrystallization during straining. It does not require an incubation time and such rapid interpass softening process can affect the mechanical properties, even when the pass strains are not large and the interpass times are short.

In most of the cases the occurrence of DRX/MDRX is extremely limited and it is only possible when certain conditions are fulfilled.

In order to have DRX the strain which the material has undergone (which is the sum between the applied strain $\varepsilon_{\text{applied}}$ during each single pass and the residual strain $\varepsilon_{\text{res}}$ due to incomplete recrystallization in the interpass time between two next couples of rolls) has to be equal or higher than a critical strain $\varepsilon_c$ ($\varepsilon = \varepsilon_{\text{applied}} + \varepsilon_{\text{res}} \geq \varepsilon_c$) function of initial grain size ($d_0$), hot rolling temperature ($T$), strain rate $\dot{\varepsilon}$ and chemical composition (from which all the numerical constants $p, q$ depend on), described by the relation:

$$\varepsilon_c = A \cdot d_0^p \cdot Z^q$$  \hspace{1cm} [1]

where $Z$ is the "Zener-Hollomon parameter" defined as:

$$Z = Z(\dot{\varepsilon}, T) = \dot{\varepsilon} \cdot \exp \left( \frac{Q}{R \cdot T} \right)$$  \hspace{1cm} [2]

$Q$ is the activation energy for recrystallization.

The situation is schematically described as in Fig.8-2.

Dynamic recrystallization can occur in the early stage during hot rolling, where the temperature is high enough to induce it even for low strain applied, or DRX can be achieved at the end, during the final rolling, when the temperature is low and the retained strain inside the material plus the applied strain reaches the critical level $\varepsilon_c$.

The grain size during DRX is proportional to the Zener-Hollomon parameter: $D \propto (Z)^p$

The kinetics involved in DRX and SRX are quite different and models are currently available to study these complex phenomena as they occur inside the materials during different stage of hot deformation in hot rolling mills.

These models make possible to schedule the thermo mechanical control process parameters to obtain the final desiderate properties.

The SRX kinetics is described by the following equations:

$$x = 1 - \exp \left( -0.693 \left( \frac{t}{t_{0.5}} \right)^n \right)$$  \hspace{1cm} [3]
\[ t_{0.5} = A \cdot d_n^m \cdot \dot{\varepsilon}^n \cdot \exp\left(\frac{Q}{R \cdot T}\right) \] [4]

For DRX (when \( \varepsilon = \varepsilon_{\text{applied}} + \varepsilon_{\text{res}} \geq \varepsilon_c \)) the relation [3] is still valid, whereas \( t_{0.5} \) follows this other equations:

\[ t_{0.5} = A \cdot d_n^m \cdot \dot{\varepsilon}^n \cdot \exp\left(\frac{Q}{R \cdot T}\right) \] [5]

\( x \) fractional softening (\%) or amount of recrystallized microstructure;
\( t \) time;
\( t_{0.5} \) time for half softening (50%);
\( A, Q, m, n, b \) materials constants.
\( D \) - DRX grain size.

Unlike carbon steel, solution heat treatment after hot rolling is usually required for normal austenitic stainless steels for the following reasons:

- to obtain a microstructural homogenization (getting new recrystallized grains without residual stresses and plastic deformations);
to improve the corrosion resistance (removing precipitates which normally forms during hot rolling and the subsequent cooling process).

This means that the microstructure of these steels is controlled mostly by annealing, during which grain sizes smaller than 100µm are hardly achieved. Solution heat treatment after hot rolling lowers the yield strength, which sometimes makes structural use of the stainless steels plates unfeasible. In certain applications where a decreased corrosion resistance in some environments or a limited ductility or formability (for the high internal stress or precipitates) is still acceptable, the annealing process can be avoided (with positive effect also on the final costs).

These are the reasons why hot rolling of austenitic stainless steels can be carried out according two modalities:

a) hot rolling with a final rolling temperature below $T_{\text{DRX}}$ (temperature at which dynamic recrystallization occurs) resulting in austenite with microstructure of fine grains slightly elongated in the rolling direction (see Fig. 8-2a);

b) hot rolling with a final rolling temperature above $T_{\text{DRX}}$, in which a more homogeneous microstructure with equiaxed grains is achieved (see Fig. 8-2b).

With the first practice higher mechanical strength are achieved, because of the fine dislocation hardened microstructure generated during hot rolling (warm-working) [Ike96, Tendo01]. In the case of normal austenitic stainless steels, warm working is carried out at temperature below about 900°C and can extend to temperatures as low as 700°C. Of course with lower finishing rolling temperatures higher strength levels are achieved.

The response to warm working not only depends on finishing temperature but is also influenced by composition.

The final mechanical properties achieved following the second possibility relies only upon the grain refining obtained during the last step of deformation, and usually are lower [Ike96, Tendo01]. Extreme grain refining can be achieved only by careful choice of hot rolling parameters among each rolling mill stage in order to avoid as much as possible any form of post dynamic softening mechanisms (Dynamic Recrystallization and Metadynamic Recrystallization Controlled Process were developed for this purposes [Cho01]). In this way grain sizes around 20µm can be obtained [Yama90].

8.3 MATERIALS AND METHODS

Hot rolling experiments at the laboratory scale were performed by means of a small hot rolling equipment with only one couple of rolls, and due to power supply limitations it was not possible to apply a big degree of deformation during a single rolling step; therefore only the influence on the final mechanical properties of the hot rolling temperature at fixed applied strain and strain rate was investigated.

Hot-rolling experiments were performed in the way shown in Fig. 8-3. Samples were put for about thirty minutes into an electric furnace $0^\circ\text{C}$ maintained at the hot rolling temperature of interest; then hot rolled in different steps down to the final thickness requested.
(a) Finish rolling temperature $< T_{\text{DRX}}$

Annealing:
coarse $\gamma$ grains

Break-down rolling:
homogenization of microstructure by multiple DRX and SRX

Finish rolling:
Work hardening
accelerated cooling
to prevent softening and precipitation $> 10 \text{ K/s}$

Carbide precipitation

$= $ austenite with small grains deformed
(high strength = grain ref. + work hard.)

(b) Finish rolling temperature $> T_{\text{DRX}}$

Annealing:
coarse $\gamma$ grains

Break-down rolling and finish rolling:
homogenization of microstructure and elevated grain refining by multiple DRX and SRX

accelerated cooling
to prevent softening and precipitation $> 10 \text{ K/s}$

Carbide precipitation

$= $ austenite with small grains

Fig.8-2: thermo mechanical controlled processing applied for austenitic stainless steel
As the small hot rolling machine could not process samples thicker than 23 mm and apply thickness reduction bigger than 1.5 mm during each step, numerous rolling steps were performed with the last one characterized by the highest deformation (being the deformation after each rolling step the ratio between the reduction in thickness and the initial thickness). After each passage between the rolls, samples were put back into the furnace for about five minutes to homogenize again the temperature.

