POLITECNICO
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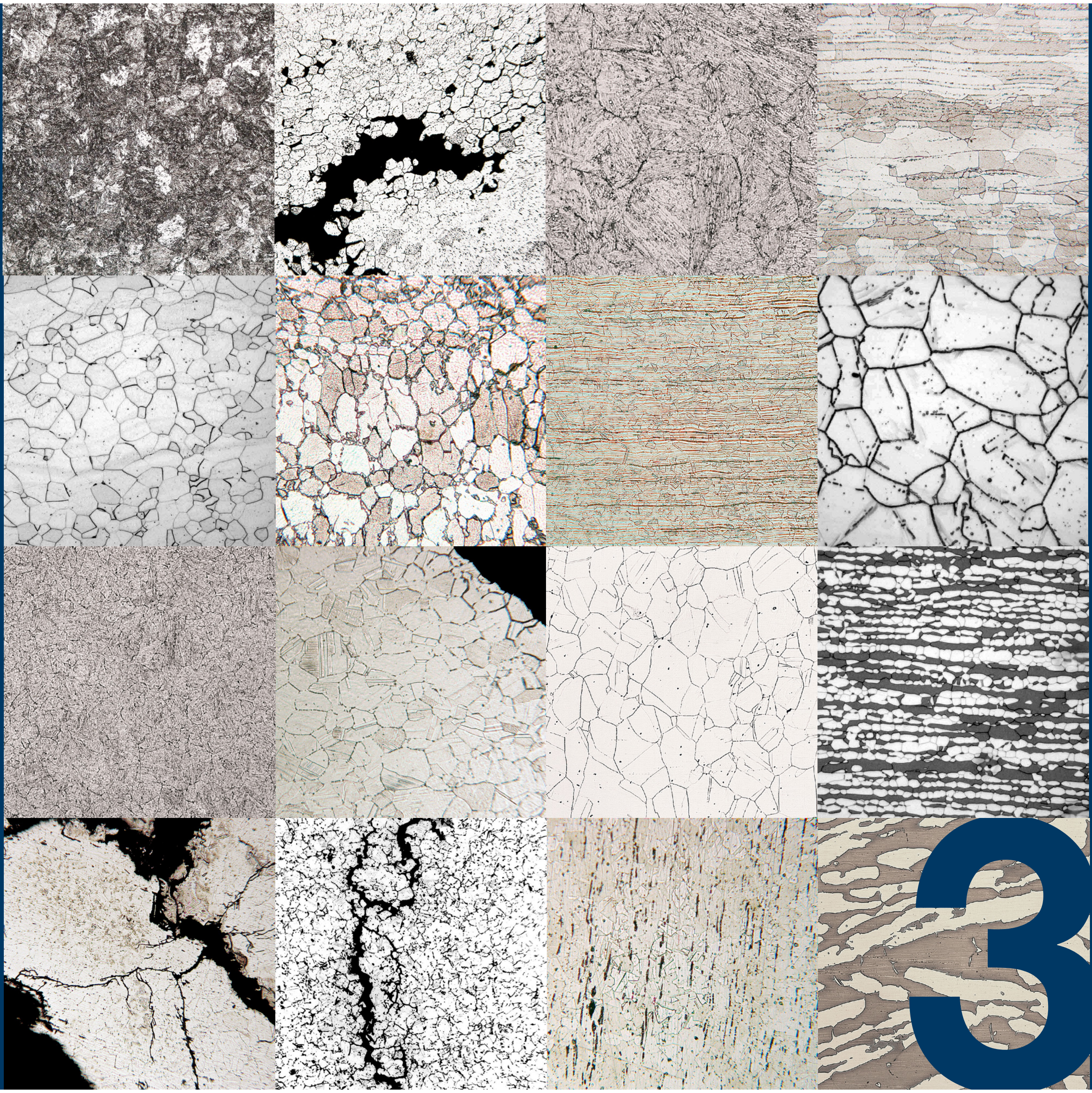
DIPARTIMENTO DI MECCANICA

Stainless steels



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Marco V. Boniardi e Andrea Casaroli

TRAFILIX
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This book is dedicated to our parents
and to all people close to us
who supported us so far
and keep on supporting us every day.

'Tis the custom of pedagogues to be eternally thundering in their pupil's ears, as they were pouring into a funnel, whilst the business of the pupil is only to repeat what the others have said: now I would have a tutor to correct this error, and, that at the very first, he should according to the capacity he has to deal with, put it to the test, permitting his pupil himself to taste things, and of himself to discern and choose them, sometimes opening the way to him, and sometimes leaving him to open it for himself; that is, I would not have him alone to invent and speak, but that he should also hear his pupil speak in turn. Socrates, and since him Arcesilaus, made first their scholars speak, and then they spoke to them.

Michel de Montaigne, 1533-1592.

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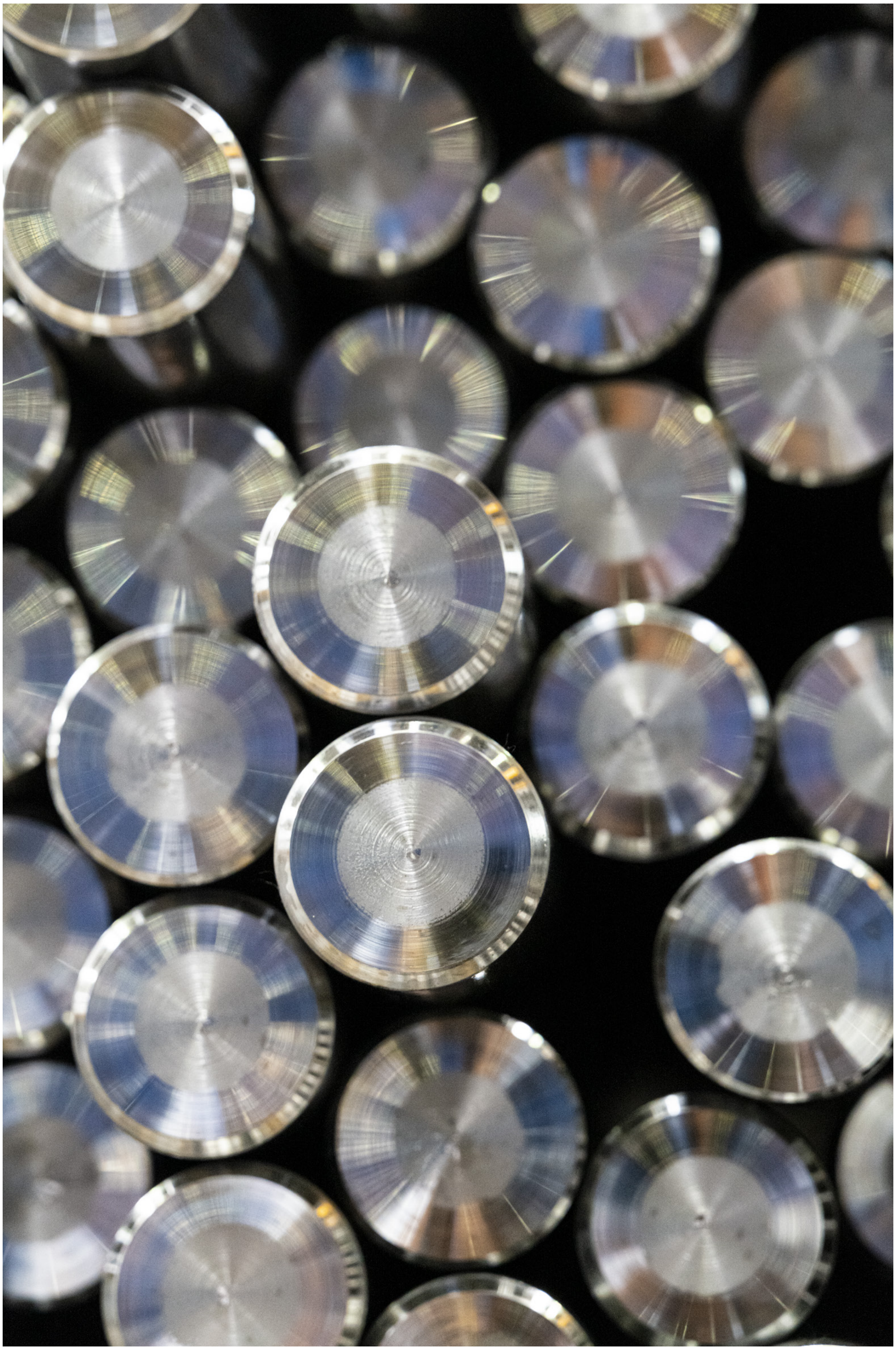

PREFACE

"Lovin' Steel": A couple of words that enclose the story, passion and future of an industrial group and summarize the reason why, since ever, the Lucefin Group has been investing in the dissemination of the culture of steel through publications, like this one, where to collect and condensate the knowledge acquired during years of experience and work.

The passion for steel is inherent in our family. My father Luigi Buzzi handed it down to me with so much intensity that I feel it my duty to keep it alive with the same enthusiasm.

Our group has always believed that experiences must be shared, that our knowledge is a valuable asset to be made widely known, mainly to those who will have the chance to engage in this field. Consequently, we made the decision to talk about stainless steel, which is our latest entrepreneurial choice, by means of this dedicated publication. Here all of its secrets are revealed and entrusted to those who for many years have been studying and teaching its intimate nature by profession or for passion, without ever forgetting that, basically, what is really important is not steel, but the world of people and situations that turn around it.

I wish to thank the authors Marco Boniardi and Andrea Casaroli and Politecnico di Milano, for selecting us to share this initiative. I thank all of our R&D staff from Trafilix and Trafitec for their valuable and essential contribution. My special thanks go to Domenico Surpi who, years ago, first provided the idea of realizing a series of technical publications for which he gladly made available his experience, knowledge, capability and perseverance. These publications, unique in the steel sector for practical usefulness, ability to précis, and plenty of technical information, have left so far and will keep on leaving a permanent sign of the Lucefin Group in our sector. Thank you very much to all from the deep of my heart!

Not a volume for a few, but for all because steel is nobody's possession, but belongs to all who love it.

Giorgio Buzzi, Esine - Brescia, 7th April 2014

ACKNOWLEDGMENTS

Some years ago, my boss Prof. Walter Nicodemi suggested to me the idea of a new book about stainless steels. Chatting before the coffee machine, he tempted me into re-writing together his book "Stainless Steels", published by Associazione Italiana di Metallurgia of Milan and one of the few books on this subject in Italian.

I immediately subscribed to his proposal, but I kept postponing his requests due to several personal problems.

A bad day, the "Prof" (as I called him) told me he had a minor health problem and had to be hospitalized for treatments.

I never met him again. I came to know that he was feeling really bad and suffering from an unforgiving disease. Still now, I regret not having visited him, but once he let out that this was what he preferred.

He would rather have all of us at Politecnico remember him as he used to be, combative and full of strength.

I wrote this book with Walter Nicodemi on my mind, his work and all that he taught me over many years.

My thanks go to Luigi and Giorgio Buzzi, Domenico Surpi, Massimo Sperto and Vittorio Boneschi of the Lucefin Group for giving me the opportunity to publish this book and to Chiara Pessognelli and Laura Bassi for their outstanding support to the graphic layout of the Italian, English and German versions.

This book is also the chance of a lifetime to thank all those who, over the time, instilled in me the passion for Metallurgy and the study of stainless steels, the leitmotif of my professional life.

I first got in touch with the world of "stainless steel" when preparing my dissertation about cold deformation of ferritic stainless steels under the guidance of Prof. Giuseppe Silva. He transmitted to me the love for teaching and I hope I have managed to put some of his passion in this book.

During the first years of my university career, I also had the chance to meet Prof. Gabriele Di Caprio who wrote the other famous reference book on stainless steels in Italian. Working with him on stainless steel small parts, I appreciated his humanity and great professional seriousness. The latter being a characteristic that today is rather hard to find in the world of work where I operate.

I am filled with gratitude towards Prof. Mario Balbi, prematurely deceased in 1997. He was a gentle man with a lot of common sense; he made me understand the great relevance of stainless steel welding and associated issues.

Surely, this book would not exist without the valuable cooperation of Centro Inox of Milan and its engineers Fausto Capelli, my all-time friend Paolo Viganò, and Vittorio Boneschi at least as long as he worked there. In addition to stainless steels, we shared some other much more important things, such as the pleasures of good food and nice walks in the mountains.

An entire industrial world is connected with stainless steel; without it, my work would be a mere theoretical experiment. My thanks go to: Emilio Rocchi from Acciai Vender, Fabio Bontempo from Ugitech, Mario Cusolito and Enrico Mariani, both from Rodacciai, Antonio Vienna, Giovanni Pattarini and Gabriele Rampinini from Forgiatura Vienna, Valentina Vicario, previously in Cogne and now with Fomas, Guido Perricone from Brembo, Francesco Ratto previously with Airliquide and now with Cryo Service.

I must also mention the support received during these years from many industrial labs that operate in close cooperation with manufacturing firms. Open exchanges with intelligent persons about technical problems help everybody increase their wealth of knowledge. These persons are the engineers Luca Bonvini, Marco Feraboli with Ms Patrizia Maio from Hammer, Alessandra Marelli, Marco Casaril and Clemente Marelli (Doctor-Engineer Honoris Causa), from Omeco, Giovanni Rivolta from Istituto Scientifico Breda, and Ms Elena Bresciani of Exova.

This book is also the result of the cooperation and unfailing support provided by all the university colleagues I worked with in the world of stainless steel over the last twenty years. Warm thanks to the metallurgy lab technicians in the Department of Mechanical Engineering of Politecnico di Milano, namely Piero Pellin, Maurizio Pardi and Luca Signorelli; to my secretary Ms Cinzia Farina; to Professors Roberto Roberti and Marina La Vecchia of the University of Brescia; to Prof. Barbara Rivolta and also Silvia Barella and Fabrizio D'Errico of Politecnico di Milano. I also owe a lot to Gianmatteo Martinelli, Mattia Bellogini, Silvia Cincera, Alessia Sironi and Chiara Tagliabue who have now transferred their sphere of interest outside the academic world.

An affectionate thank-you to Prof. Benedetto Bozzini of the University of Lecce. We have known each other since the time of our dissertations and he is both a dear friend and a colleague. Without his electrochemical advice, a significant part of this work would be missing.

The most precious aspect of Politecnico di Milano is my students, especially those engaged in writing their theses. If I am a good teacher, I think it is all thanks to them. As Ralph Waldo Emerson put it: "It is one of the most beautiful compensations of life that no person can sincerely try to help another without helping themselves".

Last but by no means least, heart-felt thanks go to Andrea Casaroli, my "merciless" co-author. Without his stubbornness, his tenacity and his "working method", this book would not exist. And this is not just for the sake of saying it!

Marco V. Boniardi, Cusano Milanino - Milano, 15th March 2014

After the appreciation words of Marco Boniardi towards me, I find it extremely difficult to write something that does not sound trivial. I have nobody to specially thank. Instead, Marco Boniardi is acquainted with very many people and has acquired a decades-long experience that I am just starting to build up.

Maybe, the only thing worth mentioning is the difference that exists between Marco and me and is definitely in terms of method and not of objectives. I think that this difference that enabled us to achieve such a complex work, peeps out from the lines of the book. However, readers will have the last word!

During the many hours we spent together to write this book, Marco and I discussed a lot, sometimes even vehemently because Marco and I, deep down, are poles apart. We are as different as day and night. You go to seaside during the day under the sun; if you want to admire the stars, you go out at night.

We are really different or, paraphrasing the comment of the Italian author Marco Paolini about rugby and soccer: "I, Andrea, am to Marco as World War I is to World War II", as trench warfare is to Blitzkrieg". Marco has a creative mind, I have my method. Had it been for Marco, he would never write a book. He is talented, he knows things and has them all in his head while I have to systematize and build my knowledge. For me, "writing a book" was like realizing something special, like erecting a tower.

Therefore, my thanks go to Marco Boniardi for the possibilities he gave me to cooperate in this successful work. I trust I did my best and hope I met his expectations.

Andrea Casaroli, Sarmato - Piacenza, 20th March 2014

Each book - and this is not a flaw - is "alive",
and wishes to continue to live.

For this to occur, your help is needed.
Any suggestions or advice you would like to give us,
and any images or micrographs you would like to send us,
will be well accepted and very appreciated. You will help
us improve the quality of the next edition.

We urge you to write to the following addresses:
marco.boniardi@polimi.it and andrea.casaroli@polimi.it

Thank you everyone in advance... for everything!

1. WHAT ARE STAINLESS STEELS?

Stainless steel is an iron-based alloy with a significant chromium content; in many cases, together with chromium, other special chemical elements are intentionally added, such as nickel and molybdenum. The main characteristics of this family of steels is resistance to wet corrosion, or electrochemical corrosion, in aggressive environments such as fresh water, sea water, contaminated water based solutions, acidic and basic environments, industrial environments, etc. Another important characteristic of this category of steel is the resistance to high temperature oxidation as typically occurs in hot gases.

The typical fields of application for stainless steel are in the chemical industry, oil industry, foodstuff and paper manufacturing, the pharmaceutical, biomedical and transport sectors, in off-shore structures, household appliances, and the construction and urban furnishing sectors.

In accordance with the European standard EN 10088, steel is classed as stainless when its chemical composition has a minimum chromium content of 10.5%. However, it should be noted that all grades of stainless steel available on market, show a chromium content greater than this value, normally ranging from 13% to 18%; in practice, a chromium content of at least 12% is needed to obtain satisfactory resistance to corrosion in water based solutions.

Chromium ensures the possibility of creating a very thin layer of oxide (also known as passive film) on steel surface, mainly made up of chromium oxides and hydroxides Cr_2O_3 and $Cr(OH)_3$: this film is insoluble, compact and adheres well to the substrate thereby protecting the base material. The passive film does not only comprise chromium oxides and hydroxides: tests performed using XPS[1] techniques have also revealed iron and molybdenum (in form of oxides and hydroxides) and have shown how nickel tends to accumulate in the interface between passive film and steel substrate (figure 1).

The film of chromium oxide/hydroxide is extremely thin - just a few nanometres - and transparent to luminous radiation, and therefore gives stainless steel its typical grey-silver metal finish, as clearly seen in cooking utensils, pans, cutlery and metal watch straps.

All the above properties are consequence of rapid reaction of chromium with oxygen. Oxidation of stainless steel, also known as passivation, occurs naturally and spontaneously in neutral oxidating environments, such as in contact with air. Otherwise, as normally occurs in industrial processes, it is induced by immersion of the semi-finished product in diluted nitric acid solution. The chromium oxide/hydroxide film acts as a sealant and creates a barrier between material and external environment. In a certain sense the term “stainless” is not appropriate; steel is, in fact, highly “oxidizable” and as it is in a stable oxide/hydroxide state, it is also highly resistant to corrosion from surrounding environment.

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[1] *XPS is the acronym for X-ray Photoelectron Spectroscopy. The sample is exposed to a flow of photons, emitted by X-ray: the interaction of photons with the material to be investigated lead to emission of electrons each of which has a specific kinetic energy. By measuring this kinetic energy, it is possible to calculate the binding energies and then the type of chemical elements. This technique is also known as ESCA, i.e. Electron Spectroscopy for Chemical Analysis.*

The passive film of chromium oxide/hydroxide has another important property: when scuffed, scratched or mechanically damaged, it spontaneously forms again on the surface of the component, thus immediately restoring protection against corrosion (figure 2).

Chromium also ensures high resistance to localised forms of corrosion such as pitting and crevice.