At the end two different quenching possibilities were investigated in order to see which route gave the best results in terms of mechanical properties:

a) hot rolling followed by direct quenching in water (HR+DQ);

b) hot rolling followed by a short period of SRX (putting back the samples in the furnace for 5 min) before final quenching in water (HR+SRX).

The list of alloys used for these preliminary investigations is reported in Tab.8-1 (Appendix 4); all alloys were homogenized at 1240°C for 8h, then hot forged in a temperature range of 1100-1200°C into 23 mm thick plates.

8.4 RESULTS

8.4.1 EFFECT OF DIFFERENT QUenchING ROUTes AFTER HOT ROLLING

8.4.1.1 HARDNESS MEASUREMENTS

The effects of two different quenching routes after hot rolling on mechanical properties, direct quenching (DQ) and post-static recrystallization before final quenching (HR+SRX), are
summarized in Fig. 8-4, which shows hardness measurement (HV10) in austenite with 1.2 wt% nitrogen on samples hot-rolled at 1020° / 1050° / 1100°C and degrees of deformation applied during a single step in the range of 20-60%; these values are the total strain which the material has undergone if complete SRX occurred during the 5 min of interpass time spent into the furnace, resulting in new unstrained grains (\(\varepsilon_{\text{res}} \approx 0\)). To achieve this condition the samples used in this investigation were very small (about 10x10x20 mm).

Samples directly quenched into water show higher level of hardness, hence mechanical strength, than the ones who have undergone post static recrystallization heat treatment before final quenching.

Hardness, hence mechanical strength, increases with increasing the degree of deformation during hot rolling at any temperature because the condition for DRX was not achieved, resulting in dislocation hardening, as shown from Fig.8-5a/b where deformed grains in the rolling direction can be seen.

Very high hardness values were measured in samples hot rolled at 1020°C where the dislocation hardening was more effective due to the lower temperature.

The effect of 5 minutes of post static recrystallization was to decrease the hardness in all conditions investigated due to SRX and grain growth resulting in bigger grains, see Fig.8-5c/d.

8.4.1.2 TENSILE PROPERTIES AND TOUGHNESS

A comparison between mechanical properties after hot rolling followed by two quenching practices, and after static recrystallization heat treatments carried out on similar materials previously cold work is summarized in Fig. 8-6 and 8-7.
Hot rolling was performed starting with a 20 mm thick plate in steps down to final thickness of 11 mm. Than tensile specimens and Charpy V notch impact energy specimens were machined. The degree of hot deformation applied during the last step was ~27%.

Static recrystallization heat treatments were carried out on samples with ~33% degree of cold work with a holding time of 15 minutes. The SRX temperature and hot rolling temperature were the same: 1000, 1050 and 1100 °C.

Fig. 8-6 shows that higher yield strength and ultimate tensile strength were achieved by direct quenching the samples after hot rolling, whereas the ductility was the lowest in this condition, even if its value of ~40%, is still very good for yield strength above 1000 MPa.

The results of impact energy tests are shown in Fig. 8-7; toughness of 40 J at room temperature was measured after hot rolling and direct quenching with a microstructure fully austenitic (Fig. 8-8a). This low value of toughness at room temperature is due to ductile to brittle transition phenomena because of the high level of nitrogen in solid solution (1.2wt%).

The lower level of toughness after post-SRX heat treatments was due to precipitation of chromium nitrides along the grain boundaries as see Fig. 8-8b/c/d.

Post-static recrystallization heat treatment after hot rolling on the alloy investigated was found to have a negative effect on the final tensile properties and toughness, as precipitation of Cr$_2$N along grain boundaries occurred as well as grain growth.
Fig. 8-6: yield strength, ultimate tensile strength and ductility of alloy containing 1.2wt% N after three different process routes: cold working (CW) + SRX; hot rolling + direct quenching (HR) and hot rolling + post-SRX before final quenching (HR+SRX).
Fig. 8-7: toughness of alloy containing 1.2 wt% N after hot rolling + direct quenching (HR) and hot rolling + post-SRX before final quenching (HR+SRX).

Even if the problem of C\textsubscript{N} precipitation could be eliminated choosing a higher temperature or alloys more thermodynamically stable, the reduction in mechanical strength by grain growth would remain, hence post-static recrystallization heat treatment after hot rolling.
should be avoided when higher mechanical properties are requested in the final state, preferring hot rolling followed by direct quenching.

8.4.2 MECHANICAL PROPERTIES OF ALLOYS HOT ROLLED AND SRX

High mechanical properties, in terms of yield strength and ultimate tensile strength, were expected by hot rolling and direct quenching fully austenitic alloys in the temperature range of 1020-1050°C, where DRX does not occur, taking advantages from work hardening (according to the hot rolling practice described in Fig.8-2a). Summaries of results of hot rolling and static recrystallization tests performed on alloys with different nitrogen and niobium contents (chemical composition in Tab.8-1) fulfilling the above-mentioned requirement are shown in Fig. 8-9/10/11 and 12. SRX heat treatments were carried out on alloys cold rolled for a degree of cold work of ~33%, then recrystallized at different temperature for 20 to 60 minutes. Alloys hot rolled had an initial thickness of 22mm (after hot forging), which was reduced to 12mm in 7 steps. The direct quenching route was followed. Fig. 8-9 shows the yield strength and the ultimate tensile strength of alloys hot rolled at different temperatures.

![Graph showing yield strength and ultimate tensile strength as function of hot rolling temperature](Fig.8-9: yield strength and ultimate tensile strength as function of hot rolling temperature)

Fig. 8-10/11/12 show the yield strength, the ultimate tensile strength and the ductility (measured as elongation to fracture) in function of the impact energy respectively. As a general trend, the toughness increases with decreasing yield strength and ultimate tensile strength but hot rolled alloys always show higher mechanical properties at the same level of toughness. The ductility increases with increasing toughness but hot rolled alloys show a lower level of toughness, compared with the same alloys SRX. The increasing in mechanical strength by dislocation hardening is gained at expense of ductility, as remarked at the end of chapter 7.
Fig. 8-10: yield strength versus toughness in alloys hot rolled and statically recrystallized

Fig. 8-11: ultimate tensile strength versus toughness in alloys hot rolled and statically recrystallized
Fig. 8-12: ductility versus toughness in alloys hot rolled and statically recrystallized.

Fig. 8-13 shows the yield strength in function of the grain size in hot rolled and SRX alloys.

As expected, hot rolled alloys showed yield strengths, higher than the ones SRX, with the same grain size, as another strengthening mechanisms were involved to determine the final properties.
Hot rolled alloys containing niobium showed smaller grain size; hence niobium is useful to control the grain growth also during hot rolling.

TEM analysis was carried out on some samples hot rolled at 1060°C (see Fig. 8-14) and 1090°C (see Fig. 8-15).

Fig. 8-14: Fe25Cr16Mn2Ni0.1C0.1Nb0.84N Hot rolled @ 1060°C

Fig. 8-15: Fe25Cr16Mn2Ni0.1C0.1Nb0.9N Hot rolled @ 1090°C

Fig. 8-14/15 show the typical “cells structure”, with very high level of dislocation density. In Fig. 8-15 the “walls” of the cells are better defined and inside the cells it is possible to see clearly a big number of dislocations. The dislocation density was higher in the sample hot rolled at lower temperature.
TEM analyses hence showed dislocation hardening as the main reason for higher tensile strength measured in hot rolled samples.

The outstanding result was to see a very high density of dislocation within the specimens hot rolled at 1050°C and 1100°C; on the contrary, in low interstitial austenite hot rolled at such high temperature recrystallization occur and warm-working cannot be used to increase the mechanical strength. In fact TMCP process in low nitrogen austenitic stainless steels carried out with finish rolling in the non recrystallization region are performed at temperature between 800–900°C, while the ones in the recrystallization regions are at 900–1000°C [Yama90].

Nitrogen in solid solution was found to have a strong effect to enhance the dynamic recrystallization temperature.

A strong effect of nitrogen on dislocation structure developed during hot rolling was also reported by other authors in AISI 316LN, with nitrogen content increased up to 0.17 wt% [Kim96], in which planar slip was found to be present at temperatures higher than 1000°C (planar slip has been mostly reported at temperatures below 900°C [Lilj72,Sas89].

It is in virtue of these results that hot rolling can be considered as a favorite processing route toward the development of ultrahigh strength austenitic stainless steels, taking the advantages of solid solution hardening by nitrogen, grain refining by niobium and warm working.

Fig. 8-16 shows the location in the diagram yield strength versus ductility of the experimental points of the hot rolled samples; the combination of strength and ductility lies on a curve near to the one at 0.9wt% N (as in alloys used to make this comparison the nitrogen content was in the range of 0.84–0.90wt%).

This was another confirmation of the conclusion in section 7.3, according which the same combination of strength and ductility is achieved independently from the strengthening mechanisms involved.

Fig.8-16: yield strength versus ductility measured in specimens hot rolled and RSX
8.4.3 ALLOYS PROPERLY DEVELOPED FOR HOT ROLLING

As explained at the end of section 8.2, hot rolling of austenitic stainless steels can be performed in two modalities depending on the final hot rolling temperature used. Therefore a decision had to be made toward the development of ultrahigh strength austenitic stainless steels, between these two further strategies:

- looking for the condition under which dynamic recrystallization can be optimized and controlled in order to achieve the smallest grain sizes;
- looking for the condition under which hot rolling can be performed in order to increase as much as possible the yield strength in austenite by warm working.

The second strategy was chosen to further explore the hot rolling of HNS during this work for two reasons:

1. if extreme grain refining by DRX cannot be achieved, dislocation hardening at the higher temperature involved during hot rolling can help to reach the final goal of an higher mechanical strength, as the same final combination of strength and ductility is achieved using different strengthening mechanisms;
2. the impossibility to study in depth the DRX phenomena, that is known to have a strong dependence on strain rate and hot rolling temperature, two processing variables that it was not possible to control extensively with the facility currently available.

Following this strategy new alloy compositions, with more stable austenite against precipitation of chromium rich nitrides or carbides, were developed in order to lower the hot rolling temperature as much as possible getting the most from warm working.

All these alloys were hot rolled staring from hot forged 23 mm thick plates down to a final thickness of 11mm by means of eight rolling steps; between two consecutive steps samples were put back into a furnace maintained at the hot rolling of interest for 5 min to homogenize the temperature.

The chemical composition of these alloys is found in Tab 8-2.

Basically these new alloys can be grouped in two classes:

- alloys containing niobium as grain refining elements;
- alloys without niobium.

The influence of different nitrogen and niobium content (in alloys of the first class) on mechanical strength and toughness was investigated, with the final aim to achieve a compromise between high strength and high toughness.

Fig. 8-17 shows the yield strength and ultimate tensile strength in alloys containing different nitrogen content in function of the hot rolling temperature; the grain size was found in the range of 10-60 μm.

Fig. 8-18 shows the yield strength and ultimate tensile strength in alloys containing different nitrogen and niobium content in function of the hot rolling temperature; the grain size was found in the range of 10-25 μm.

Niobium containing alloys showed an average grain size two to three times smaller than the ones without niobium, but the grain size dependence on hot rolling temperature was found
very irregular, without any trend. This was considered as a strong indication that during the 5 minutes of interpass time into the furnace, partially SRX occurred resulting in a microstructure partially recrystallized and deformed.

Fig.8-17: yield strength (solid lines) and ultimate tensile strength as function of hot rolling temperature

Fig.8-18: yield strength (solid lines) and ultimate tensile strength as function of hot rolling temperature

Fig.8-19 shows the combination in yield strength and ultimate tensile strength in function of the toughness, whereas Fig. 8-20 shows the ductility, in the two groups of alloys investigated.
Even if the scattering of the experimental data shown in Fig.8-19/20 is quite big, due to very irregular grain size, some trend between alloys with and without niobium and alloys within each group seems to appear.
A high level of nitrogen (> 1.2wt%), together with a high level of niobium (0.10wt%) results in high strength (Rp0.2 > 1000 MPa, Rm > 1100 Mpa) but with a very low level of toughness (< 50 J) due to the ductile to brittle transition (as the microstructure was always fully austenitic). Very high level of toughness (> 200 J) and high level of mechanical properties (Rp0.2 from 800 ÷ 1000 MPa and Rm from 1100 ÷ 1200 MPa), where reached in alloys with nitrogen content between 0.85 ÷ 0.90wt%. The ductility increases with increasing toughness in all alloys; niobium containing alloys with the same nitrogen content showed a lower level of ductility compared to alloys without niobium, but the mechanical properties were higher in the first one due to grain refining. In the alloys characterized by high toughness the ductility was found in the range 35-45%.