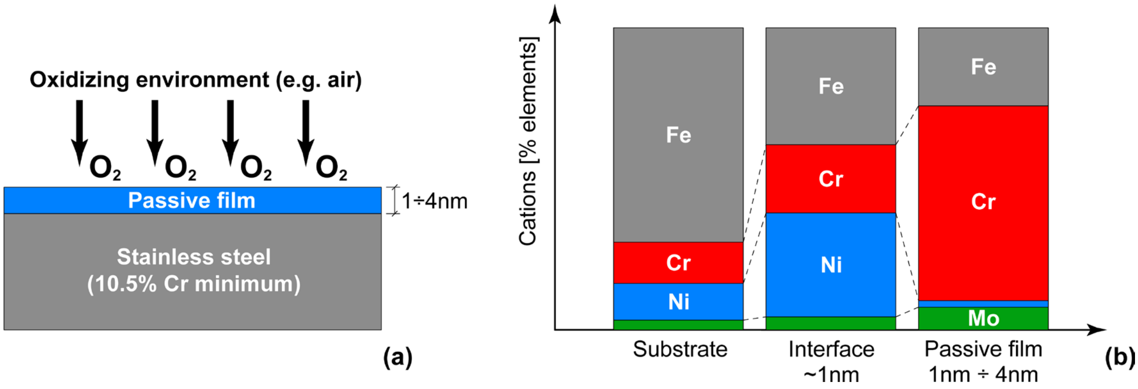


Figure 1 – (a) Mechanism of stainless steel passivation and (b) chemical elements in the passive film, in the interface and in the substrate of a stainless steel grade 18%Cr - 14,3%Ni - 2,5%Mo [from Olefjord and Elfstrom 1982].

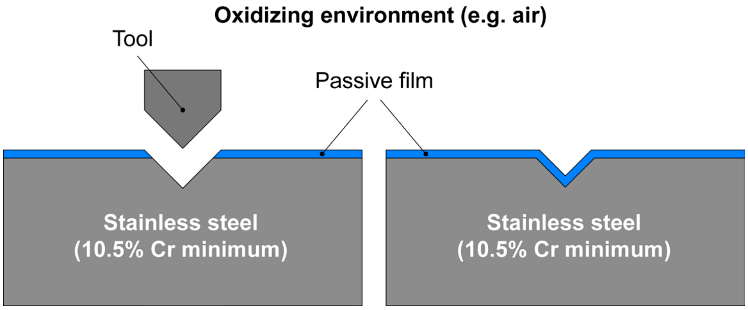


Figure 2 – Mechanical damage of the passive film and subsequent re-passivation of stainless steels [from Baddoo 1995].

The chromium oxides are also highly stable at high temperatures, then stainless steels are highly resistant to oxidation and corrosion when subject to heat.

In very general terms, it can be concluded that the greater the quantity of chromium, the greater the resistance of stainless steel to corrosion. This applies both in conditions of wet corrosion and under the effect of high temperature oxidation. As an example, figure 3 shows the corrosion speed in terms of weight loss of chromium-iron alloys in diluted solutions of nitric acid or sulphuric acid (figure 3a) and in conditions of high temperature oxidation (figure 3b).

Note that nitric acid is an oxidizing acid that can cause passivation of chromium, in this case the steel's resistance to corrosion increases in proportion to the increase in chromium content, whereas in the presence of a reducing acid, such as sulphuric acid, the speed of corrosion follows a similar trend in reverse.

An additional effect of the chromium is to improve the creep resistance; this is the reason why stainless steels are widely used at high temperature in conditions where the damage mechanism is predominantly caused by creep.

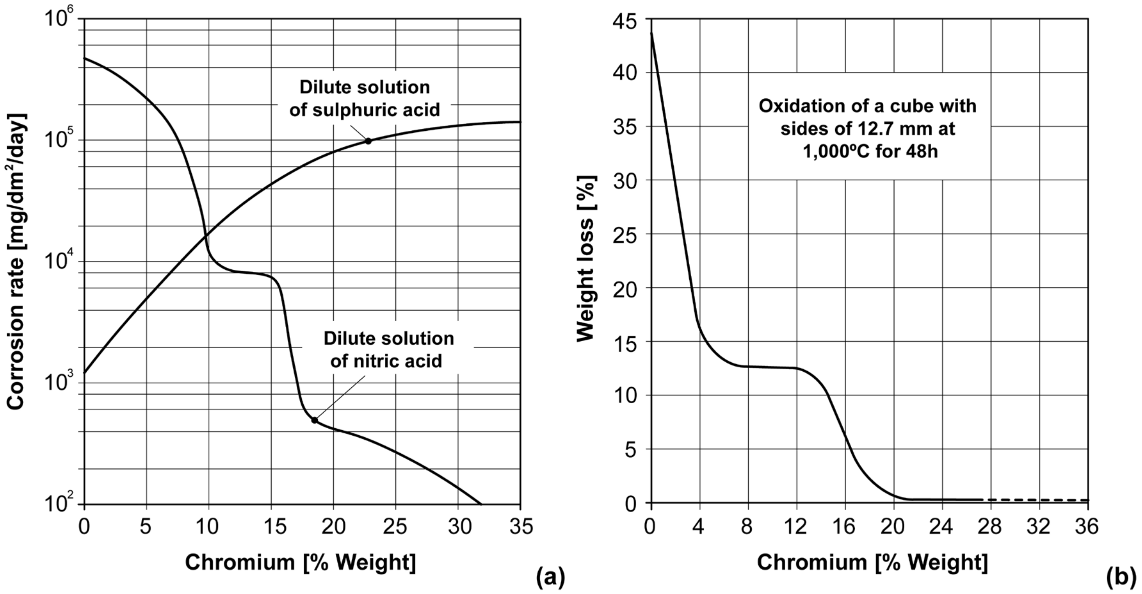
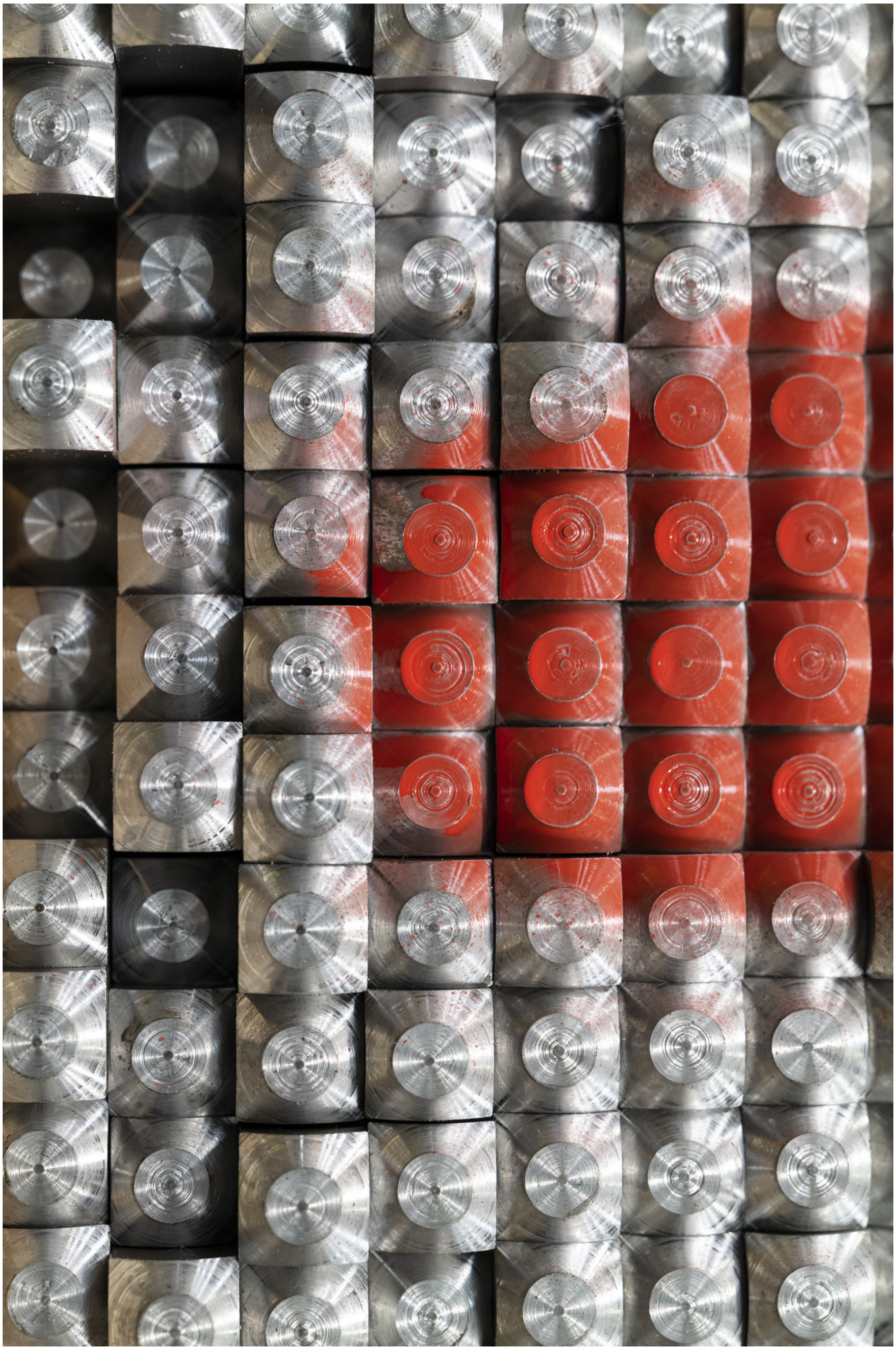


Figure 3 – Corrosion speed, in terms of weight loss of iron-chromium alloys (a) in diluted solutions of nitric acid or sulphuric acid and (b) in conditions of high temperature oxidation [from Verhoeven 2007].



2. THE FAMILY TREE OF STAINLESS STEEL

The main stainless steel grades available on market can be summarised in a simple family tree view (figure 4).

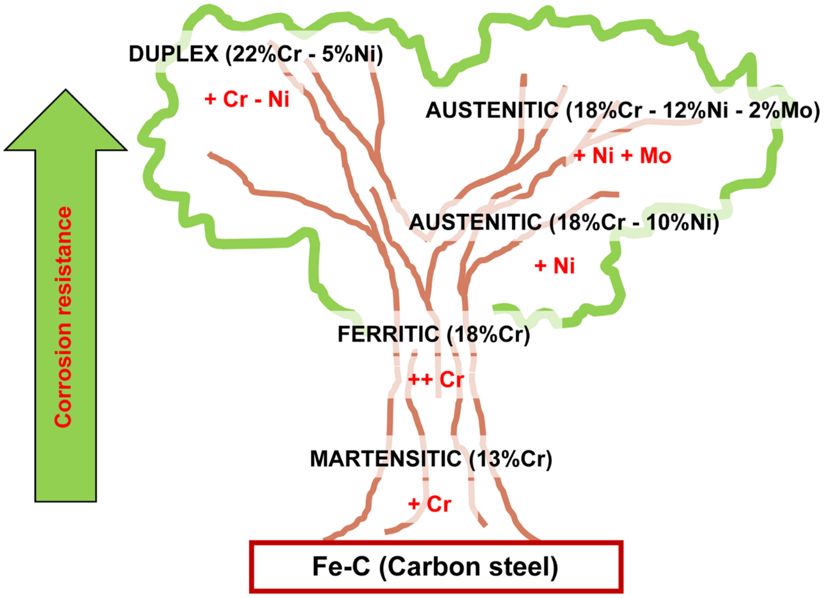


Figure 4 – Evolution of stainless steels starting from carbon steels: the family tree of stainless steel.

To begin with, we consider a medium-carbon steel, such as steel grade EN C30: it is sufficient to add a set content of chromium (~13%) to obtain a first type of stainless steel. This is grade EN X30Cr13.

This type of stainless steel can undergo heat treatment and, after quenching and tempering, it forms tempered martensite at room temperature. It also has good resistance to corrosion, combined with high mechanical properties.

To further increasing corrosion resistance a larger quantity of chromium needs to be added, while the carbon content should be reduced. In this case the steel grade obtained will be the grade EN X6Cr17, with a ferritic structure at room temperature, due to the high level of chromium, that has notable ferrite forming properties. The corrosion resistance of the new steel will be greater than that of EN X30Cr13; on the contrary the mechanical resistance of the grade EN X6Cr17 will be lower because no hardening heat treatment will be possible.

To obtain a steel with even greater corrosion resistance, the increase of chromium content and the addition of nickel and molybdenum will be essential.

In this case, there are two alternative procedures:

a) starting with grade EN X6Cr17, nickel could be added to obtain stainless steel grade EN X5CrNi18-10 or both nickel and molybdenum to obtain the grade EN X5CrNiMo17-12-2: in this way the microstructure at room temperature will be asutenitic, due to the austenite stabilizing properties of nickel that prevail over the ferrite forming effect of chromium.

b) alternatively, smaller quantities of nickel, along with greater quantities of chromium and a set percentage of molybdenum, can be added to grade EN X6Cr17 to obtain the stainless steel grade EN X2CrNiMoN22-5-3: in this way a two-phase structure of ferrite and austenite is obtained.

The four steel grades described above also represent the four main families of stainless steels currently used; these families, all defined on the basis of their microstructure at room temperature, are:

- martensitic stainless steels (such as grade EN X30Cr13),
- ferritic stainless steels (such as grade EN X6Cr17),
- austenitic stainless steels (such as grade EN X5CrNi18-10 and grade EN X5CrNiMo17-12-2),
- austenitic-ferritic stainless steels also called duplex stainless steels (such as grade EN X2CrNiMoN22-5-3).

A fifth category can be added to the previous four, i.e. the precipitation hardening stainless steels: this family is not defined by microstructure at room temperature but rather by strengthening mechanism used to produce it (precipitation hardening).

3. METALLURGY OF STAINLESS STEELS

As described in the previous chapter, the four main families of stainless steels are classified on the basis of their microstructure at room temperature, in other words:

- martensitic stainless steels (with a martensitic microstructure),
- ferritic stainless steels (with a ferritic microstructure),
- austenitic stainless steels (with an austenitic microstructure),
- austenitic-ferritic stainless steels (with a mixed austenitic and ferritic microstructure).

To understand how it is possible to obtain such diverse microstructures, a thorough analysis of the alloying element effect on phase diagram of stainless steels is needed: only a careful examination of these phase diagrams will enable a full understanding of how such different structures and properties can be obtained within the same family of materials.

On analysis of phase diagrams, it must always be taken into account that these diagrams are valid only in equilibrium cooling conditions, i.e. only when the specified alloy is cooled very slowly from melting point to room temperature.

3.1 Iron-chromium

The first phase diagram to be considered is the *Fe-Cr* diagram (figure 5) because chromium is the chemical element that gives to stainless steels their excellent corrosion resistance.

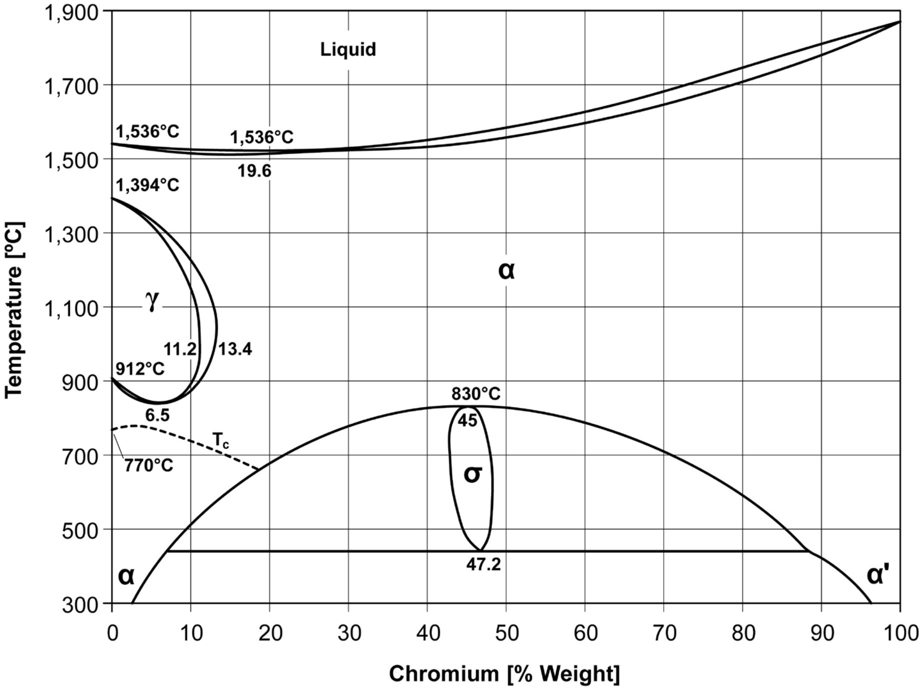


Figure 5 – *Fe-Cr* phase diagram [from ASM-H.3 1992].

Chromium is a ferrite forming element and it aids the expansion of the α-phase field; for this reason the *Fe-Cr* phase diagram highlights a closed γ-phase field, with upper and lower limits corresponding respectively to 11.2% and 13.4%. If chromium content exceeds 13.4% the iron-chromium alloy will have α-lattice and stable ferritic structure[2] from the melting point to room temperature. On the contrary, if chromium content is lower than 13.4%, the standard transformation $\gamma \rightarrow \alpha$ will occur.

While closure of the γ-phase field is caused by addition of ferrite forming elements such as chromium, aluminium, vanadium, silicon, molybdenum, titanium, niobium or tungsten, the austenitizing elements such as nickel, manganese, carbon or nitrogen expand the γ-phase field.

All these factors are critical because, as seen in figure 6, an addition of carbon, nitrogen or nickel expands the γ-phase field significantly. In this conditions it is possible to obtain a stable γ-phase at high temperatures (900°-1000°C) even with chromium contents higher than 13.4%.

These characteristics of *Fe-Cr* phase diagram enable an explanation for existence of two important stainless steel families.

On one hand, if chromium content is around 16-17% and carbon level is very low (less than 0.1%), there are no structural transformations and microstructure will be ferritic (ferritic stainless steels); on the other hand, when chromium content is around 13% and carbon level is around 0.2-0.3%, the alloy undergoes $\gamma \rightarrow \alpha$ transformation and may form martensite (martensitic stainless steel).

Another notable characteristics of *Fe-Cr* phase diagram is σ-phase, i.e. an intermetallic compound between iron and chromium with a tetragonal lattice (and a variable chromium content, ranging approximately between 40% and 50%). σ-phase is formed on grain boundary and increases the levels of hardness and brittleness of steel. As σ-phase has high chromium content, it tends to significantly worsen corrosion resistance of stainless steels (removing the same element that gives steel its corrosion resistance): σ-phase formation should therefore be avoided at all costs, taking care not to expose the material to temperatures between 550°-850°C for time intervals of 100-1,000 hours. Bear in mind that the specified temperature range (550°-850°C) applies exclusively to alloys made up of iron and chromium; if other alloying elements are present, such as molybdenum, σ-phase may also form at temperatures up to 980°C. The phenomena caused by σ-phase are also called "800°C embrittlement".

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[2] *When speaking of stainless steels, the α-phase is often called δ-phase. The distinction (α and δ) between the two names used to define the same phase is conventional: usually the body-centred cubic phase is known as δ if found at high temperature, while α is used when referring to room temperature.*

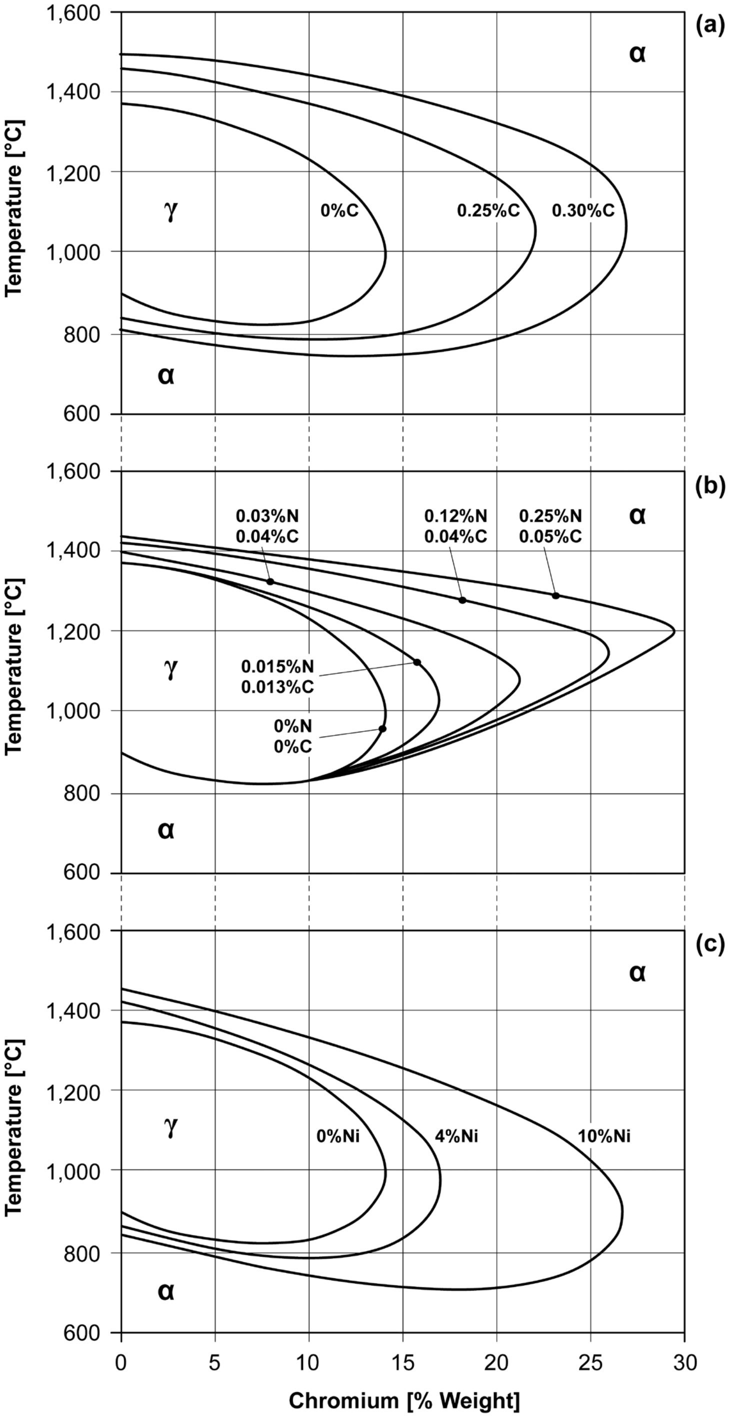

Figure 6 – Effect of (a) carbon, (b) nitrogen and (c) nickel on dimension of γ-phase field in *Fe-Cr* phase diagram [from Lacombe et al. 1993].

On *Fe-Cr* phase diagram, there also exists α'-phase: this phase forms at temperatures ranging from approximately 350°C to 550°C for different holding times[3]. The most critical condition occurs at 475°C, after at least on hour and is known as "475°C embrittlement".

The α'-phase forms within ferrite grains and has a body-centred cubic structure: it is a phase rich in iron and chromium, in line with the steel α-matrix, with sub-microscopic dimensions.

The α'-phase is a decomposition/transformation of ferrite structure, not identifiable by means of standard metallographic analysis or by X-rays, due to the sub-microscopic dimensions and lattice parameters identical to those in α'-phase[4].

The α'-phase leads to a progressive embrittlement of steel, as well as to a decline in corrosion resistance. The phenomenon occurs on alloys with a chromium content of more than 14% with kinetics that increase in proportion to the increase of alloying elements.

3.2 Iron-Nickel

We will now look into the effect of nickel (*Fe-Ni* phase diagram), i.e. the other alloying element always present in austenitic and in austenitic-ferritic stainless steels.

Nickel affords ductility and toughness to material at cryogenic temperatures; it also contributes to increase the corrosion resistance of stainless steels, because it aids repassivation of the steel[5] and increases corrosion resistance in reducing environments. Just as in case of chromium, nickel gives stainless steel optimal resistance to high temperature oxidation and creep.

Nickel opens γ-phase field and at the same time closes α-phase field (figure 7).

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[3] *According to most authors, the α'-phase is obtained by spinodal decomposition, in other words by decomposition of an unstable phase (the original α-phase) which forms two separate solid solutions with the same crystalline structure but a different chemical composition (α'-phase is the new modified α-phase); however a minority of authors affirm that α'-phase forms by nucleation and growth from α-phase.*

[4] *The symbol α' is also currently attributed to martensite obtained by cold work of austenitic stainless steels. As the two microstructure (α'-martensite and α'-ferrite from spinodal decomposition) must not be confused, we have used the term "475°C embrittlement" rather than the term α'-ferrite.*

[5] *If the passive film is subject to mechanical damages or worse, if it is chemically damaged, nickel aids the film to forms again, restoring the original corrosion resistance.*

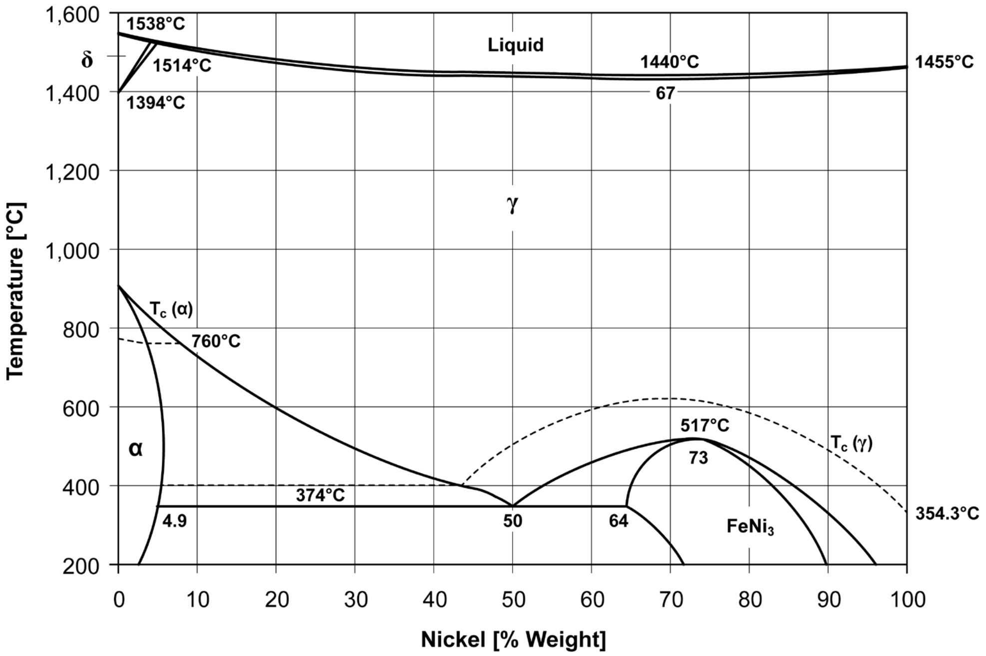

Figure 7 – *Fe-Ni* phase diagram [from ASM-H.3 1992].

The addition of nickel tends to open the γ-phase field and to shift the critical points of γ⟶α transformation at very low temperatures: the structure is therefore not subject to any transformation on cooling, remaining austenitic at room temperature. The *Fe-Ni* phase diagram also shows the Ni_3Fe phase, which however is of little practical interest with regard to stainless steels.

For *Fe-Ni* alloys the amount of nickel that is needed to form only γ-phase at room temperature is around 30%; if, on the other hand, 17% of chromium is added, 8% of nickel is sufficient to form a stable austenitic structure: this is the reason why stainless steels with 17-18% chromium and 10-12% nickel has only austenite at room temperature (figure 8).

3.3 Iron-Chromium-Nickel

For a better understanding of phenomena described above, it is worth considering the *Fe-Cr-Ni* ternary diagram. However, in consideration of the difficulty of plotting ternary diagrams (which would have a three dimensional structure), it is more common to use a representation in form of binary sections.

The *Cr-Ni* binary section of the *Fe-Cr-Ni* ternary diagram, with an iron content of 70% (figure 9) is very useful for this purpose[6].

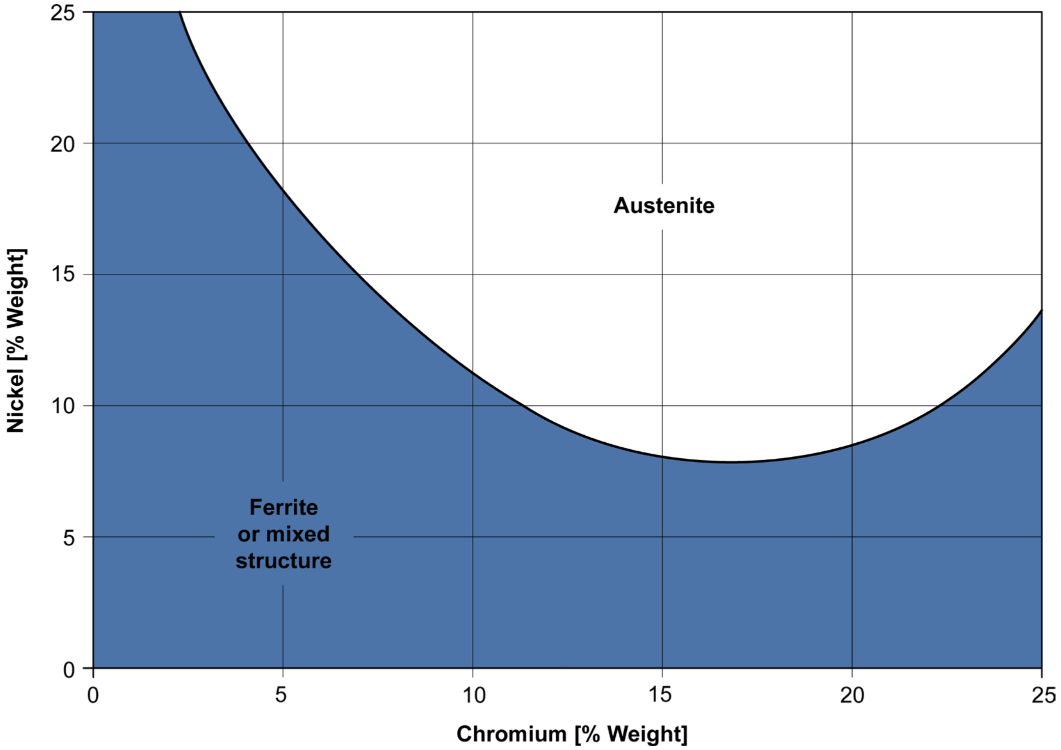

Figure 8 – Effect of nickel on formation of austenite in relation to chromium content: steels of various chemical compositions with *C* = 0.1% solution annealed in water from 1,100°C [from Peckner and Bernstein 1977].

The ternary section shown in figure 9 highlights the absence of critical points and explains the existence of austenitic stainless steels or duplex stainless steels in relation to chromium and nickel contents; for example a chromium content of 17-18% and nickel of 10-12% produced austenitci structure, while a chromium content of 22-25% and nickel at 4-8% forms austenitic-ferritic structure.

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[6] *Austenitic stainless steels alloyed with chromium and nickel or with chromium, nickel and molybdenum do not have a completely austenitic structure at room temperature. A small percentage of ferrite is always present (up to 5%): this is normally an advantage as it reduces the steel's susceptibility to hot cracks during welding.*

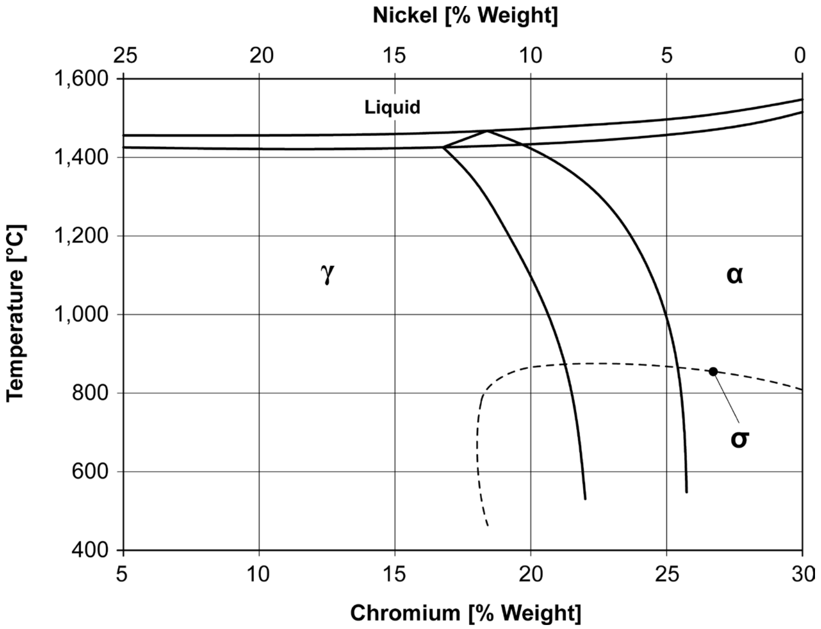

Figure 9 – *Cr-Ni* binary section of the *Fe-Cr-Ni* ternary diagram (with *Fe* = 70%) [from Lippold and Kotecki 2005].

3.4 Other alloying elements

As well as chromium and nickel, stainless steels contain other chemical elements that modify both metallurgical/mechanical properties and corrosion resistance of steel, creating additional properties.

Stainless steels are steel, so carbon is always present. Carbon is an austenitizing element and it increases steel hardness and mechanical resistance. Carbon has a close affinity with chromium and therefore forms chromium carbides, such as $Cr_{23}C_6$, particularly detrimental to corrosion resistance. Chromium carbides form on grain boundary at temperatures between 450°-900°C and they leading to a localised depletion of chromium. As a consequence the chromium level near the grain boundaries falls below the passivation threshold (10.5% chromium) giving rise to intergranular corrosion even if enviroments is only slightly aggressive[7]. The corrosion level depends both on amount of carbide precipitation and ability of chromium to spread in steel lattice[8] (figure 10).

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[7] *The mechanism of deterioration generated by σ-phase is very similar to what occurs with chromium carbides, leading to localised depletion of chromium and intergranular corrosion.*

[8] *In ferritic stainless steels the depletion of chromium caused by carbides is long range because the diffusivity of chromium is high; on the contrary in austenitic stainless steels (low chromium diffusivity) chromium depletion remains short range. As a consequence intergranular corrosion are much more dangerous in austenitic stainless steels compared to ferritic stainless steels.*

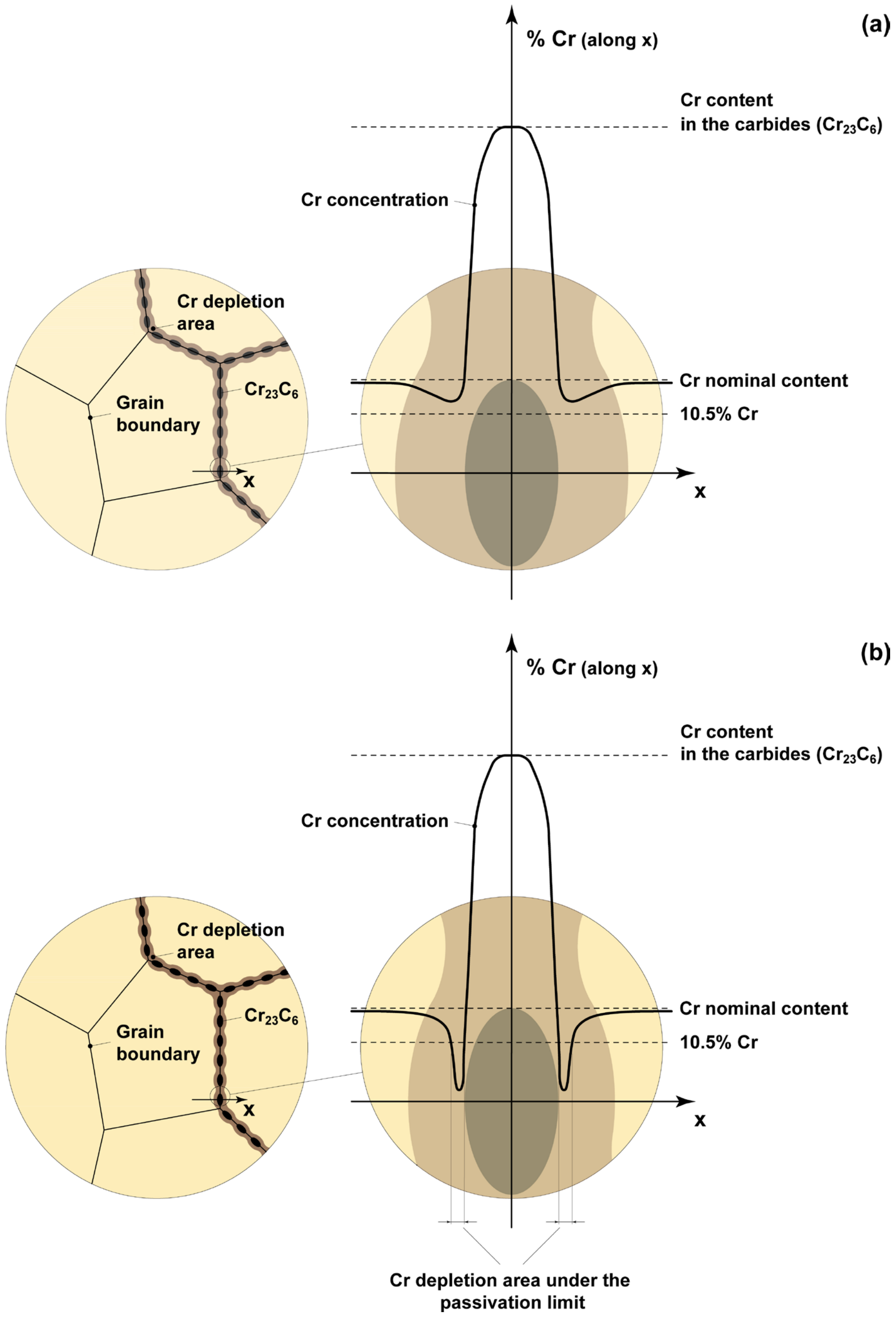

Figure 10 – Chromium concentrations at grain boundary after chromium carbide precipitation: a) ferritic stainless steel (high diffusivity of chromium), b) austenitic stainless steel (low diffusivity of chromium).

The chromium carbide precipitation can be avoided by minimising carbon content or attempting to neutralise its effect by combining it with other chemical elements.

After chromium, nickel and carbon, the fourth significant chemical element in stainless steels is molybdenum, another ferritising element.

This element significantly increases resistance to corrosion, with particular regard to localised attack, such as pitting and crevice corrosion. Molybdenum also increases oxidation resistance at least up to medium temperatures; however, at temperatures over 800°C, it tends to form liquid oxides (MoO_3) leading to catastrophic phenomena.

There is then another series of alloying elements often present in stainless steels, but these are less important with respect to those above. They are manganese, titanium, niobium, sulphur, nitrogen and copper.