8.5 DISCUSSION

Nitrogen in solid solution was found to have a profound influence on the temperature of dynamic recrystallization and hence on the thermomechanical processing and the resulting properties. In particular, nitrogen makes dislocation hardening very active and increases the mechanical strength even at temperatures above 1000°C. In this way, by means of hot rolling, dislocation hardening was added to the solid solution hardening and grain boundary hardening to develop ultrahigh strength austenitic stainless steels in relative large quantity (bulk material). Best results in term of combination strength-toughness-ductility were found after hot rolling at 1050°C an austenite with chemical composition: Fe 25Cr 16Mn 3Ni 0.10C 0.85N, which gave: Rp0.2 ~ 1000 MPa, Rm ~ 1200 MPa, A5 ~ 35% and Av ~ 200 J. Unfortunately during hot rolling it was not possible to control the grain size properly, resulting in a big scatter of data; however, hot rolling of HNS has all the potentiality to give ultrahigh strength austenitic stainless steels in large quantities and in a wide range of product forms.
9. APPLICATIONS OF HIGH NITROGEN AUSTENITIC STAINLESS STEELS.

High nitrogen austenitic stainless steels are currently produced by powder metallurgy and pressure metallurgy routes, hence are quite expensive. Therefore they have found limited applications, in fields where the high cost of investment can be tolerated due to requirements of very high mechanical properties and resistance to corrosion in many aggressive environments.

Generator rotor retaining rings are a classical application of high nitrogen austenitic stainless steels. These components serve on all generators in all power stations of the world and are thus indispensable for electric power generators. The function of the retaining rings is to hold the copper conductor winding against the centrifugal forces. Generator rotor retaining rings may be small or huge forgings and because of the high rotating frequencies are some of the most highly stressed parts of the machine. Moreover, because of the energy loss due to Eddy currents the retaining rings should not be ferromagnetic materials. Thus, generator rotor retaining rings need to be made of high strength non-magnetic materials: these are generally cold worked, high nitrogen austenitic stainless steels [Stein99].

Because of their superior property combinations concerning strength, ductility and corrosion resistance, high nitrogen austenitic stainless steels are presently used also in the building industry for bolts and other fixations were resistance to stress corrosion cracking is important because the components are stressed in aggressive environments for very long time [Stein99b]. For this application they are cold worked to over 2000 MPa yield strength.

It would be now possible to produce wires with yield strength over 3000 MPa converting them into rivets, nails or bolts. Moreover, ultrahigh strength wires have application potential, for example in bridge building.

High nitrogen nickel-free austenitic stainless steels have recently been introduced to applications where human body fluids are in contact with the metal. Such components can be made by melting an forging, or alternatively by powder metallurgical methods, particularly metal injection moulding [Wohl98,Uggo96,Menz96]. Some applications are concerning; watch cases, dental correction devices.

Anyway, even if the list of applications could continue, they all are very limited applications.

This situation might change in the future because now high nitrogen austenitic stainless steels to be made without overpressure, providing the proper know-how is used, have been developed.

In this way they could be produced by means of traditional steel making facilities, they could be cheaper than traditional austenitic stainless steel grades as they contain no or very low nickel.

Thus wide applications of ultrahigh strength low nickel nigh nitrogen austenitic stainless steels in the automotive industry and construction and civil engineering industry would be possible. In each cases the compromise among ductility, strength, corrosion resistance and moderate price will be weighted differently.
10. OUTLOOK

Without any doubt the best way towards a more wide applications of HNS pass trough thermo mechanical controlled process (TMCP), for the production of diversified wrought products with high mechanical strength and corrosion resistance.
To reach this final goal further researches should be focused on the hot workability of HNS in as-cast condition, as the final behaviour during hot rolling is dictated by this microstructure. Hot workability tests should start with high nitrogen steels with chemical composition Fe25Cr16Mn3Ni0.1Co.9N or the niobium alloyed version Fe25Cr16Mn3Ni0.1Co.9N0.1Nb; and eventually more investigations related to study of other important parameters, such as strain rate and strain during hot rolling, should be performed in order to get the best from the TMCP. For these purposes “hot rolling simulation” on HNS should be performed with the final aim to improve the hot workability of these steels in the as-cast condition.
The grain refining effect by niobium addition and strengthening by dislocation hardening during hot rolling on corrosion resistance (crevice, pitting, stress corrosion cracking) was not investigated during this work, hence further studies in this direction are necessary.
Even if with the new possibility to melt HNS with traditional steel making facilities without overpressure, the welding problems of HNS should partially be solved, when this joining practice has to be followed, more investigations in this direction are necessary.
The effect of very small grains (less than 20µm) on the ductile to brittle transition temperature on high nitrogen austenitic stainless steels is still not clear; small samples and hence down-scaled Charpy V notch impact specimens are necessary in order to achieve very small grain size.
Appendix 1

DECOMPOSITION OF AUSTENITE IN AUSTENITIC STAINLESS STEELS.

Three main kinds of precipitation may take place during decomposition of austenite in austenitic stainless steels:

1) intermetallic phases;
2) carbides;
3) nitrides,

although other phases may also be present, such as sulphides and borides (in boron containing steels) [Padi02, Proc89, ASM94, Gav99].

A.1 INTERMETALLIC PHASES

Intermetallic phases formed between transition elements belonging to so called B-group (Mn, Fe, Co, Ni etc.) and A-group (Ti, V, Cr, Mo etc.).

The three intermetallic phases most frequently found in austenitic stainless steels are:

- sigma phases (σ);
- chi phases (χ);
- Laves phase (η).

Other intermetallic phases that can also occasionally be found are:

- G phase;
- R phase;
- Mu (µ) phase;
- gamma prime (γ');
- gamma double prime (γ'');
- η- Ni₃Ti phase;
- δ- Ni₃Nb phase.

Precipitation of intermetallic phases from austenite is normally associated with undesirable consequence like matrix depletion in alloying elements (like Cr, Mo and Nb) and reduction in ductility, toughness and corrosion resistance.

Exceptions are γ' Ni₃(Al, Ti) in precipitation-hardening iron based superalloys and the Laves phases Fe₅Nb in austenitic stainless steels since their occurrence can result in precipitation hardening.

Tab.A-1 summarized results concerning crystal structures and compositions of intermetallic phases, which may appear in austenitic stainless steels.
### Tab.A-1: intermetallic phases

<table>
<thead>
<tr>
<th>phase</th>
<th>Unit cell</th>
<th>Atoms per cell</th>
<th>Principal metallic element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sigma (σ)</td>
<td>bct</td>
<td>30</td>
<td>(Fe,Ni)x(Cr,Mo)y</td>
</tr>
<tr>
<td>Chi (χ)</td>
<td>bcc</td>
<td>58</td>
<td>(Fe,Ni)30Cr12Mo10</td>
</tr>
<tr>
<td>Laves (η)</td>
<td>hcp</td>
<td>12</td>
<td>Fe₂Mo; Fe₂Nb; Fe₂Ta; Fe₂Ti; Fe₂W</td>
</tr>
<tr>
<td>G</td>
<td>fcc</td>
<td>116</td>
<td>Ni₁₆Nb₁₆Si₇; Ni₁₆Ti₁₆Si₇; (Ni,Fe,Cr)₁₆(Nb,Ti)₆Si₇</td>
</tr>
<tr>
<td>R</td>
<td>hcp</td>
<td>53</td>
<td>Fe₂₃Mo₁₈Cr₁₃; (Fe,Ni)₁₀Cr₅Mo₃Si₂</td>
</tr>
<tr>
<td>Mu (μ)</td>
<td>rhombohedral</td>
<td>13</td>
<td>(Fe,Co)₇(Mo,W)₆; (Cr,Fe)₇Mo₃(Cr,Fe,Mo)₄</td>
</tr>
<tr>
<td>γ'</td>
<td>fcc</td>
<td>4</td>
<td>(Ni,Co,Fe,Cr)₁₂(Al,Ti)</td>
</tr>
<tr>
<td>γ''</td>
<td>bct</td>
<td>8</td>
<td>Ni₃Nb</td>
</tr>
<tr>
<td>η</td>
<td>hcp</td>
<td>8</td>
<td>Ni₃Ti</td>
</tr>
<tr>
<td>δ</td>
<td>orthorhombic</td>
<td>8</td>
<td>Ni₃Nb</td>
</tr>
</tbody>
</table>

A.1.1 SIGMA FASE (σ)

Sigma phase precipitation in austenitic stainless steels occurs between 550 and 900 °C. It has a body centered tetragonal crystal lattice with a composition, in austenitic stainless steels, that can be approximately written as (Fe, Ni)x(Cr, Mo)y.

Alloying elements like Cr, Mn, Mo, W, Si, Ti, Nb and Ta assist its formation being dissolved in it; whereas Ni, Co, Al, C and N hinder its precipitation and they do not dissolve in it.

Sigma phase precipitates mainly on grain boundaries depleting the adjacent matrix in Cr and Mo causing dissolution of carbides in these regions.

Sigma phase precipitation has a very slow kinetics, for at least three reasons:

1. carbon and nitrogen are insoluble in σ-phase, as a consequence σ-phase normally appears only after carbide and nitride precipitation has already taken place and the matrix is depleted in C and N;
2. its nucleation is difficult due to complex crystal structure very different from the parent austenite;
3. it is very rich in substitution elements thus requiring protracted diffusion times.

Cold deformation accelerated sigma phase precipitation, especially if there is recrystallization during annealing treatment.

Being extremely brittle, sigma phase precipitation has deleterious effect on toughness and ductility in austenitic stainless steels, its other harmful effect results in intercrystalline corrosion, as it is not chemically resistant.

Nitrogen alloying suppresses σ phase formation, which precipitates after relatively longer time and lower temperature, compare to standard austenitic steels.
A.1.2. CHI PHASE (χ)

The χ-phase is a carbon-dissolving compound that can be interpreted either as an intermetallic phase or as carbide M13C. It has a bcc α-Mn type crystal structure. Precipitation can only occur if Mo or/and Ti is present. χ-phase is found mainly on the grain boundaries, incoherent twin boundaries, coherent twin boundaries and on dislocation within the matrix. χ-phase precedes σ-phase formation and cold working accelerates its nucleation. Nitrogen alloying shifts χ phase precipitation to longer time and reduces the temperature range for precipitation. M₆C carbide tends to appear instead of the χ phase with increasing nitrogen content.

A.1.3. LAVES PHASE (η)

Laves phases in austenitic stainless steels have hexagonal close packed structure of MgZn₂ type. The most common are Fe₂Mo, Fe₂Nb and Fe₂Ti, or a combination of all three, for example, Fe₂(Mo,Ni,Ti). The Fe₂Nb Laves phase precipitation can cause significant precipitation hardening in austenitic stainless steels with high amount of Nb. Laves phases precipitation occurs along grain boundaries, incoherent and coherent twin boundaries and within the grain. In high nitrogen austenitic stainless steels with Mo η phase precipitation is shifted to higher temperature and it is accelerated by nitrogen.

A.2. CARBIDES PRECIPITATION

Carbon content in wrought austenitic stainless steels is usually between 0.05-0.25 weight percent, depending on the steel grades [ASM94]. Carbon solubility in austenite decreases rapidly as the temperature decreases and high Ni content furthermore reduces it, as consequence precipitation of M₂₃C₆ carbide, where M represents Cr, Fe, Mo and Ni, is a very common phenomenon. The addition of “stabilizing elements” such as Ti, Nb and V decreases the carbon solubility even further resulting in MC type carbides, where M represents Ti, Nb and/or V. The presence of Mo in certain alloys can cause the precipitation of η-type carbide M₆C, where M represents Fe, Mo and Cr. Tab A-2 summarized results concerning crystal structures and compositions of carbides which may appear in austenitic stainless steels.

<table>
<thead>
<tr>
<th>Carbides</th>
<th>Unit cell</th>
<th>Atoms per cell</th>
<th>Principal metallic element</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₂₃C₆</td>
<td>fcc</td>
<td>116</td>
<td>Cr, Fe, Mo, Ni</td>
</tr>
<tr>
<td>MC</td>
<td>ord fcc</td>
<td>8</td>
<td>Ti, Nb, V and/or Zr</td>
</tr>
<tr>
<td>M₆C</td>
<td>fcc</td>
<td>112</td>
<td>Fe, Mo, Cr</td>
</tr>
<tr>
<td>M₇C₃</td>
<td>hcp</td>
<td>40</td>
<td>Cr, Fe</td>
</tr>
</tbody>
</table>

Tab A-2: carbides
A.2.1. M$_{23}$C$_6$ CARBIDES

M$_{23}$C$_6$ is the main carbide that may precipitate in austenitic steels. It has fcc structure and Fe, Mo and Ni can substitute for Cr. The M$_{23}$C$_6$ carbide is normally undesirable since its presence is associated with sensitisation or intergranular corrosion by depletion in chromium content at grain boundaries, where it mainly precipitates, as well as a decrease in ductility and toughness.

Nitrogen alloying inhibits M$_{23}$C$_6$ precipitation.

M$_{23}$C$_6$ carbide is normally the first phase that may form in austenitic stainless steels. Depending on carbon content significant amount of carbides can form after only few minutes between 650 and 750°C.

In the case of stabilized steels M$_{23}$C$_6$ dissolution takes place due to precipitation of the more stable MC carbides.

In non-stabilized steels M$_{23}$C$_6$ dissolution may also occur if there is significant precipitations of intermetallic phases such as σ phase, χ phase and Laves phase. Intermetallic phases precipitation lower the Cr and Mo content of the matrix increasing carbon solubility and leading to partial dissolution of the M$_{23}$C$_6$ carbide.