Manganese is normally present in stainless steels at percentages lower than 2% as it is used in steel making by virtue of its deoxidizing properties[9]; at values greater than 2% it is used as a replacement for nickel due to its austenitizing properties. High levels of manganese (> 2%) improves the work hardening properties of stainless steel, but reduces its corrosion resistance.

Titanium and niobium are both ferritising elements, and in the case of stainless steels, are known as stabilizing elements. These two elements have a great affinity with carbon and can form carbides or carbo-nitrides of titanium or niobium such as MC or $M_x(NC)_y$ (with $M = Ti$ or Nb): in this way carbon can not form carbide with chromium, and corrosion resistance is preserved[10].

Sulphur can be added to improve machinability of stainless steels: sulphur forms manganese and/or chromium sulphides that contribute to break chips during machining of the workpiece. However the use of sulphur has a series of negative effects: it reduces corrosion resistance and the UTS/Impact strength of stainless steel, as well as its hot deformability and weldability.

Nitrogen is a highly austenitizing element added to austenitic and austenitic-ferritic stainless steels to increase both mechanical strength and resistance to localised corrosion.

Lastly, copper, another austenitizing element added in small percentages (maximum 1%) to improve cold deformability of austenitic stainless steels. However, copper slightly reduces corrosion resistance, as well as weldability and hot deformability.

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[9] *Silicon is used in a similar way, as a strong deoxidizing agents of liquid metal bath.*

[10] *Tantalum may also be added as an alternative to titanium and niobium.*

3.5 Schaeffler diagram and De Long diagram

Stainless steels have many alloying elements and it is important to uderstand their overall effect on microstructure at room temperature. The phase diagrams are useless to solve this problem and a more simple instrument is needed.

For this purpose, a different diagram has been developed by Schaeffler and subsequently modified by other researchers. This diagram enables to identify the stainless steel microstructures at room temperature after rapid cooling, starting from the steel chemical composition. Although the diagram lacks the solid thermodynamic background typical of equilibrium diagrams, it is still very useful for a great number of practical applications (figure 11).

On the X-axis, the Schaeffler diagram shows the sum of ferritising elements (known as equivalent chromium, Cr_{eq}) while the Y-axis shows the sum of austenitizing elements (known as equivalent nickel, Ni_{eq}). Each element is weighed with its specific coefficient, set at 1 for chromium and nickel.

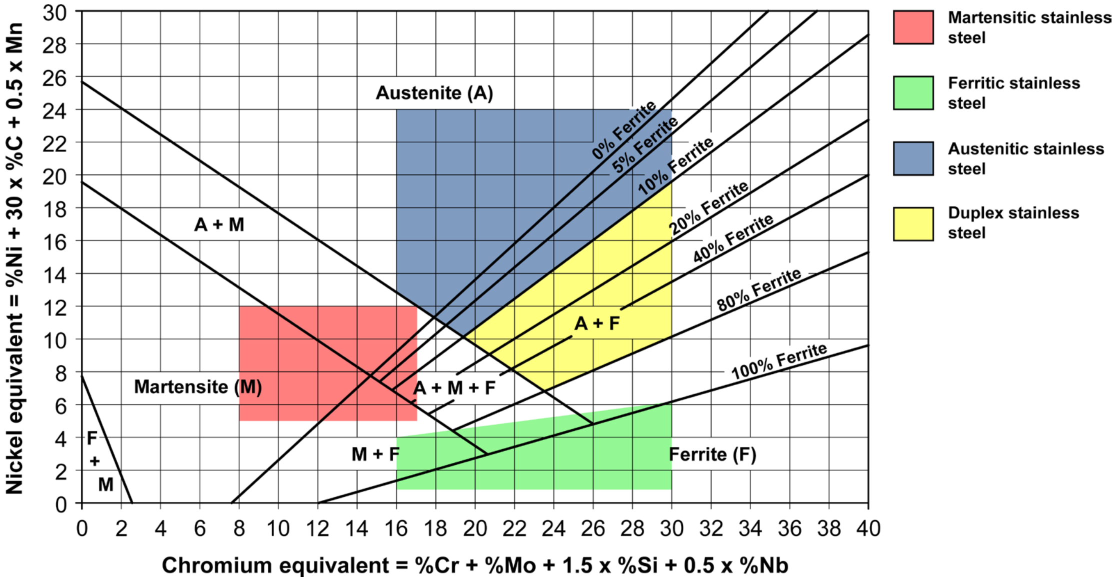

Figure 11 – Schaeffler diagram [from Krauss 2005]; the main families of stainless steel are highlighted with different colors.

The Schaeffler diagram is divided into four areas that correspond to the four typical microstructures of the four main of stainless steel grades (martensite, ferrite, austenite and austenite-ferrite). Microstructures and stainless steel grades can be identified from the steel chemical composition.

As can be observed, the Schaeffler diagram does not mention nitrogen among the alloying elements: to remedy this problem austenitic and austenitic-ferritic fields of Schaeffler diagram were amended by De Long in 1970s (figure 12). A more precise diagram became essential when addition of controlled amounts of nitrogen as alloying element became common to increase hardness and mechanical strength of austenitic and austenitic-ferritic stainless steels.

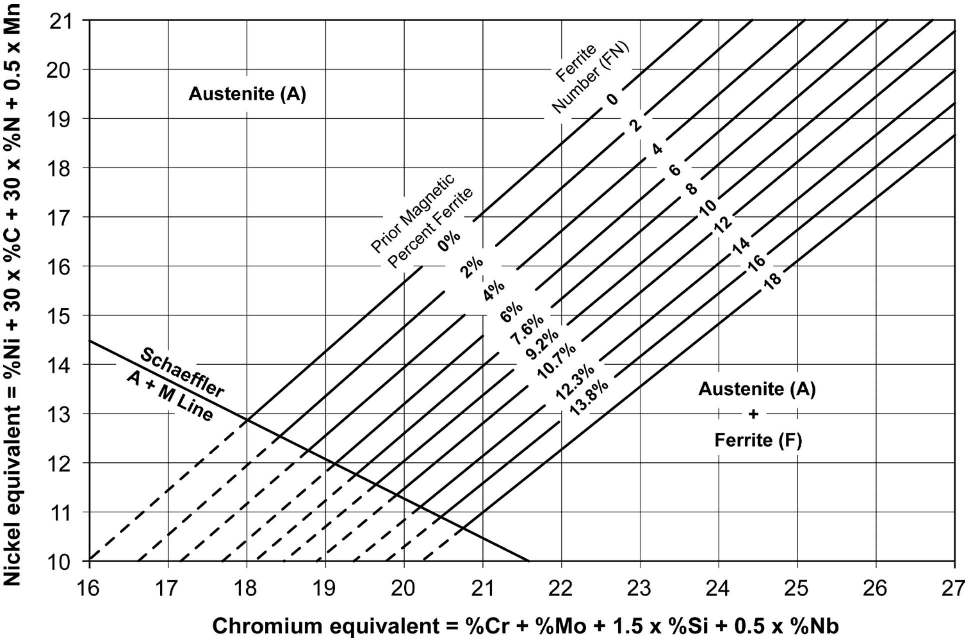

Figure 12 – De Long diagram [from Krauss 2005]. The Ferrite Number (or FN) is a description of the ferrite content of a weld metal determined using a standardized magnetic-inductive procedure.

Lastly it is worth to reiterate that both Schaeffler and De Long diagrams refer to alloys cooled rapidly from melting point to room temperature, such as welding beads: these diagrams provide reliable results only in these specific conditions.

However in many cases the two diagrams are used as an approximate guideline to evaluate microstructures of semi-finished products in fully annealed or solution annealed state (castings, hot rolled plates, forged components, cold drawn bars, etc.)[11].

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[11] *The Schaeffler diagram must never be used to define the microstructure of stainless steel semi-finished products based on their chemical composition. Indeed, the microstructures are always influenced by the heat treatment, as well as the presence of local irregularities in chemical composition, in addition to values of* Cr_{eq} *and* Ni_{eq}.


2

4. STAINLESS STEEL REFERENCE STANDARDS

The European reference standard for stainless steels is EN 10088, parts 1 to 5: this standards list the various grades of stainless steel, their chemical compositions, their physical and mechanical properties, their heat treatments and their technical delivery conditions for flat and long semi-finished products.

As well as the European standard, the AISI (American Iron and Steel Institute) standards are also used, even if , the last edition dates back to the 1980s: this standards, as all US standards, identify each stainless steel grade with progressive number. The AISI standards was then taken over by the ASTM (American Society for Testing and Materials) which quotes the AISI references in its own standards[12].

The AISI standards divide stainless steels into different series; the most common are the following:

- 200 series: chromium-manganese austenitic stainless steels,
- 300 series: chromium-nickel austenitic stainless steels,
- 400 series: martensitic and ferritic stainless steels,
- 600 series: precipitation hardening stainless steels.

An approximate correspondence can nevertheless be established between European and AISI standards. The AISI references for some of the most used types of stainless steels are as follows[13]:

- martensitic stainless steel grade EN X30Cr13 is similar to AISI 420,
- ferritic stainless steel grade EN X6Cr17 is similar to AISI 430,
- austenitic stainless steel grades EN X5CrNi18-10 and EN X5CrNiMo17-12-2 are similar to AISI 304 and AISI 316.

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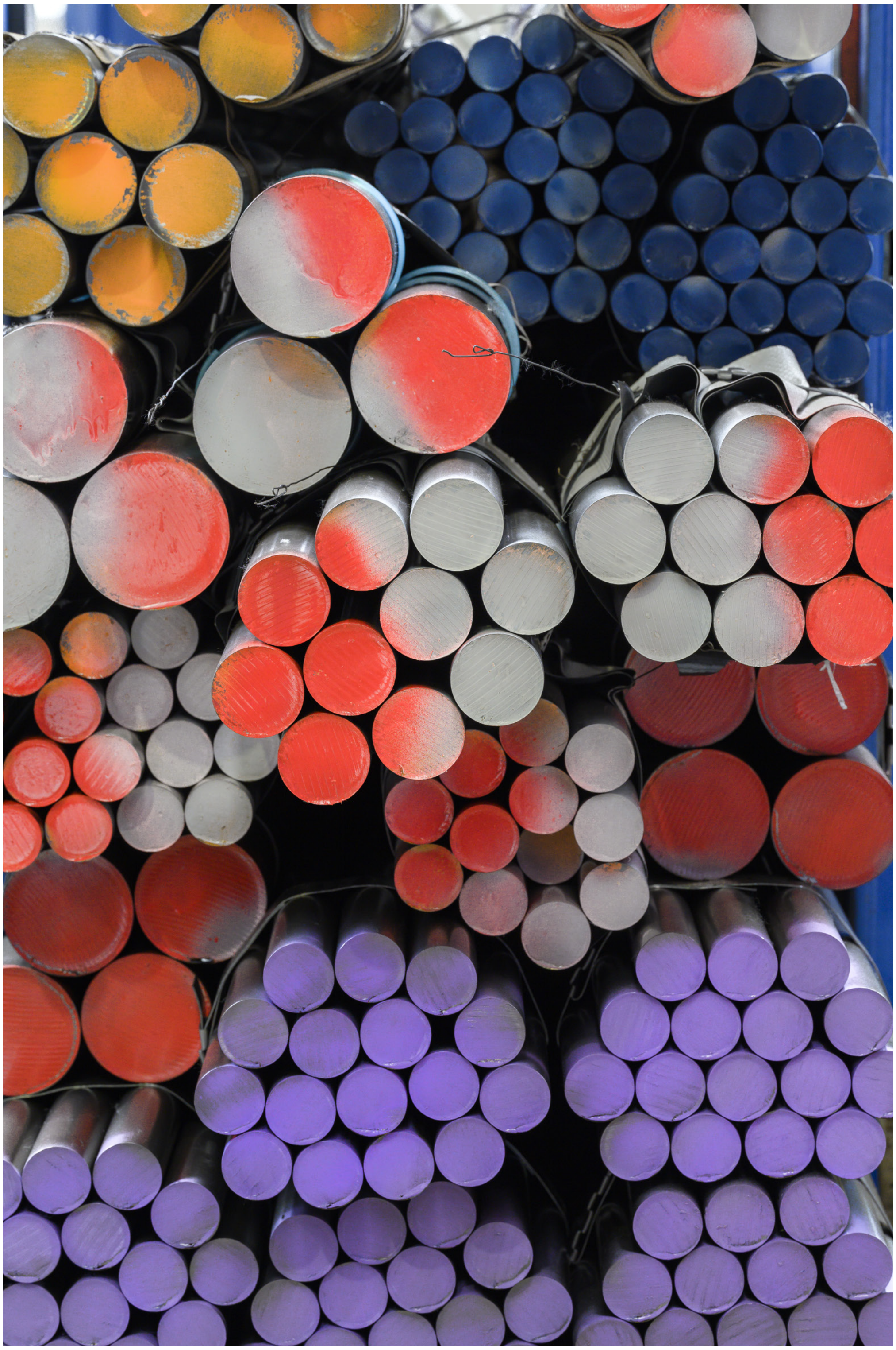
[12] *This is the case, for example, of ASTM A240/A240M entitled "Standard Specification for Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General Applications" or ASTM A473 entitled "Standard Specification for Stainless Steel Forgings" which state AISI references together with UNS references (Unified Numbering System).*

[13] *It was decided to use the terms "similar to" to avoid the reader's presumption that AISI and EN standards are identical to one another.*



5. NOTES ON THE MARKET OF STAINLESS STEELS

Although the production of stainless steels represents just a fraction of the overall production of steel (approx. 2% of all semi-finished products) it nevertheless is very important, both in terms of high unit value of marketed product (with a market share of around 15%) and in terms of type of application: in many industrial sectors stainless steel is essential.

Approximately three quarters of the world production of stainless steel is for flat semi-finished articles (sheets, strips, etc.); only one quarter derives from long semi-finished products (bars, rods, wires, etc.).

As a consequence the production of long semi-finished products has a more flexible response to market demands (with more types and formats available) with respect to flat semi-finished products, which are more standardised.

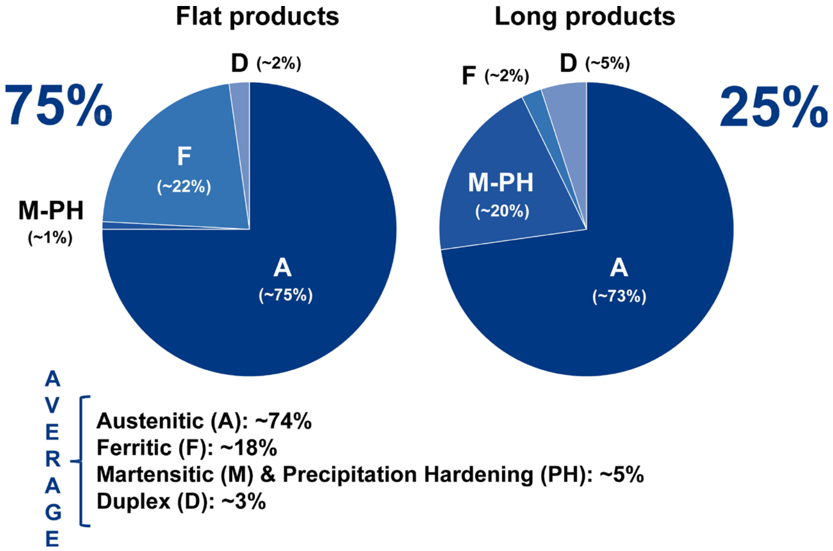


Figure 13 – Schematic representation of world production/use of stainless steels, divided by flat and long semi-finished products.

Figure 13 shows a schematic representation of world production of stainless steels, divided by flat and long semi-finished products. The austenitic stainless steel grades cover the most important applications and consequently this type represents the most significant part of world stainless steel production.

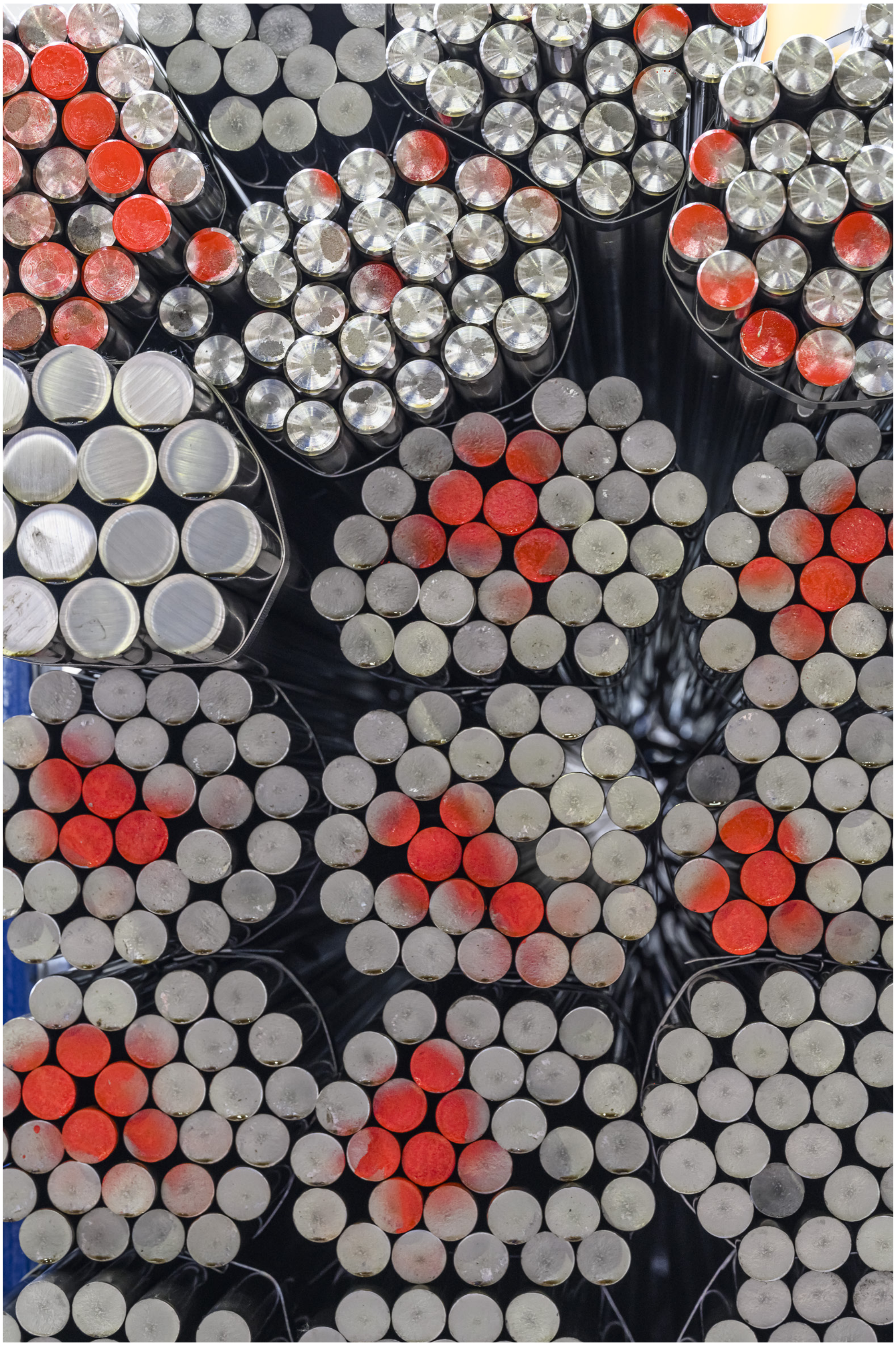
Ferritic and martensitic stainless steels are less used, but not less important, than the austenitic ones. Instead, austenitic-ferritic and precipitation hardening are used for very specific applications.

The main fields of application of stainless steels are summarised in table 1.

SECTOR AND/OR APPLICATIONS	%
Petrochemical and energy (On-shore and off-shore plants, oil extraction and production industries, natural gas transportation systems, subsea equipment, geothermic, solar and photovoltaic plants, etc.)	12-14
Process industries (chemical, petrochemical and pharmaceutical industries, transformation and production of semi-finished products, food industries, pulp and paper industries, water treatment and desalination plants, etc.)	18-20
Transport (Cars, bicycles and motorcycles, heavy goods vehicles, trains, ships and boats etc.)	12-14
Building, architecture and urban furnishing (Monuments and structures, facades and roofs, flues and chimneys, handrails and railings, escalators and elevators, pipes, etc.)	16-18
Appliances and household items (Pots, cutlery, washing machines, dishwashers, sinks, taps and general cooking utensils etc.)	34-36
Other	~3

Table 1 – Main fields of application of stainless steel.

Bear in mind that approximately 55% of the stainless steel is normally used to manufacture components for industrial plants, buildings and means of transport, while 45% is used for appliances and household items. These two markets differ significantly: while in the first case the final user looks mainly to the metallurgical and mechanical properties, comparing performance and costs with other materials such as galvanised steel, aluminium alloys, plastic materials etc., in case of household items the material properties are less important than final products cost and market trends.



6. MARTENSITIC STAINLESS STEELS

6.1 Metallurgy

Martensitic stainless steels have limited chromium content (normally between 11.5% and 18%) and the highest carbon content among the most commonly used stainless steels (generally between 0.1% and 1%). Chromium, a ferritising element, and carbon, an austenitizing element, are balanced in order to form austenitic structure at high temperature and martensitic structure at room temperatures after quenching.

The high carbon content is essential to ensure high hardness and high mechanical strength to steel but, at the same time, it promotes chromium carbide precipitation. Therefore martensitic stainless steels are the least resistant to corrosion and their field of application is limited to slightly aggressive environments.

The chemical composition of the main grades of martensitic stainless steels and their designation are shown in table 2.

Figure 14 shows the main grades of martensitic stainless steels. The diagram starts from grade EN X30Cr13 (similar to AISI 420B), the ancestor of this family, that is still used today to produces blades and knives.

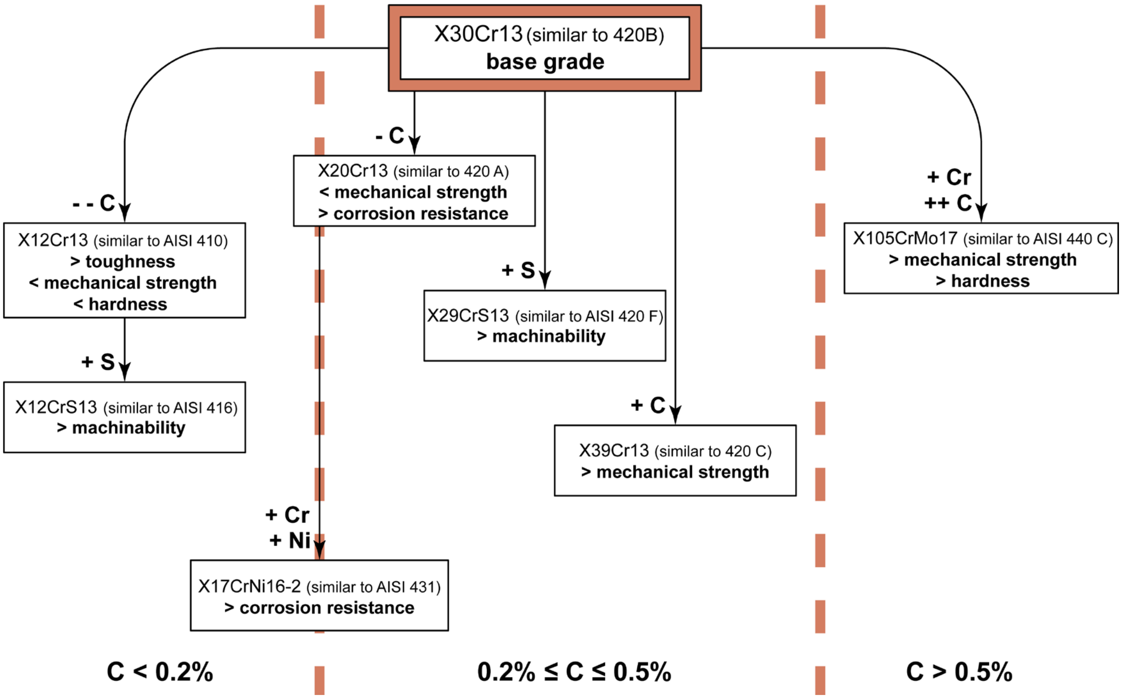


Figure 14 – Main types of martensitic stainless steels, starting from grade EN X30Cr13 (similar to AISI 420B), ancestor of this family.

EN Designation	%C	%Si	%Mn	%P	%S	%Cr	Other	AISI approximate correspondence
X12Cr13 (1.4006)	0.08-0.15	≤ 1.00	≤ 1.50	≤ 0.040	≤ 0.015	11.5-13.5	1	AISI 410
X12CrS13 (1.4005)	0.08-0.15	≤ 1.00	≤ 1.50	≤ 0.040	0.15-0.35	12.0-14.0	2	AISI 416
X20Cr13 (1.4021)	0.16-0.25	≤ 1.00	≤ 1.50	≤ 0.040	≤ 0.015	12.0-14.0	---	AISI 420 (420A) (*)
X30Cr13 (1.4028)	0.26-0.35	≤ 1.00	≤ 1.50	≤ 0.040	≤ 0.015	12.0-14.0	---	AISI 420 (420B) (*)
X39Cr13 (1.4031)	0.36-0.42	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	12.5-14.5	---	AISI 420 (420C) (*)
X29CrS13 (1.4029)	0.25-0.32	≤ 1.00	≤ 1.50	≤ 0.040	0.15-0.25	12.0-13.5	3	AISI 420F
X17CrNi16-2 (1.4057)	0.12-0.22	≤ 1.00	≤ 1.50	≤ 0.040	≤ 0.015	15.0-17.0	4	AISI 431
X105CrMo17 (1.4125)	0.95-1.20	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	16.0-18.0	5	AISI 440C
X3CrNiMo13-4 (1.4313)	≤ 0.050	≤ 0.70	≤ 1.50	≤ 0.040	≤ 0.015	12.0-14.0	6	---
X4CrNiMo16-5-1 (1.44185)	≤ 0.060	≤ 0.70	≤ 1.50	≤ 0.040	≤ 0.015	15.0-17.0	7	---

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 420B).

Notes:

1: %Ni ≤ 0.75.
2: %Mo ≤ 0.60.
3: %Mo ≤ 0.60.
4: 1.50 ≤ %Ni ≤ 2.50.
5: 0.40 ≤ %Mo ≤ 0.80.
6: 3.50 ≤ %Ni ≤ 4.50; 0.30 ≤ %Mo ≤ 0.70; %N ≤ 0.020.
7: 4.00 ≤ %Ni ≤ 6.00; 0.80 ≤ %Mo ≤ 1.50; %N ≤ 0.020.

Table 2 – Chemical composition of the main types of martensitic stainless steels [from EN 10088].

The phase diagrams (figures 15 and 16) show the existence of critical points, i.e. the transformation $\gamma \rightarrow \alpha$ already observed in the *Fe-C* phase diagram. For example, this is what happens when carbon content is around 0.3%, such as for EN X30Cr13 (similar to AISI 420B) or when it is around 1%, such as for EN X105CrMo17 (similar to AISI 440C).

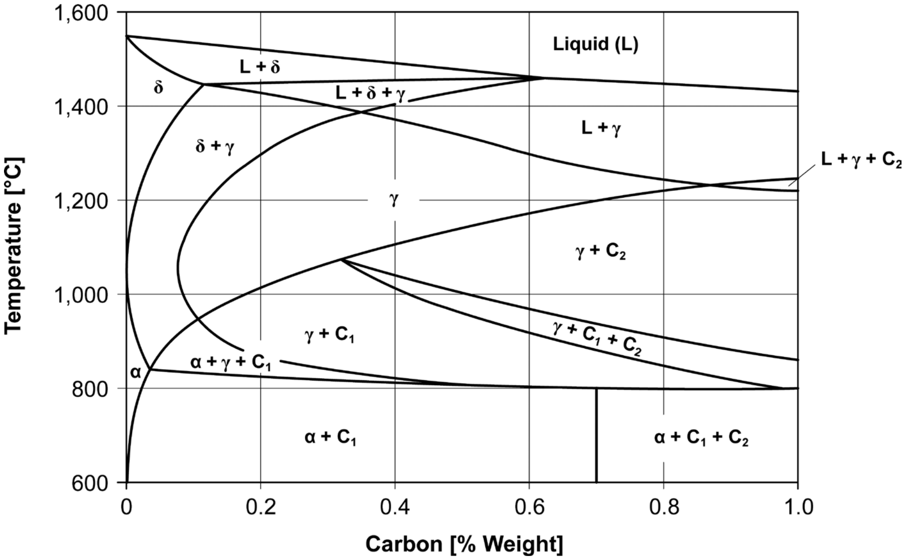


Figure 15 – Two-dimensional section of *Fe-Cr-C* ternary phase diagram, isopleth for %Fe-13%Cr-%C alloys. C_1 carbides type $(Cr,Fe)_{23}C_6$, C_2 carbides type $(Cr,Fe)_7C_3$ [from Lippold and Kotecki 2005].

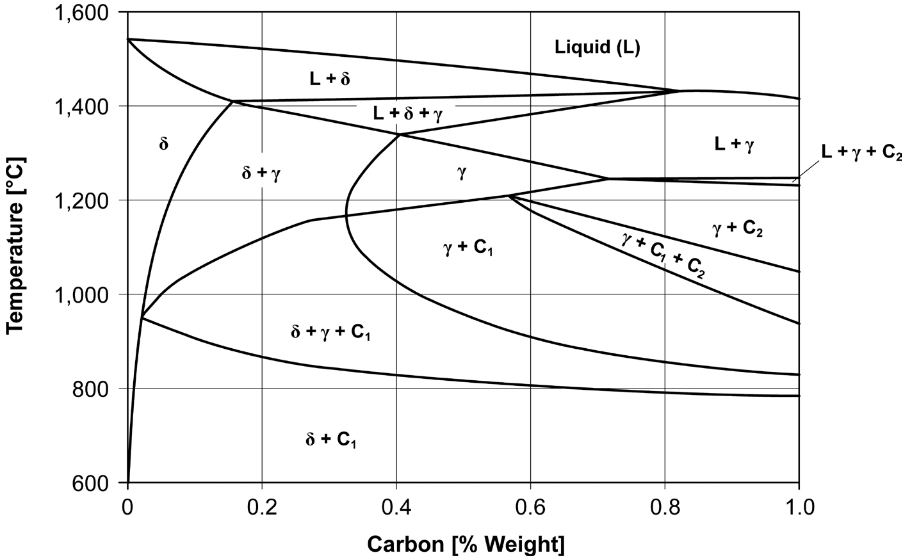


Figure 16 – Two-dimensional section of *Fe-Cr-C* ternary phase diagram, isopleth for %Fe-17%Cr-%C alloys. C_1 carbides type $(Cr,Fe)_{23}C_6$, C_2 carbides type $(Cr,Fe)_7C_3$ [from Lippold and Kotecki 2005].

Therefore when the steel is heated above critical points, the original microstructure transforms completely into austenite plus carbides, that become martensite plus carbides after cooling in oil or in air.

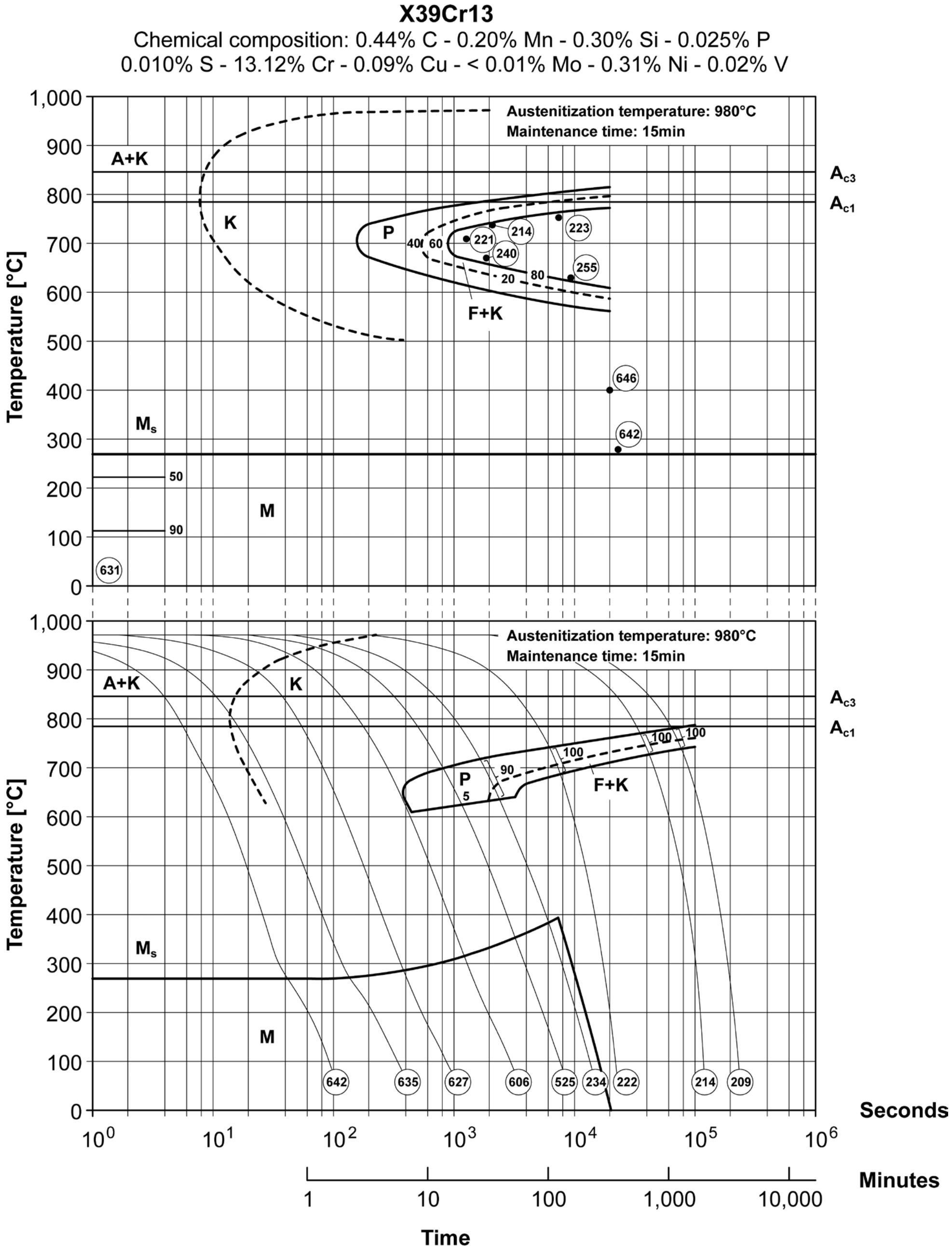
Note that the addition of carbon (or nitrogen or nickel) expands the γ-phase field and causes the martensitic transformation, after quenching, for chromium contents above the threshold of 13.4% set by the *Fe-Cr* phase diagram (figure 5).

The existence of critical points also allows to trace the T.T.T. and C.C.T. diagrams (figure 17). The presence of carbides, both at high and low temperatures, can be explained due to the high carbon content, which promotes carbide formation.

The great amount of alloying elements also shift T.T.T. and C.C.T. diagrams to the right and downwards, with respect to temperature-time axes. This shift causes an increase both in steel hardenability and quantity of retained austenite and, therefore, raises the risk of cracks formation during quenching and tempering. For these reasons, martensitic stainless steels are considered air-hardening steels.

6.2 Heat treatments

Semi-finished products in martensitic stainless steel must undergo heat treatment to increase machinability. For this purpose an annealing process could be performed (full or isothermal annealing). However, in practice, a sub-critical annealing is used on martensitic stainless steels, i.e. a heat treatment at temperatures from 730°-830°C for several hours, followed by gradual cooling in furnace or air: this heat treatment forms a globular pearlitic microstructure characterised by a matrix of α-phase with globular carbides of Fe_3C phase. During the heat treatments, special attention must always be paid to surface decarburisation and chromium oxidation phenomena, due to oxygen in heat treatment atmosphere. To avoid these problems it is useful to perform heat treatments in a neutral or reducing atmosphere. The production of a martensitic steel components always starts from a semi-finished product in fully annealed state. The second step is rough-machining of semi-finished product to obtain a workpiece with shape and dimensions close to those of finished component.



A + K	Austenite and carbides	**RA**	Retained Austenite
K	Carbides	**F**	Ferrite
P	Pearlite	**F + K**	Non lamellar eutectoid
○	Vickers Hardness, HV	**A_{c1}**	= 790°C
M	Martensite	**A_{c3}**	= 850°C
B	Bainite	**M_s**	= 280°C

Figure 17 – T.T.T. and C.C.T. diagrams for martensitic stainless steel grade EN X39Cr13 (similar to AISI 420C) [from Wever et al. 1954/56/58].

After rough machining, workpiece is quenched and tempered to obtain mechanical properties and corrosion resistance required by design. The last step is finish machining in order to give final dimensions and tolerances to the finished component.

The technological process required to produce a component in martensitic stainless steel is shown in figure 18.

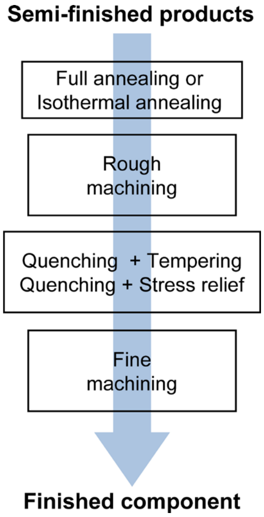


Figure 18 – Technological process required to produce a component in martensitic stainless steel.

Many important factors must be taken into account with regard to quenching of martensitic stainless steels. Heating must be carried out with care. Martensitic stainless steels, as the case of all stainless steels, have very low thermal conductivity: to avoid irreversible deformation or cracks heating must be controlled. A great deal of attention should be paid to heating rate of workpieces to be treated, especially for components with large size and/or complex geometry.

As an example a step heating cycle can be carried out with pre-heating between 550°C and 800°C. The soaking phase is performed at higher temperature than carbon steel. Martensitic stainless steels are heated and held at temperature between 950°-1100°C[14]. The high tempererature promotes both the formation of austenite and dissolution of any carbides. This process increases the carbon content in solid solution and therefore increases the martensite hardness after quenching as well (figure 19).

---

[14] *The increase of carbon (and chromium) causes a proportional increase in steel austenitization temperature.*

However, there is an optimal temperature for austenitization; if this temperature is exceeded, grains undergo a large growth which causes a strong reduction in the steel mechanical properties (figure 20).