In high nitrogen austenitic stainless steels nitrogen shifts M$_{23}$C$_6$ precipitation to longer times due to a retardation of M$_{23}$C$_6$ nucleation because this carbides does not contain nitrogen.

A.2.2. MC CARBIDES

The MC (M = Ti, Zr, Hf, V, Nb and Ta) carbides are very stable and are present in stabilized austenitic stainless steels such as AISI 321 (Ti stabilized), AISI 347 and 348 (Nb stabilized). Addition of strong MC carbides former elements hinders M$_{23}$C$_6$ precipitation. However Ti, Zr or Hf addition results, unavoidably, in formation of MN nitrides and M$_4$C$_2$S$_2$ carbosulphides that are even more stable than the MC carbide.

MC carbides having fcc lattice are formed in austenitic CrNi steels containing Ti or Nb. They reduce the carbon content in the matrix and prevent M$_{23}$C$_6$ precipitation. Along with a stabilising effect, their precipitation can be used for strengthening.

Nitrogen can partially substitute for carbon in these carbides. They are referred to as carbonitrides M(C,N) existing in a wide range of interstitial contents.

The MC carbide precipitation is predominantly intergranular, on dislocations and stacking fault however MC precipitation at grain boundaries can also occur.

A.2.3. M$_6$C CARBIDES

The carbides of the type M$_6$C (M = Fe, Cr, Mo, W, Nb and V), also known as η-carbide, are often found in austenitic stainless steels containing Mo, W and Nb. They contain more than one metallic element, requiring the presence of at least three types of atoms and usually represented by the formulae A$_3$B$_2$C or A$_4$B$_2$C (i.e. Fe$_3$Mo$_2$C in Mo containing steels).

This type of carbide has fcc, diamond type, structure.

Nitrogen additions favour M$_6$C precipitation instead of the detrimental M$_{23}$C$_6$, because the former is able to dissolve more nitrogen than the latter. Nitrogen atoms replace carbon atoms in the lattice.
This type or carbide is very common in superaustenitic stainless steels due to their high Mo content (>6wt%).

A.3. NITRIDES

Nitrides in austenitic stainless steels can be grouped in two classes:

1. primary nitrides of type MN (M = Zr, Ti, Nb and V) formed in stabilized steels containing residual amounts of nitrogen (<0.1wt%);
2. secondary nitrides of the type M₂N (M = Cr, Fe) formed in stainless steels containing high levels of nitrogen (>0.1wt%).

Tab A-3 summarized results concerning crystal structures and compositions of nitrides which may appear in austenitic stainless steels.

<table>
<thead>
<tr>
<th>Nitrides</th>
<th>Unit cell</th>
<th>Atoms per cell</th>
<th>Principal metallic element</th>
</tr>
</thead>
<tbody>
<tr>
<td>MN</td>
<td>Ord fcc</td>
<td>8</td>
<td>ZrN; TiN; NbN; VN</td>
</tr>
<tr>
<td>M₂N</td>
<td>hcp</td>
<td>9</td>
<td>(Cr,Fe)₂N</td>
</tr>
<tr>
<td>Z-phase</td>
<td>tetragonal</td>
<td>6</td>
<td>CrNNb</td>
</tr>
</tbody>
</table>

Tab A-3: nitrides

A.3.1 PRIMARY NITRIDES MN

The MN nitrides have the same crystalline structure as MC carbides but they are even more stable and do not dissolve during solution annealing. They can dissolve small amounts of other metallic elements present in the matrix such as Fe, Cr and Ni, but only very small amounts of C. Chromium nitride precipitation in austenitic stainless steels with low levels of nitrogen (less than 0.1wt%) usually occurs in continuous mode on grain boundaries, inside the grains and on dislocations.

A.3.2 SECONDARY NITRIDES M₂N

In high nitrogen austenitic stainless steels (Cr,Fe)₂N type nitrides form below 1000°C, with an hexagonal closed packet lattice (hcp ε-nitride); discontinue precipitation is common observed giving a cellular structure referred sometimes as “false perlite” [Sim96]. Nitrogen depletion in the matrix due to nitrides precipitation can make austenite unstable and formation of ferrite and sigma phase is possible. Furthermore (Cr,Fe)₂N precipitation has adverse effect on toughness and on the corrosion resistance of austenitic stainless steels. Nitrogen in solid solution delays the precipitation of phases, which do not dissolve or at least in very small quantity nitrogen, such as M₂₃C₆, σ, χ and Laves phase. In stainless steels containing Nb and more than 0.4% nitrogen, precipitation of Z phase can occur. Z phase is a nitride, with a tetragonal lattice structure, which contain Cr, Mo, Nb; it forms on grain boundaries and within grains with different morphologies.
Appendix 2

INTERACTION PARAMETERS ACCORDING TO ZHENG

First order parameters:

\[ e_{Cr}^N = \frac{320.6}{T} + 0.1127 \]
\[ e_{Ni}^N = \frac{16.0}{T} + 0.00288 \]
\[ e_{Mn}^N = \frac{135.5}{T} + 0.03567 \]
\[ e_{Mo}^N = \frac{417}{T} + 0.2426 \]
\[ e_{V}^N = \frac{-1540}{T} + 0.79 \]
\[ e_{Nb}^N = \frac{-173}{T} \]
\[ e_{Co}^N = \frac{28}{T} - 0.004 \]
\[ e_{Si}^N = \frac{274}{T} + 0.11 \]
\[ e_{C}^N = 0.12 \]
\[ e_{P}^N = 0.05 \]

Second order parameters:

\[ r_{Cr}^N = \frac{6.41}{T} + 0.0028 \]
\[ r_{Ni}^N = 1.887 \cdot 10^{-4} \]
\[ r_{Mn}^N = \frac{2.789}{T} - 0.001245 \]
\[ r_{CrNi}^N = \frac{7.0}{T} - 0.005 \]
\[ r_{CrMn}^N = \frac{7.23}{T} - 0.00165 \]
\[ r_{CrCrMn}^N = -1.06 \cdot 10^{-4} \]
Alloys used in this work were produced in a vacuum induction furnace, see Fig. A-1, using pure elements like Ni, Cr, Mn, Fe, Cu and binary alloys of Fe-Mo, Fe-Nb, Fe-V, Mn-N and Cr-N, with chemical composition listed in Tab. A-4.

The melting practice by VIM was carried out following these guidelines.

Once the initial iron and eventually nickel charge into the crucible was completely melted in a vacuum of $10^{-2}$ mbar, nitrogen gas was introduced into the vacuum chamber up to a pressure of 900-950 mbar (maintained stable until extraction of cast ingots after cooling).

Then, the other alloying elements progressively added to the melt at a temperature estimated around 1550°C following the sequence: Cr, Fe-Mo, Fe-V, Fe-Nb, Mn.
When complete dissolution of all raw materials occurred, 20g of CaSi together with 5g of aluminum foil were added as a deoxidizing medium. After a couple of minutes power was decreased to reach a liquid temperature in the range 1450-1460°C before the addition of C, Cu, Cr2N in this order.

Nitrogen solubility in the liquid phase is strongly affected by the bath temperature, namely it decreases with increasing the liquid temperature, and hence in order to avoid nitrogen escape from the melt during Cr2N addition, the liquid temperature should be the lowest possible. A good compromise between bath fluidity and nitrogen solubility was achieved at 1450-1460 °C (lower temperatures gave rise to solidification around the crucible’s walls).

Casting was performed pouring the liquid metal into cold steel cylinders with a copper plate on the bottom. To accelerate nitrogen take up chromium nitrides were added slowly to the melt (alloy composition of course take also in consideration the chromium contained in the added nitrides). After cooling an ingot of about 10Kg weight with a diameter of 85 mm was extracted from the furnace. For some experiments three smaller ingots of about 3 kg weights with a diameter of 45 mm were cast.

All the ingots were subsequently homogenized in an electric furnace in air, with a combination of temperature and time depending upon alloy composition before hot forging, necessary to modify the coarse microstructure resulting from casting into a more uniform with homogenous grains.

Hot forging was carried out by the company Burgher & Co (Schafisheim-AG, Switzerland) with a hammer machine between 1100 and 1200 °C, in order to obtain plates with a rectangular cross section of approximately 70mm x 17mm (if not otherwise specified), See Fig. A-2.

Ingots were heated up to forging temperature in an oven (gas furnace) and water quenched after forging.

Fig.A-2: two different phases during hot forging of alloys developed in this work.
Appendix 4

ALLOYS CHEMICAL COMPOSITION

$Ty =$ minimum annealing temperature to have fully austenitic microstructure, without precipitation of $M_23C_6$ or $Cr_2N$, after one hour.

<table>
<thead>
<tr>
<th>ETH Nr.</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>Nb</th>
<th>V</th>
<th>$Ty$ [°C]</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1863</td>
<td>23</td>
<td>15</td>
<td></td>
<td>0.20</td>
<td>0.73</td>
<td></td>
<td></td>
<td>1050</td>
<td>Carbon effect</td>
</tr>
<tr>
<td>1883</td>
<td>23</td>
<td>17</td>
<td></td>
<td>0.19</td>
<td>0.75</td>
<td></td>
<td></td>
<td>1050</td>
<td></td>
</tr>
<tr>
<td>2029</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>0.72</td>
<td></td>
<td></td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>2066</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.15</td>
<td>0.74</td>
<td></td>
<td></td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>2067</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.14</td>
<td>0.74</td>
<td></td>
<td></td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>2068</td>
<td>23</td>
<td>16</td>
<td>2</td>
<td>0.10</td>
<td>0.72</td>
<td></td>
<td></td>
<td>925</td>
<td></td>
</tr>
<tr>
<td>2108</td>
<td>23</td>
<td>16</td>
<td>1</td>
<td>0.12</td>
<td>0.72</td>
<td></td>
<td></td>
<td>975</td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>0.78</td>
<td>0.15</td>
<td></td>
<td>1000</td>
<td>Niobium effect</td>
</tr>
<tr>
<td>2012</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>0.76</td>
<td>0.30</td>
<td></td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>2037</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>0.75</td>
<td>0.10</td>
<td></td>
<td>1000</td>
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<td>0.05</td>
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<td>975</td>
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</tr>
<tr>
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<td>1</td>
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<td>0.10</td>
<td></td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>2137</td>
<td>25</td>
<td>15</td>
<td>3</td>
<td>0.08</td>
<td>0.83</td>
<td>0.02</td>
<td></td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>2138</td>
<td>26</td>
<td>15</td>
<td>3</td>
<td>0.08</td>
<td>0.87</td>
<td>0.02</td>
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</tr>
<tr>
<td>1956</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>0.95</td>
<td>0.50</td>
<td></td>
<td>1150</td>
<td>Vanadium effect</td>
</tr>
<tr>
<td>1957</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>1.06</td>
<td>1.00</td>
<td></td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>2035</td>
<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>0.75</td>
<td>0.60</td>
<td></td>
<td>1150</td>
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<tr>
<td>2111</td>
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<td>1</td>
<td>0.12</td>
<td>0.88</td>
<td>0.60</td>
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<td>1200</td>
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</tr>
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<td>23</td>
<td>16</td>
<td></td>
<td>0.17</td>
<td>0.75</td>
<td>0.60</td>
<td></td>
<td>1100</td>
<td>Niobium and Vanadium effect</td>
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<td>2141</td>
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<td>15</td>
<td>3</td>
<td>0.08</td>
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<td>0.30</td>
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<td>1050</td>
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Tab 6-1: alloys used for study the grain reeling by Nb and V addition (Chapter 6)

<table>
<thead>
<tr>
<th>ETH Nr.</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>Nb</th>
<th>$Ty$ [°C]</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>2139</td>
<td>30</td>
<td>15</td>
<td>3</td>
<td>0.08</td>
<td>1.20</td>
<td>0.02</td>
<td>1050</td>
<td>Same as 2238</td>
</tr>
<tr>
<td>2212</td>
<td>25</td>
<td>16</td>
<td>2</td>
<td>0.10</td>
<td>0.90</td>
<td></td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>2218</td>
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<td>16</td>
<td>2</td>
<td>0.10</td>
<td>0.84</td>
<td>0.10</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>2237</td>
<td>25</td>
<td>16</td>
<td>3</td>
<td>0.10</td>
<td>0.88</td>
<td></td>
<td>1025</td>
<td></td>
</tr>
<tr>
<td>2245</td>
<td>30</td>
<td>16</td>
<td>4</td>
<td>0.12</td>
<td>1.34</td>
<td></td>
<td>1100</td>
<td></td>
</tr>
</tbody>
</table>

Tab 7-1: alloys used for study the influence of different nitrogen content and strengthening mechanism on mechanical properties of HNS (Chapter 7)
### Tab 7-3: alloys used for study the influence of grain size and yield strength on the ductile to brittle transition temperature in HNS (Chapter 7)