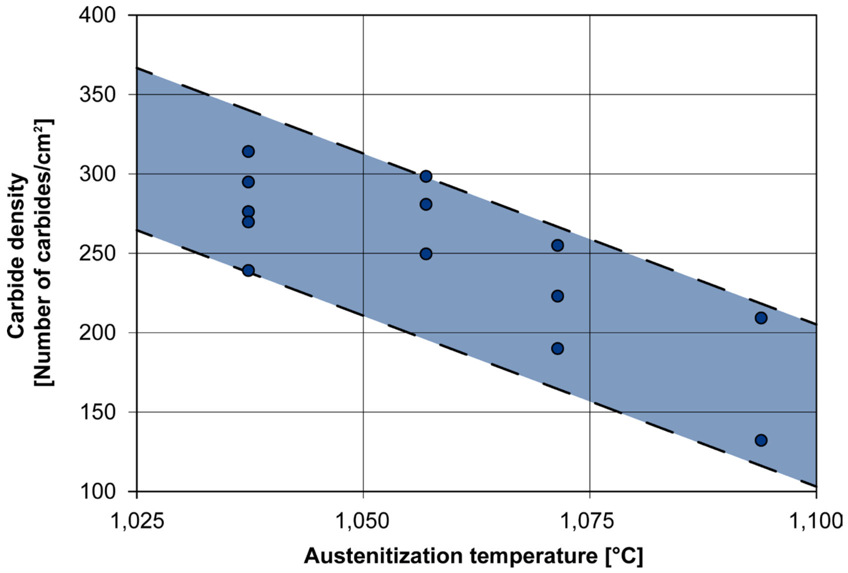


Figure 19 – The effect of austenitization temperature on chromium carbide density after quenching on martensitic stainless steels (0.65%C-12.8%Cr-0.4%Si-0.65%Mn) [from Verhoeven 2007].

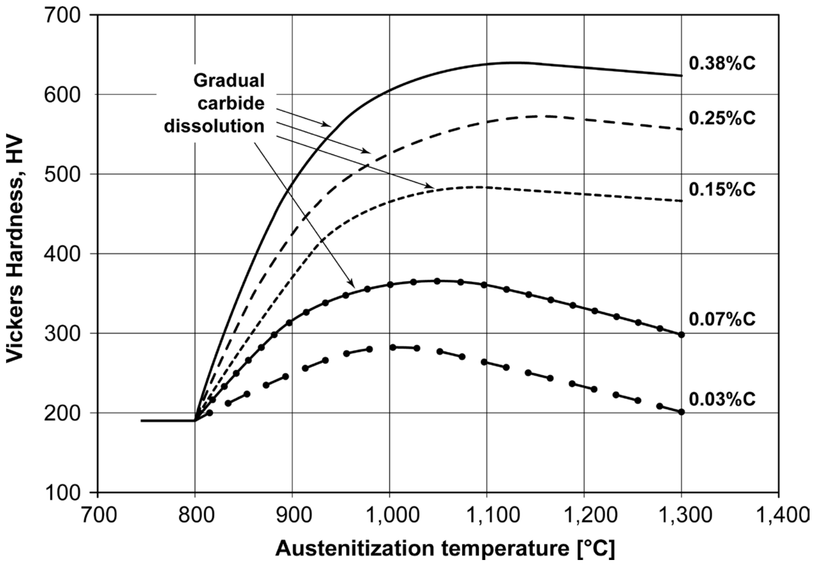


Figure 20 – The effect of austenitization temperature on hardness of a martensitic stainless steel with 13%Cr and an increasing carbon content (quenched in oil and tempered at 200°C) [from Lacombe et al. 1993].

The austenitization temperature of martensitic stainless steels however must not be increased as required: this would increase both the risk of grain growth and formation of retained austenite at room temperature, especially for steels with high carbon content (figure 21).

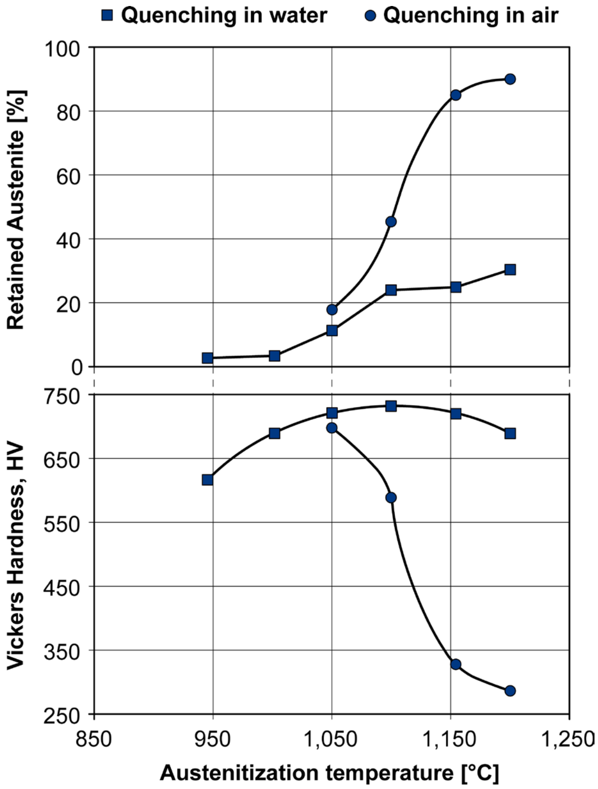


Figure 21 – The effect of austenitization temperature and quenching media on hardness and quantity of retained austenite in martensitic stainless steel (0.4%C-16%Cr-0.9%Mo-0.5%Ni) [from Lacombe et al. 1993].

As previously noted, martensitic stainless steels are air-hardening steels; however oil cooling is used as well, especially for large to medium size components in order to increase uniformity of microstructure and homogenize mechanical properties along the component section.

Tempering also has a number of special features. This heat treatment is performed after quenching to reduce both brittleness of the as-quenched martensite and residual stresses generated during quenching.

Generally, tempering of martensitic stainless steels is performed at low temperatures (below 400°C) or high temperatures (over 640°C). Great care is taken to prevent tempering between 450°C and 600°C: this interval is critical as it increases brittleness and reduces corrosion resistance (figure 22).

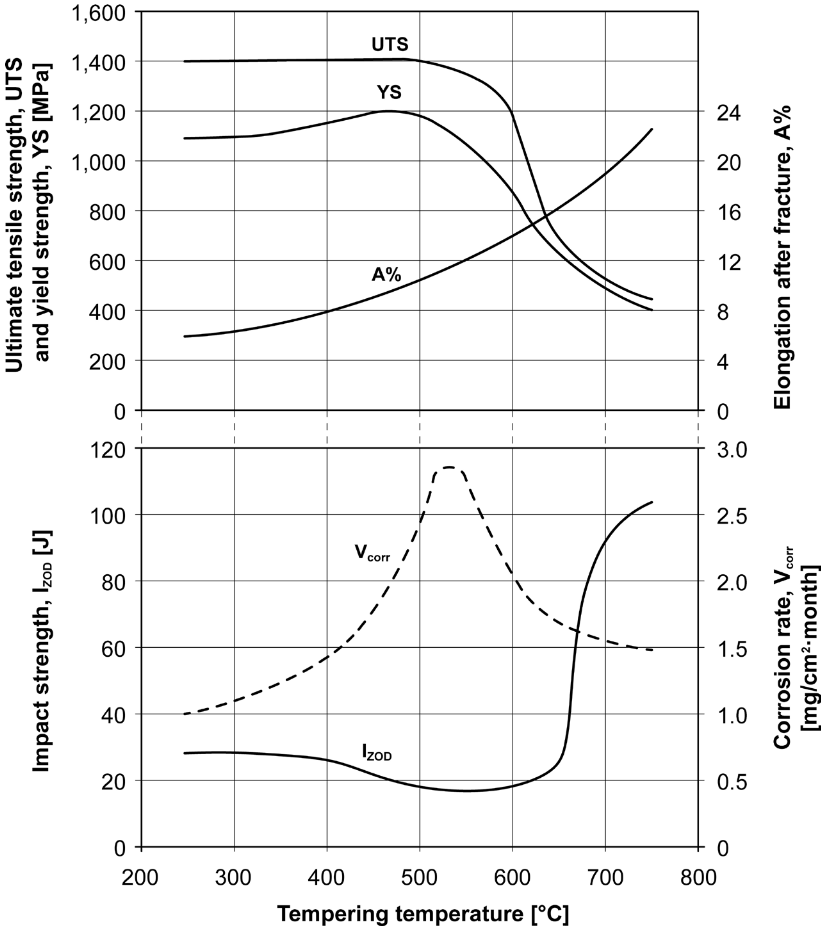


Figure 22 – The effect of tempering temperature on mechanical properties and corrosion resistance of a martensitic stainless steel grade EN X20Cr13 (similar to AISI 420A) [from Sedriks 1996].

Tempering performed below 400°C produces the highest values of hardness, tensile strength and corrosion resistance. Tempering at low temperature is the method normally performed on small size components in martensitic stainless steel.

Alternatively tempering can be performed at temperatures over 640°C (up to 750°C): in this second case fracture toughness and impact strength are maximized at the expense of hardness and corrosion resistance. The heat treatments for the most common martensitic stainless steels are summarised in table 3.

EN Designation	Full annealing Subcritical annealing	Cooling medium	Austenitization	Quenching medium	Tempering	AISI approximate correspondence
X12Cr13 (1.4006)	820°-900°C 730°-790°C	furnace air	930°-1,010°C	oil, air	600°-750°C 150°-400°C	AISI 410
X12CrS13 (1.4005)	820°-900°C 730°-790°C	furnace air	930°-1,010°C	oil, air	600°-750°C 150°-400°C	AISI 416
X20Cr13 (1.4021)	840°-900°C 730°-790°C	furnace air	950°-1,050°C	oil, air	600°-750°C 150°-400°C	AISI 420 (420A) (*)
X30Cr13 (1.4028)	840°-900°C 730°-790°C	furnace air	950°-1,050°C	oil, air	600°-700°C 150°-400°C	AISI 420 (420B) (*)
X39Cr13 (1.4031)	840°-900°C 730°-790°C	furnace air	950°-1,050°C	oil, air	600°-700°C 150°-400°C	AISI 420 (420C) (*)
X29CrS13 (1.4029)	840°-900°C 730°-790°C	furnace air	950°-1,050°C	oil, air	600°-700°C 150°-400°C	AISI 420F
X17CrNi16-2 (1.4057)	840°-900°C 680°-790°C	furnace air	950°-1,050°C	oil, air	600°-700°C 150°-400°C	AISI 431
X105CrMo17 (1.4125)	840°-900°C 730°-770°C	furnace air	1,010°-1,070°C	oil, air	150°-400°C	AISI 440C
X3CrNiMo13-4 (1.4313)	hot forming (**)	air	950°-1,050°C	oil, air	600°-700°C	---
X4CrNiMo16-5-1 (1.4418)	hot forming (**)	air	950°-1,050°C	oil, air	600°-700°C	---

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 420B).
(**) These steels are cooled in air after hot deformation and can be used with or without heat treatment (quenching and tempering).

Table 3 – Characteristics of heat treatment on the main types of martensitic stainless steels.

6.3 Physical and mechanical properties

The physical properties of martensitic stainless steels are very similar to those of medium carbon steels (table 4). The mechanical properties depend on the heat treatment applied. While in fully annealed state hardness values are around 160-250HB, after quenching most martensitic stainless steels have a Ultimate Tensile Strength (UTS) between 700MPa and 1,700MPa, depending on chemical composition and tempering temperature; the fatigue limit is around 0.45·UTS.

Table 5 shows mechanical properties for different grade of martensitic stainless steel after heat treatments.

Brittle fracture also strongly depends on chemical composition and heat treatment.

Both impact strength and ductile to brittle transition temperature worse as mean grain size, carbon content and phosphorous content increase.

Figure 23 shows the ductile to brittle transition for three commonly used martensitic stainless steels: note the behaviour is similar to that of medium carbon steels.

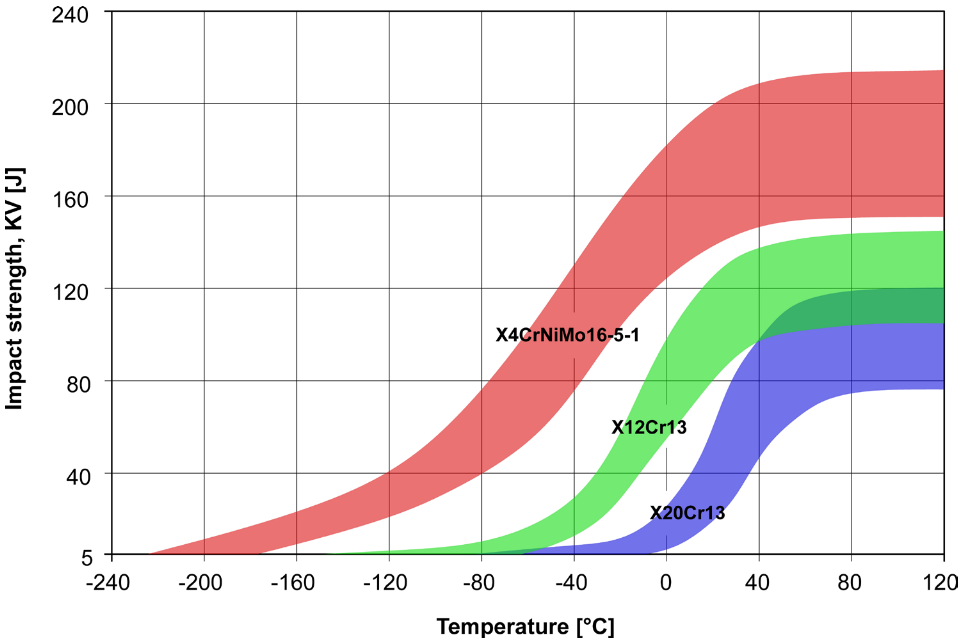


Figure 23 – Ductile to brittle transition for three commonly used martensitic stainless steels after quenching and tempering at 650°C.

EN Designation	Density [kg/dm³]	Specific heat at 20°C [J·kg⁻¹·K⁻¹]	Electrical resistance at 20°C [W·mm²·m⁻¹]	Thermal conductivity [W·m⁻¹·K⁻¹]	Mean coefficient of thermal expansion [10⁻⁶·K⁻¹]		Elastic modulus [GPa]		AISI approximate correspondence
					between 20°C and 100°C	between 20°C and 200°C	at 20°C	at 200°C	
X12Cr13 (1.4006)	7.7	460	0.60	30	10.5	11.0	215	205	AISI 410
X12CrS13 (1.4005)	7.7	460	0.60	30	10.5	11.0	215	205	AISI 416
X20Cr13 (1.4021)	7.7	460	0.60	30	10.5	11.0	215	205	AISI 420 (420A) (*)
X30Cr13 (1.4028)	7.7	460	0.65	30	10.5	11.0	215	205	AISI 420 (420B) (*)
X39Cr13 (1.4031)	7.7	460	0.55	30	10.5	11.0	215	205	AISI 420 (420C) (*)
X29CrS13 (1.4029)	7.7	460	0.55	30	10.5	---	215	205	AISI 420F
X17CrNi16-2 (1.4057)	7.7	430	0.70	25	10.0	10.5	215	205	AISI 431
X105CrMo17 (1.4125)	7.7	460	0.80	15	10.4	10.8	215	205	AISI 440C
X3CrNiMo13-4 (1.4313)	7.7	430	0.60	25	10.5	10.9	200	185	---
X4CrNiMo16-5-1 (1.4418)	7.7	430	0.80	15	10.3	10.8	200	185	---

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 420B).

Table 4 – Physical properties of the main types of martensitic stainless steels [from EN 10088].

EN Designation	Heat treatment condition	YS [MPa]	UTS [MPa]	A [%]	Hardness	AISI approximate correspondence
X12Cr13 (1.4006) X12CrS13 (1.4005) (#)	A	300-400	500-600	18-28	160-200HB	AISI 410 AISI 416
	A + CD (**)	450-900	650-1,000	12-18	---	
	Q T 200°C	1,000-1,250	1,350-1,500	11-16	42-46HRC	
	Q T 350°C	950-1,150	1,250-1,400	11-17	40-44HRC	
	Q T 650°C	550-700	650-850	18-24	16-24HRC	
X20Cr13 (1.4021) X17CrNi16-2 (1.4057)	A	350-450	550-700	16-26	220-260HB	AISI 420 (420A) (*) AISI 431
	A + CD (**)	500-900	700-1,100	12-18	---	
	Q T 200°C	1,050-1,300	1,350-1,550	11-16	42-46HRC	
	Q T 350°C	1,000-1,200	1,250-1,450	11-17	40-44HRC	
	Q T 650°C	600-800	750-950	16-20	21-25HRC	
X30Cr13 (1.4028) X39Cr13 (1.4031) X29CrS13 (1.4029) (#)	A	350-450	550-700	14-24	180-220HB	AISI 420 (420B) (*) AISI 420 (420C) (*) AISI 420F
	A + CD (**)	600-1,000	700-1,200	10-16	---	
	Q T 200°C	1,250-1,400	1,550-1,750	10-15	48-52HRC	
	Q T 350°C	1,200-1,350	1,450-1,650	10-16	45-49HRC	
	Q T 650°C	650-900	800-1,050	14-18	22-28HRC	
X105CrMo17 (1.4125)	A	400-550	650-800	12-20	230-270HB	AISI 440C
	A + CD (**)	600-900	750-1,100	8-14	---	
	Q T 200°C	1,650-1,900	1,900-2,100	4-8	56-60HRC	
	Q T 350°C	1,600-1,750	1,750-1,900	4-8	54-58HRC	
X3CrNiMo13-4 (1.4313) X4CrNiMo16-5-1 (1.4418)	Hot formed Q T 650°C	550-750	650-900	18-24	16-24HRC	---
		650-850	750-1,000	16-22	24-32HRC	

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term “type” (for example type 420B).
A: Annealed.
A + CD: Annealed and Cold Drawn.
Q T: Quenched and Tempered.
(**) The mechanical properties after A + CD depend on cold drawn level.
(#) The types with sulphur have a slightly lower elongation after fracture compared to those without sulphur.

Table 5 – Mechanical properties of the main types of martensitic stainless steels.

6.4 Types and applications

The semi-finished products in martensitic stainless steel commercially available are either fully annealed or quenched and tempered, predominantly in form of long semi-finished products (bars and rods); flat semi-finished products are manufactured only in few cases (strips and sheets), especially for cutting blades.

The martensitic stainless steels most commonly used are EN X30Cr13 (similar to AISI420B[15]) and EN X12Cr13 (similar to AISI 410): the first has high carbon content and is very hard, while the second has high fracture toughness and impact strength.

These two steels are widely used where high mechanical strength and wear resistance are required. Corrosion resistance is good, especially in rural environments, fresh water not contaminated by chlorides, in contact with food, or with weak acids (such as organic acids), with petroleum products and with oxidizing solutions (chromates, permanganates, etc.).

They are frequently used for production of kitchen or industrial knives, surgical instruments, rasors, scissors, callipers, gun barrels; they are also used to produce moulds for plastic materials and springs.

Another use of this steel grade is for power drive shafts in mildly aggressive environments, steam turbine blades or compressor blades, connecting rods, bushings for pumps and compressors, filters, bathroom fittings, threaded fasteners, handles, coins and medals.

Grade EN X29CrS13 (similar to AISI420F) and grade EN X12CrS13 (similar to AISI 416) are similar to EN X30Cr13 and EN X12Cr13 but with improved machinability due to the high content of sulphur (approx. 0.2%). At the same time, however, sulphur reduces mechanical strength, corrosion resistance and, above all, wedability.

Grade EN X17CrNi16-2 (similar to AISI 431[16]) has higher corrosion resistance than stainless steels described above, due to the increased chromium content: it also has higher impact strength due to nickel, not present in grades EN X30Cr13 and EN X12Cr13.

The steel grade EN X17CrNi16-2 is used for marine propeller shafts, pump components, valves, turbine blades and wear-resistant components in petroleum-refining plants.

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[15] *The AISI standard divides type 420 into three sub-groups, with low, medium and high carbon content. Type 420A with an average carbon content of 0.2%, type 420B with an average carbon content of 0.3% and type 420C with an average carbon content of 0.4%: the increase of carbon causes the increase of hardness and sensitivity to carbide precipitation.*

[16] *The AISI standard provides two martensitic stainless steels with nickel contents between 1.25% and 2.5%: AISI 414 and AISI 431. AISI 414 has a carbon content of approximately 0.15% while AISI 431 has approximately 0.20% of carbon. For EN 10088 standard, the grade EN X17CrNi16-2 has a carbon content ranging from 0.12% to 0.22%.*

The martensitic stainless steel grade EN X105CrMo17 (similar to AISI 440C[17]) is also noteworthy: this steel has high content of chromium and carbon and offers good corrosion resistance (similar to that of grade EN X12Cr13). After quenching and tempering it ensures excellent wear resistance but it has very low fracture toughness.

Grade EN X105CrMo17 is used to produce components resistant to wear and oxidation or to wear and corrosion, such as chains working at high temperatures, ball bearings and surgical instruments for special applications.

Lastly, the grades EN X3CrNiMo13-4 and EN X4CrNiMo16-5-1 known as "super-martensitic", represent two examples of martensitic stainless steel with low carbon, nickel and molybdenum. These materials have good mechanical strength and high fracture toughness at the end of manufacturing process (for example after hot rolling), without heat treatment.

Tubes manufactured with these steels are used in chemical and oil sector as fluid carriers or as structural elements or, also, for heat exchangers. These steels offer optimal corrosion resistance in environments rich in H_2S e CO_2 , where they can be used without the addition of corrosion inhibitors.

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[17] *The AISI standard provides three levels of carbon content: low (AISI 440A with %C 0.60-0.75), medium (AISI 440B with %C 0.75-0.95%) and high (AISI 440C with %C 0.95-1.20%) for stainless steel type AISI 440.*

7. FERRITIC STAINLESS STEELS

7.1 Metallurgy

When the chromium content reaches values of 17% (or greater) and, at the same time, the carbon content is reduced (below 0.1%), the ferritising effect of chromium is no longer balanced by austenitizing action of carbon and, therefore, stainless steel micro-structure will be ferritic at room temperatures. This is what occurs on stainless steel grade EN X6Cr17 (similar to AISI 430), the ancestor of ferritic stainless steels.

Ferritic stainless steels however are not limited to grade EN X6Cr17, there are in fact various grades, divided into three families, according to chromium content.

Figure 24 shows the main grades of ferritic stainless steels sold on market, starting from grade EN X6Cr17, the ancestor of this family; on the other hand, table 6 shows the chemical composition of the main types of ferritic stainless steels and their designation.

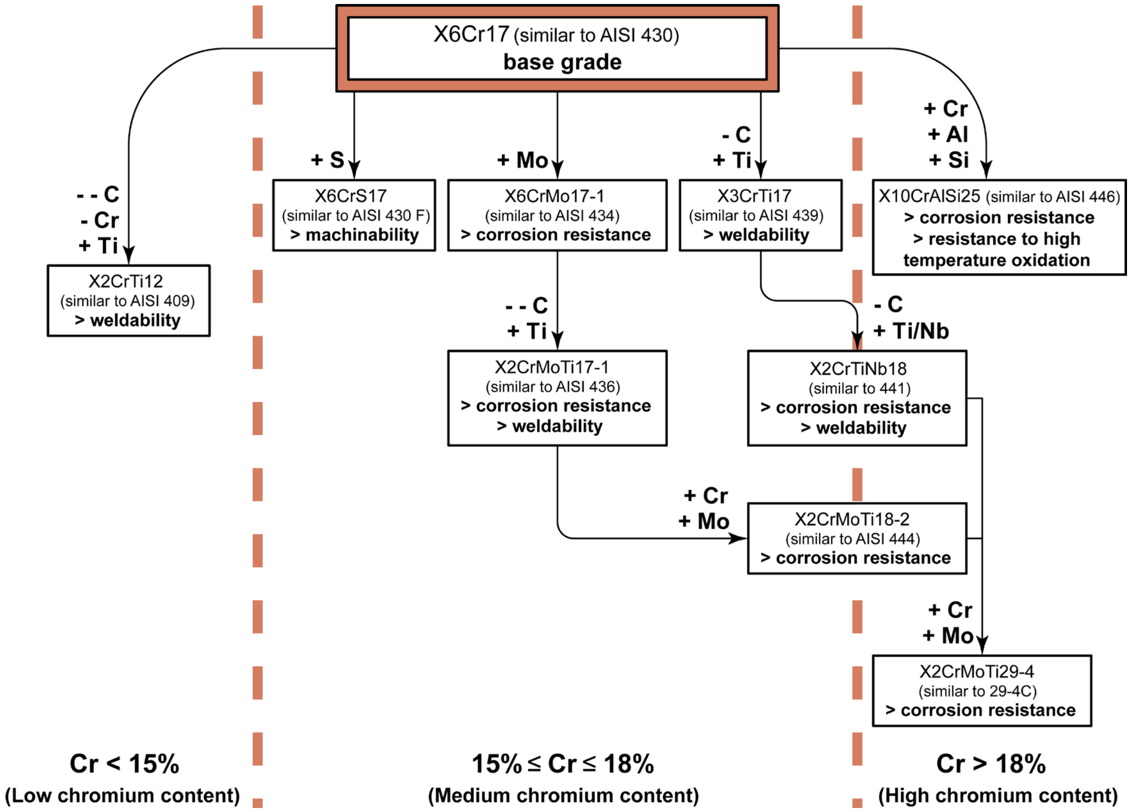

Figure 24 – Main types of ferritic stainless steels, starting from grade EN X6Cr17 (similar to AISI 430), ancestor of this family.

EN Designation	%C	%Si	%Mn	%P	%S	%Cr	%Mo	Other	AISI approximate correspondence
X2CrTi12 (1.4512)	≤ 0.03	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	10.5-12.5	---	1	AISI 409
X6Cr17 (1.4016)	≤ 0.08	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	16.0-18.0	---	---	AISI 430
X6CrMoS17 (1.4105)	≤ 0.08	≤ 1.50	≤ 1.50	≤ 0.040	0.15-0.35	16.0-18.0	0.20-0.60	---	AISI 430F
X3CrTi17 (1.4510)	≤ 0.05	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	16.0-18.0	---	2	AISI 439 (430Ti) (*)
X6CrMo17-1 (1.4113)	≤ 0.08	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	16.0-18.0	0.90-1.40	---	AISI 434
X2CrMoTi17-1 (1.44513)	≤ 0.025	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	16.0-18.0	0.80-1.40	3	AISI 436
X2CrMoTi18-2 (1.4521)	≤ 0.025	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	17.0-20.0	1.80-2.50	4	AISI 444
X2CrTiNb18 (1.4509)	≤ 0.03	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	17.5-18.5	---	5	441 (*)
X10CrAlSi25 (1.4762)	≤ 0.12	0.70-1.40	≤ 1.00	≤ 0.040	≤ 0.015	23.0-26.0	---	6	AISI 446
X2CrMoTi29-4 (1.4592)	≤ 0.025	≤ 1.00	≤ 1.00	≤ 0.030	≤ 0.010	28.0-30.0	3.50-4.20	7	29-4C (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 441).
1: $\%Ti = [6 \times (C + N)]-0.65$.
2: $\%Ti = [4 \times (C + N)+0.15]-0.80$.
3: $0{,}30 \leq \%Ti \leq 0.60$; $\%N \leq 0.020$.
4: $\%Ti = [4 \times (C + N) + 0.15]-0.80$; $\%N \leq 0.030$.
5: $0{,}10 \leq \%Ti \leq 0.60$; $[3 \times C + 0.30] \leq \%Nb \leq 1.00$.
6: $1{,}20 \leq \%Al \leq 1.70$; $1.20 \leq \%Si \leq 1.70$.
7: $\%Ti = [4 \times (C + N) + 0.15]-0.80$; $\%N \leq 0.045$.

Table 6 – Chemical composition of the main types of ferritic stainless steels [from EN 10088].

The first family has a chromium content ranging from 15.5% to 18%: the largest number of ferritic stainless steel types sold on market belongs to this family. The second and third ones are characterised rispectively by chromium content ranging from 11.5% to 14.5% (ferritic stainless steels with low chromium content) and chromium content over than 18% (known as "super-ferritic" stainless steels).

All the families - with low, medium and high chromium content - have other alloying elements: these include aluminium and silica, that stabilize the ferritic micro-structure and improve resistance to high temperature oxidation, molybdenum, that improves corrosion resistance, titanium and niobium, that inhibit the chromium carbide precipitation.

To understand the microstructure of ferritic stainless steels with high chromium and very low carbon content, it is useful to consider their phase diagram.

In this regard it is worth noting that the *Fe-Cr* diagram (figure 5) is modified by the presence of 0.05% of carbon (figure 25).

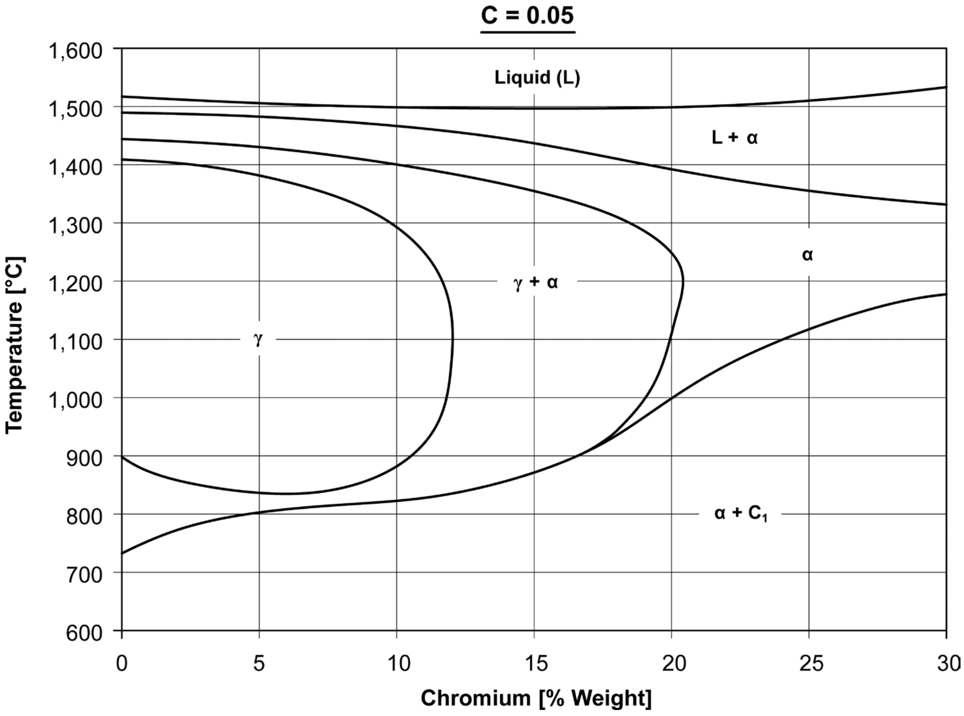

Figure 25 – Two-dimensional section of *Fe-Cr-C* ternary phase diagram, isopleth for %Fe-%Cr-0.05%C alloys. C_1 carbides type $(Cr,Fe)_{23}C_6$ [from McGuire 2008].

Grade EN X6Cr17 has an initial solidification as α-phase followed by partial transformation in γ-phase when temperature falls the two-phase field $\gamma+\alpha$; subsequently, from temperatures of 900°-950°C through to room temperature[18], the chemical system returns to form homogeneous grains of α-phase (ferrite). If we attempt to quench this steel, for example by heating around 800°C and then cool it in water, no changes would occur and therefore there would be no significant increase in mechanical strength. Between 20°-900°C there are no critical points to enable austenite ⟶ martensite transformation and therefore it would not be possible to apply quenching to increase tensile strength.

Above 900°-950°C, as already observed, there is the two-phase field of γ+α[19]: this is typical of non-stabilized ferritic stainless steels with chromium content of 16-17% .

On one hand, small percentages of austenite at high temperatures is positive because avoids grain growth during annealing heat treatments. On the other hand the existence of austenite at high temperatures causes an additional problem: if rapid cooling is performed immediately after the heating phase, austenite transforms into martensite, causing intergranular brittleness.

However, when ferritic stainless steels contain stabilizing alloying elements, such as titanium and niobium, and/or high content of chromium (more than 18%) or molybdenum (1-2%), their microstructure will be completely ferritic starting from melting point through to room temperature; in this way it is possible to improve weldability of these stainless steels compared to non-stabilized grades.

An additional metallurgical problem is related to precipitation of chromium carbides, type $Cr_{23}C_6$ that can lead to intergranular corrosion problems. This phenomenon is due to the high chemical affinity between chromium and carbon. In this regard is worth noting that it is practically impossible to eliminate chromium carbide precipitation in ferritic stainless steels: the solubility of carbon in body centred cubic lattice is very low. On the other hand the high diffusivity of chromium in the α-phase lattice produces lower decrease of chromium near grain boundaries with respect to austenitic stainless steels (figure 10).

For this reason intergranular corrosion problems are negligible in ferritic stainless steels compared to austenitic ones.

The only way to eliminate chromium carbides is to add stabilizing alloying elements, such as titanium and niobium, during the steel making process. Semi-finished products should also undergo full annealing before being used.

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[18] *The transformation temperature from two-phase field, γ+α, to one-phase field, α, depends on chromium content. The value of 900°-950°C referred to a stainless steel with approximatly 17% of chromium. Temperature increases or decreases if chromium content is respectively higher or lower than 17%.*

[19] *However, the amount of austenite at high temperatures in non-stabilized ferritic stainless steels is small (max 20%).*

Two further problems should be noted in relation to ferritic stainless steels: (i) formation of σ-phase and (ii) 475°C embrittlement.

The σ-phase is a *Fe-Cr* phase which causes considerably reduction both in corrosion resistance and mechanical strength. The σ-phase formation is a problem exclusively for stainless steels with high contents of chromium and molybdenum (super-ferritic).

Molybdenum also forms other harmful phases, such as χ and *Laves* phase, that are both *Fe-Cr-Mo* phases. To eliminate σ, χ and *Laves* phases stainless steel should be heated to temperatures of around 1,050°C followed by rapid cooling in water. This heat treatment, called solution annealing, dissolves chromium carbides χ and *Laves* phase and inhibit their formation during the cooling phase. Figure 26 shows a typical example of time-temperature diagram used to describe precipitation of chromium carbides and σ-phase for varius stainless steels.

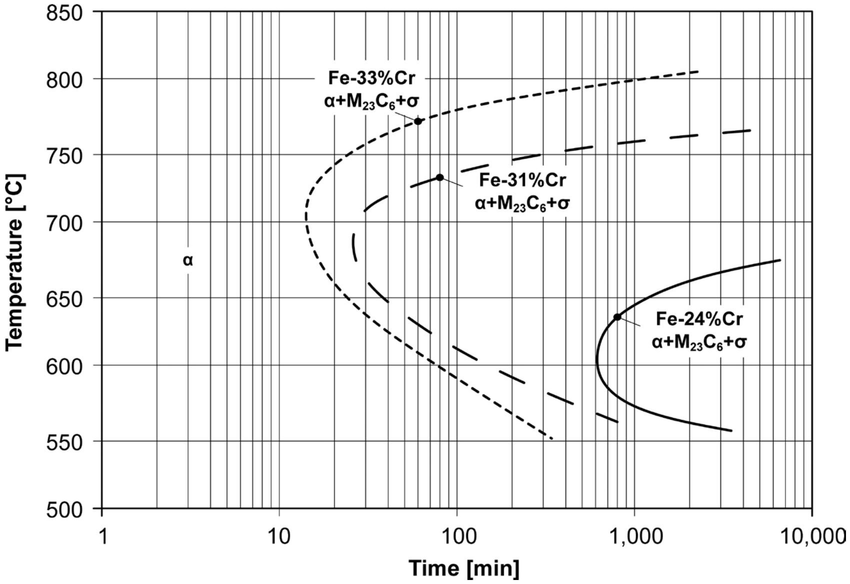

Figure 26 – Time-temperature diagram used to describe precipitation of chromium carbides and σ-phase for various stainless steels [from Vander Voort 1991].

The 475°C embrittlement is a more significant problem than σ-phase formation, because it affects a greater number of ferritic stainless steels with the only exception of those with chromium content below 14%.

The 475°C embrittlement is described by diagrams similar to those used for σ-phase (figure 27). Figure 28 shows another useful diagram illustrating the decrease in impact strength according to temperature and exposure time.

The effect of 475°C embrittlement is eliminated by annealing at 550°-600°C for time intervals that do not lead to formation of chromium carbides or σ-phase; cooling phase must be in air or water.

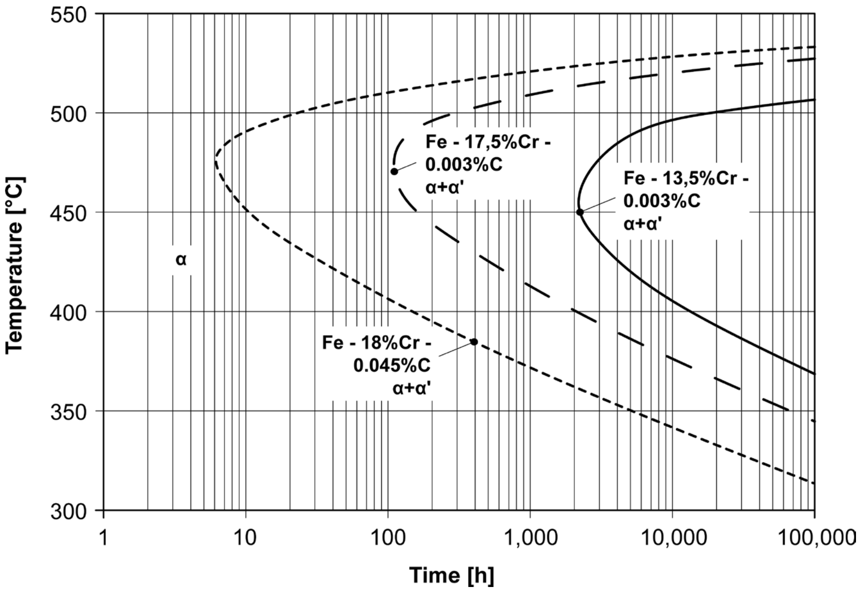

Figure 27 – Time-temperature diagram used to describe 475°C embrittlement (spinodal decomposition of α-phase) for various stainless steels [from Grobner 1973].