<table>
<thead>
<tr>
<th>ETH Nr.</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>Nb</th>
<th>Ty [°C]</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>2262</td>
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<td>16</td>
<td>3</td>
<td>0.09</td>
<td>1</td>
<td>0.06</td>
<td>1050</td>
<td>With Nb effect</td>
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<tr>
<td>2267</td>
<td>25</td>
<td>16</td>
<td>3</td>
<td>0.10</td>
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<td>0.05</td>
<td>1100</td>
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<tr>
<td>2268</td>
<td>30</td>
<td>15</td>
<td>3</td>
<td>0.08</td>
<td>1.25</td>
<td>0.05</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>2265</td>
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<td>3</td>
<td>0.10</td>
<td>0.94</td>
<td>0.05</td>
<td>1050</td>
<td>Only N effect</td>
</tr>
<tr>
<td>2266</td>
<td>30</td>
<td>15</td>
<td>3</td>
<td>0.08</td>
<td>1.24</td>
<td>0.05</td>
<td>1100</td>
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</tr>
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<td>2278</td>
<td>27</td>
<td>16</td>
<td>3</td>
<td>0.10</td>
<td>1.03</td>
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<td>1000</td>
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<td>3</td>
<td>0.10</td>
<td>0.88</td>
<td></td>
<td>1000</td>
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</tbody>
</table>

### Tab 8-1: alloys used during hot rolling experiments as well comparison between mechanical properties after SRX and hot rolling (Chapter 8)

<table>
<thead>
<tr>
<th>ETH Nr.</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>Nb</th>
<th>Ty [°C]</th>
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<tbody>
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<tr>
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<td>16</td>
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</tr>
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### Tab 8-2: alloys developed to be hot rolled (Chapter 8)

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<th>ETH Nr.</th>
<th>Cr</th>
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<th>Ni</th>
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Appendix 5

EMPIRICAL MODEL FOR NITROGEN SOLUBILITY IN THE SYSTEM Fe-Cr-Mn-Ni-Mo-C-N WITHOUT OVERPRESSURE

Production of high nitrogen austenitic stainless steels by means of traditional steel making facilities, without overpressure, requires a balanced chemical composition of nitrogen solubility enhancer elements to prevent pore formation during the solidification. Although many models for nitrogen solubility calculation exist in the literature of HNS and software like ThermoCalc are widely used among alloy developers, some kind of empirical models for nitrogen solubility evaluation, based on analysis of a large number of experimental data, may be very useful for a first estimation of the nitrogen content that might be expected on the base of the only chemical composition.

From a large number of high nitrogen austenitic steel grade developed at the ETH Zurich, the following model for nitrogen solubility was found (alloying elements in weight percent):

\[ N = 0.05 \cdot Cr + 0.03 \cdot Mn - 0.75 \]  \[1\]

During this work many other high nitrogen austenitic stainless steels were melted, enriching the experimental databank for nitrogen solubility, and a new correlation was proposed fitting better the experimental data, as shown in Fig.A-3:

\[ N = 0.066 \cdot Cr + 0.02 \cdot Mn + 0.19 \cdot C - 0.025 \cdot Ni + 0.05 \cdot Mo - 1.05 \]  \[2\]

Fig.A-3: nitrogen solubility measured and calculated by equations \[1\] and \[2\] in austenitic stainless steels with chemical composition in the range:

- 17-78wt% Cr
- 0-30wt% Mn
- 0-49wt% Ni
- 0-7.3wt% Mo
- 0-0.3wt% C
- 0.3-1.5wt% N

Equation \[2\] should be considered only as a rough estimation for nitrogen solubility as other important effects, like the temperature, are not included.

Anyway, even with this limitation a good fit within an error of about 15% was found.
Appendix 6

EMPIRICAL CORRELATION BETWEEN HARDNESS $HV_{10}$ AND YIELD STRENGTH $R_{p0.2}$ IN HIGH NITROGEN AUSTENITIC STAINLESS STEELS

During this work high nitrogen austenitic stainless steels were developed with yield strength in the range 400-3600 Mpa. Results from tensile tests and hardness measurements were collected from a large number of experimental conditions in many different austenitic alloys; the common feature was a fully austenite microstructure free of any kind of precipitates. A good correlation between yield strength $R_{p0.2}$ and hardness $HV_{10}$ was found. Experimental data were analysed by regression analysis using the last square method with the final goal to achieve the best fit among all experimental data regardless the form of the equation used for. In this way an easy tool for a good estimation of yield strength (within an error of +/- 5%) on the base of only hardness test was found.

Fig. A-4 shows how the best fit was found by means of this equation:

$$R_{p0.2} = 0.0037(HV_{10})^2 + 1.4716HV_{10} - 49.8 \quad [\text{MPa}]$$

Fig. A-4: experimental correlation between hardness and yield strength in high nitrogen austenitic stainless steels

$R^2=0.9842$
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PERSONAL DATA

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Date of Birth: Dec 25, 1968
Place of Birth: Salo’ (Brescia), Italy
Nationality: Italian
Marital Status: single

EDUCATION

2000 – 2003 PhD-Student in Material Science, Institute of Metallurgy, Swiss Federal Institute of Technology, Zurich (ETHZ)
Research project: Development of ultrahigh-strength austenitic stainless steels alloyed with nitrogen

1997-1999 Research Assistant in Metallurgical Engineering, University of Padova (Italy).
Research project: Damage for Rolling Contact Fatigue in perlitic steels for train wheels.

1989-1997 Mechanical Engineering Diploma (mark: 110/110 cum laude), University of Brescia (Italy).
Dissertation: The phenomenon of the load relaxation in steels used for high strength bolts.

1990-1991 Military service in Italian Army as radio operator and teletypist


1979-1982 Middle school study in Gargnano (Brescia), Italy.

1975-1979 Elementary school study in Gargnano (Brescia), Italy.
WORKING EXPERIENCE

Jan 2000 – Jan 2003 Graduate Research Assistant/ Ph.D. at the Institute of Metallurgy, Swiss Federal Institute of Technology, Zurich (ETHZ), Switzerland

Jan 1999 – Dec 1999 Graduate Research Assistant at the Metallurgical Engineering Department of Padova University (Italy).

Jan 1998 – Dec 1998 Graduate fellow (Academic Guest) at the Institute of Metallurgy, Swiss Federal Institute of Technology, Zurich (ETHZ), Switzerland

Mar 1997 – Nov 1997 Graduate Research Assistant at the Mechanical Engineering Department of Brescia University (Italy)

SKILLS

1. LANGUAGE

- Mother tongue: Italian
- Fluently: English
- Basic knowledge: German, French

2. SOFTWARE

Thermocalc: used for thermodynamic simulation in equilibrium, phase diagrams, others;
Word, Excel, Power Point, Corel Draw, Photoshop: for general purposes;
Basic, Pascal, LabView: basic knowledge of programming.

3. PRACTICAL

Operations with vacuum inductive furnace;
Hot rolling and hot forging.

HOBBIES

Music, dancing, travelling, reading, airplanes and flight simulations on PC.