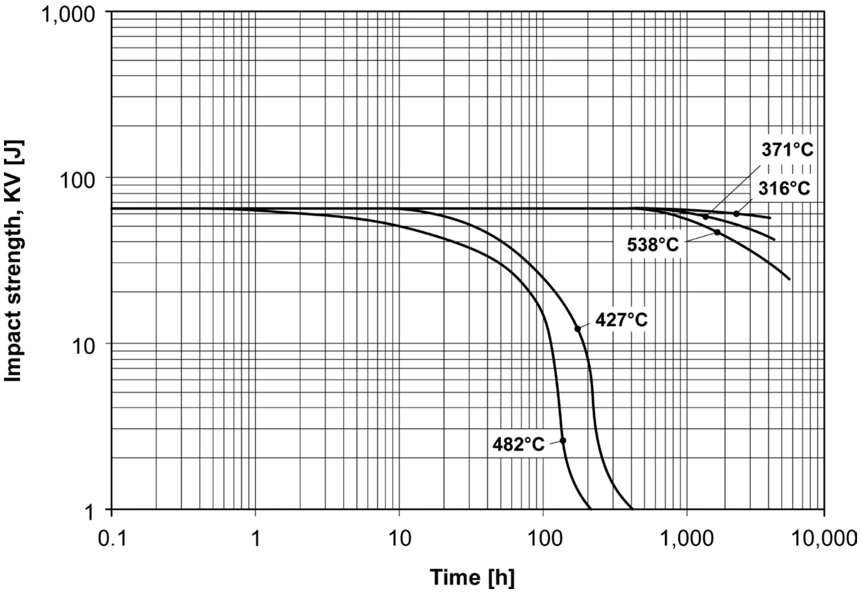

Figure 28 – Impact strength of ferritic stainless steels with 18% chromium after aging at 316°C, 371°C, 427°C, 482°C and 538°C [from Grobner 1973].

7.2 Heat treatments

The only heat treatment used for ferritic stainless steels is full annealing: its role is to optimise corrosion resistance aiding uniform chromium distribution[20].

Full annealing of ferritic stainless steels is performed at different temperatures depending on steel chemical composition. The selection of temperature and holding time is very important because ferritic stainless steels are very sensitive to grain growth. Table 7 shows the heat treatments adopted for the most common types of ferritic stainless steels.

The cooling phase is always performed in air for thin, flat semi-finished products or for long semi-finished products with small diameter, or in water for components with larger sections; otherwise water cooling is compulsory for ferritic stainless steels with higher content of chromium to avoid 475°C embrittlement.

The full annealing of ferritic stainless steels also serve to re-crystallise cold-worked metal, i.e. to reform new grains starting from the original ones that was extended by cold deformation. These new grains are finer than the original hot formed grains (figure 29).

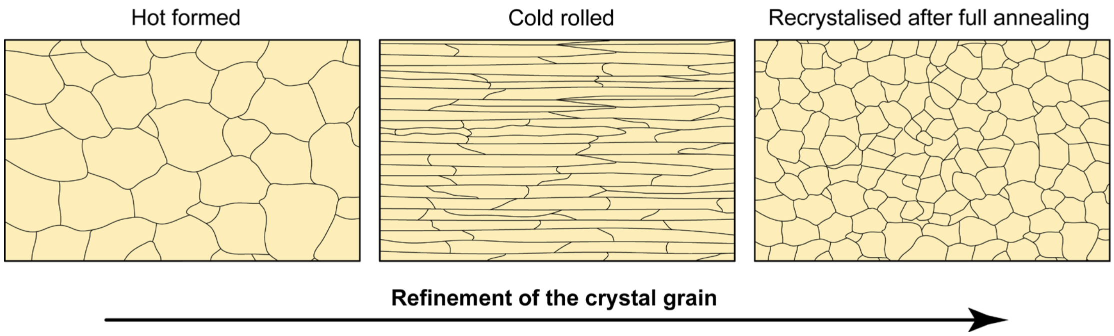

Figure 29 – The effect of full annealing on ferritic stainless steels.

The semi-finished products must be cleaned thoroughly to remove oils, grease or carbon residue before heat treatments; otherwise there is risk of surface carburisation.

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[20] *Full annealing do not dissolves chromium carbides but through the diffusion mechanisms it aids redistribution of chromium. Therefore, the chromium content will be restored above the passivation threshold avoiding the intergranular corrosion due to carbide precipitation.*

EN Designation	Full annealing	Cooling medium	AISI approximate correspondence
X2CrTi12 (1.4512)	770°-850°C	air, water	AISI 409
X6Cr17 (1.4016)	770°-850°C	air, water	AISI 430
X6CrMoS17 (1.4105)	770°-850°C	air, water	AISI 430F
X3CrTi17 (1.4510)	770°-850°C	air, water	AISI 439 (430Ti) (*)
X6CrMo17-1 (1.4113)	770°-850°C	air, water	AISI 434
X2CrMoTi17-1 (1.4513)	800°-880°C	air, water	AISI 436
X2CrMoTi18-2 (1.4521)	800°-880°C	air, water	AISI 444
X2CrTiNb18 (1.4509)	850°-930°C	air, water	441 (*)
X10CrAlSi25 (1.4762)	800°-880°C	air, water	AISI 446
X2CrMoTi29-4 (1.4592)	900°-1,000°C	air, water	29-4C (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term “type” (for example type 441).

Table 7 – Characteristics of full annealing heat treatment on the main types of ferritic stainless steels.

7.3 Physical and mechanical properties

The physical properties of the most common types of ferritic stainless steels are shown in table 8. An important physical property of ferritic stainless steels is magnetically soft behaviour, which is enhanced by full annealing for extended holding times (figure 30).

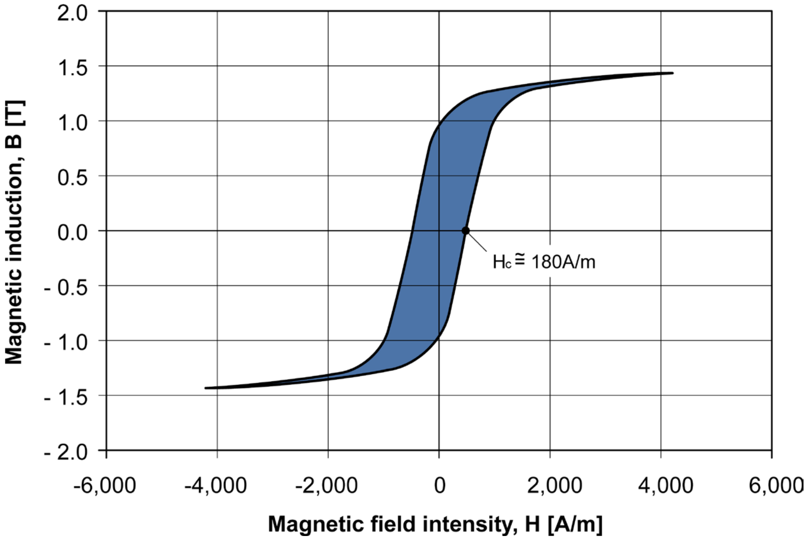

Figure 30 – Hysteresis curve up to 4200 A/m of ferritic stainless steel grade EN X6Cr17 (similar to AISI 430) [from Oxley et al. 2009].

The mechanical strength of ferritic stainless steels are not very high; these steels are made up of ferrite grains and are used in fully annealed state. The UTS ranges between 450MPa and 600MPa with hardness values of 150-220HB.

Table 9 shows the typical mechanical properties for some types of ferritic stainless steels.

Ferritic stainless steels cannot be hardened by quenching: the only way to increase tensile strength is by cold deformation processes, such as cold drawing or rolling: in this case the UTS can reach up to 900-1,000MPa (figure 31).

The impact strength of ferritic stainless steels is highly variable but it can be said that the ductile to brittle transition temperature increases with increasing of chromium content (figure 32).

EN Designation	Density $[kg/dm^3]$	Specific heat at 20°C $[J \cdot kg^{-1} \cdot K^{-1}]$	Electrical resistance at 20°C $[W \cdot mm^2 \cdot m^{-1}]$	Thermal conductivity $[W \cdot m^{-1} \cdot K^{-1}]$	Mean coefficient of thermal expansion $[10^{-6} \cdot K^{-1}]$		Elastic modulus [GPa]		AISI approximate correspondence
					between 20°C and 100°C	between 20°C and 200°C	at 20°C	at 200°C	
X2CrTi12 (1.4512)	7.7	460	0.60	25	10.5	11.0	220	210	AISI 409
X6Cr17 (1.4016)	7.7	460	0.60	25	10.0	10.0	220	210	AISI 430
X6CrMoS17 (1.4105)	7.7	460	0.70	25	10.0	10.5	220	210	AISI 430F
X3CrTi17 (1.4510)	7.7	460	0.60	25	10.0	10.0	220	210	AISI 439 (430Ti) (*)
X6CrMo17-1 (1.4113)	7.7	460	0.70	25	10.0	10.5	220	210	AISI 434
X2CrMoTi17-1 (1.4513)	7.7	460	0.70	25	10.0	10.5	220	210	AISI 436
X2CrMoTi18-2 (1.4521)	7.7	430	0.80	23	10.4	10.8	220	210	AISI 444
X2CrTiNb18 (1.4509)	7.7	460	0.60	26	10.0	10.0	220	210	441 (*)
X10CrAlSi25 (1.4762)	7.7	500	1.10	17	---	10.5	220	210	AISI 446
X2CrMoTi29-4 (1.4592)	7.7	440	0.67	17	11.5	---	220	210	29-4C (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 441).

Table 8 – Physical properties of the main types of ferritic stainless steels [from EN 10088].

EN Designation	Heat treatment condition	YS [MPa]	UTS [MPa]	A [%]	Hardness [HB]	AISI approximate correspondence
X2CrTi12 (1.4512)	A	250-350	400-500	27-32	140-180	AISI 409
X6Cr17 (1.4016)	A	300-400	450-550	25-30	150-200	AISI 430
	A + CD (**)	550-850	650-950	5-18	---	
X6CrMoS17 (1.4105)	A	250-350	450-550	20-25	150-200	AISI 430F
	A + CD (**)	400-700	600-850	5-15	---	
X3CrTi17 (1.4510)	A	250-350	450-550	25-30	150-200	AISI 439 (430Ti) (*)
	A + CD (**)	500-800	600-900	5-20	---	
X6CrMo17-1 (1.4113)	A	300-400	480-580	22-28	150-200	AISI 434
X2CrMoTi17-1 (1.4513)	A	250-350	420-520	25-30	140-180	AISI 436
X2CrMoTi18-2 (1.4521)	A	350-450	480-580	25-30	160-220	AISI 444
X2CrTiNb18 (1.4509)	A	250-350	450-550	20-25	150-200	441 (*)
X10CrAlSi25 (1.4762)	A	350-450	550-650	12-18	170-230	AISI 446
X2CrMoTi29-4 (1.4592)	A	450-550	560-660	22-27	150-200	29-4C (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 441).
A: Annealed.
A + CD: Annealed and Cold Drawn.
(**) The mechanical properties after A + CD depend on cold drawn level.

Table 9 – Mechanical properties of the main types of ferritic stainless steels.

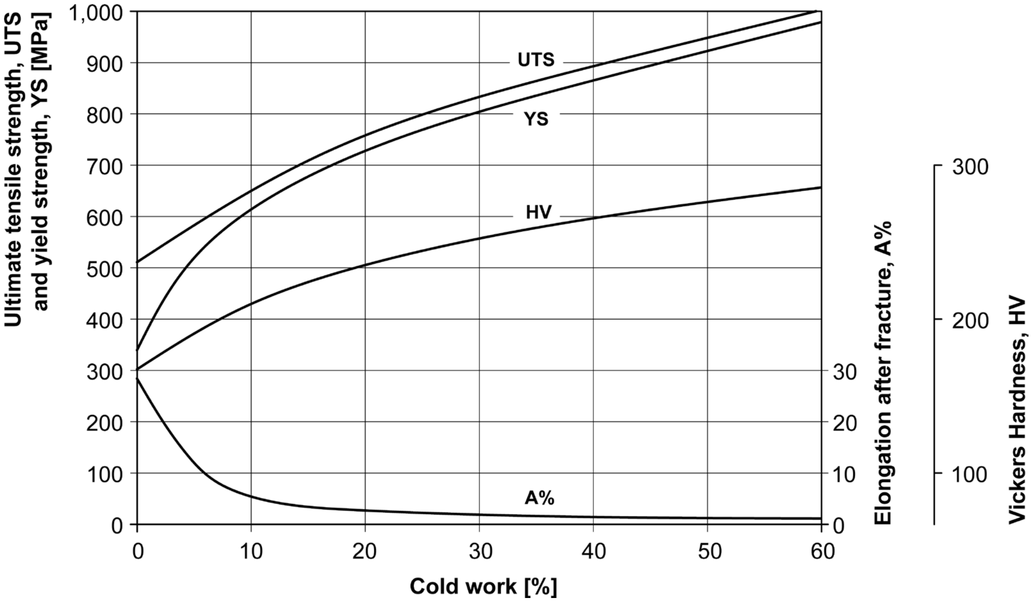

Figure 31 – The effect of cold work on mechanical properties of ferritic stainless steel grade EN X6Cr17 (similar to AISI 430) [from Lacombe et al. 1993].

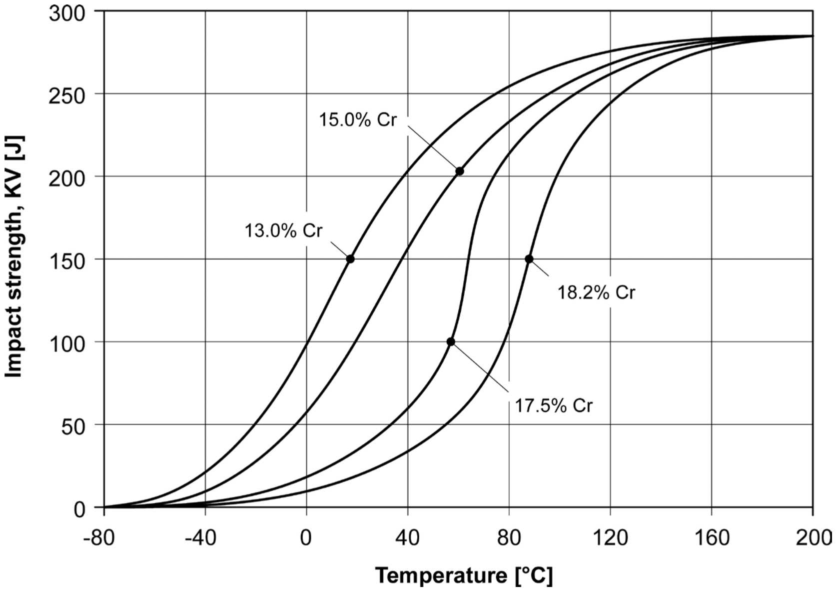

Figure 32 – The effect of chromium on ductile to brittle transition of iron-chromium alloys (carbon is ~0.01%) [from Sedriks 1996].

The impact strength also depends on other metallurgical parameters. The ductile to brittle transition temperature increases with increasing of interstitial elements (carbon and nitrogen) and decreases with decreasing of average grain size; the thickness of semi-finished products also has an effect on brittle fractures of ferritic stainless steels (figure 33).

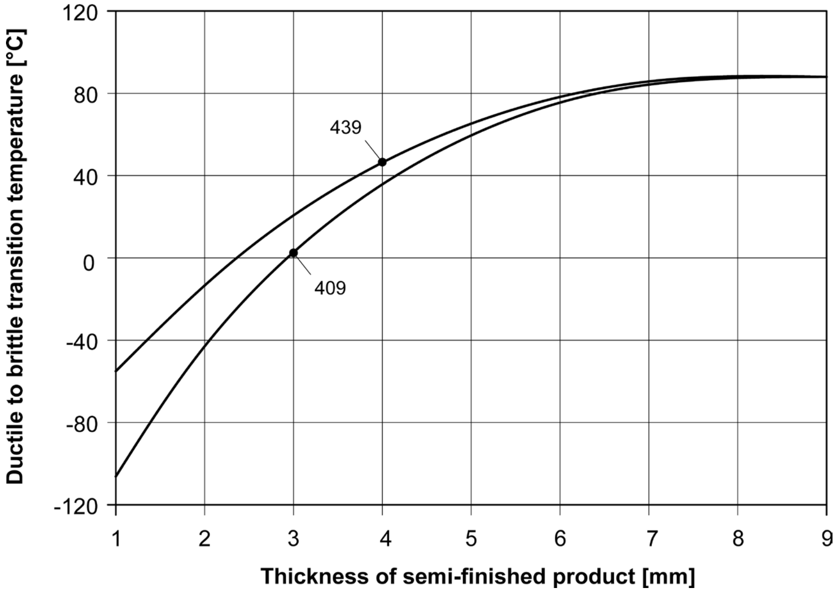

Figure 33 – Effect of thickness of semi-finished product on ductile to brittle transition temperature of two ferritic stainless steels [from Sedriks 1996].

7.4 Types and applications

Semi-finished products in ferritic stainless steels are available on market mainly in form of sheets or strips; a more limited percentage is also available as long semi-finished products, such as bars and rods.

The ferritic stainless steels most commonly used are grades EN X6Cr17 (similar to AISI 430) and EN X2CrTi12 (similar to AISI 409).

The EN X6Cr17 is a traditional ferritic stainless steel with good cold deformability and machinability; it has higher corrosion resistance than martensitic stainless steels especially in nitric acid (up to 90% in cold water-based solutions and up to 10% in hot water-based solutions).

For this reason EN X6Cr17 is used for production and transformation of nitric acid (tanks, condensers, pipelines, coils, etc.); it is also widely used for cracking and reforming plants in oil sector, for production of low cost cutlery, household appliances, decorative elements and furnishing accessories, bar counters and tables, and kitchen extractor hoods. It is also used for many applications in milk dairy sector and for train carriages and buses manufacture.

Ferritic stainless steel EN X6Cr17 is also used in components operating at temperatures up to 750°-800°C due to its good resistance to high temperature oxidation.

Grade EN X6CrMoS17 (similar to AISI 430F) is similar to EN X6Cr17, but with improved machinability due to high amount of sulphur: this steel is used to produce bars and rods (long semi-finished products) used for solenoid valves[21] and small mechanical parts.

The other widely used ferritic stainless steel is grade EN X2CrTi12 (similar to AISI 409) that has lower corrosion resistance with respect to EN X6Cr17 but increased cold deformability and improved weldability due to the stabilization effect of titanium; it also has lower cost than EN X6Cr17.

Grade EN X2CrTi12 is widely used for catalytic converters and exhaust system for cars, lorries and motorcycles: this field of application represents the single most important market for a specific type of stainless steel.

Grade EN X3CrTi17 has been developed to improve weldability without reducing corrosion resistance compared to EN X6Cr17. Grade EN X3CrTi17 has 0.025% of carbon and it is stabilized with titanium.

Grade EN X3CrTi17 is used in similar applications of EN X6Cr17, at least in all cases where good wedability is required. One typical application are washing machine drums produced by welding.

Other ferritic stainless steels have been developed to increase corrosion resistance of the traditional EN X6Cr17. Grades EN X6CrMo17-1 (similar to AISI 434), EN X2CrTiNb18 (known also as 441) and EN X2CrMoTi17-1 (similar to AISI 436) can be used in aggressive environments. The addition of molybdenum improves corrosion resistance and allows to use these ferritic stainless steel grades for car exhaust systems, escalators, lifts and conveyor belts, drinking water pipelines, or as supports for photovoltaic cells. Ferritic stainless steel grades EN X2CrMoTi18-2 (similar to AISI 444) and EN X2CrMoTi29-4 (also known as 29-4C) represent a further improvement in terms of corrosion resistance, due to addition of high amounts of chromium and molybdenum: these grades are widely used for heat exchangers, boilers and hot water storage tanks.

Lastly, the ferritic stainless steel EN X10CrAlSi25, with high content of chromium, silicon and aluminium has elevated resistance to high temperature oxidation (up to 1100°C).

Grade EN X10CrAlSi25 also has good resistance in sulphurous environments (diesel fuel combustion products, sulphur oxides, etc.) in which austenitic stainless steels have poor performance. This type is widely used for ovens and boilers, crucibles, hydrogenetion plant (also with oils rich in sulphur) and superheater pipelines.

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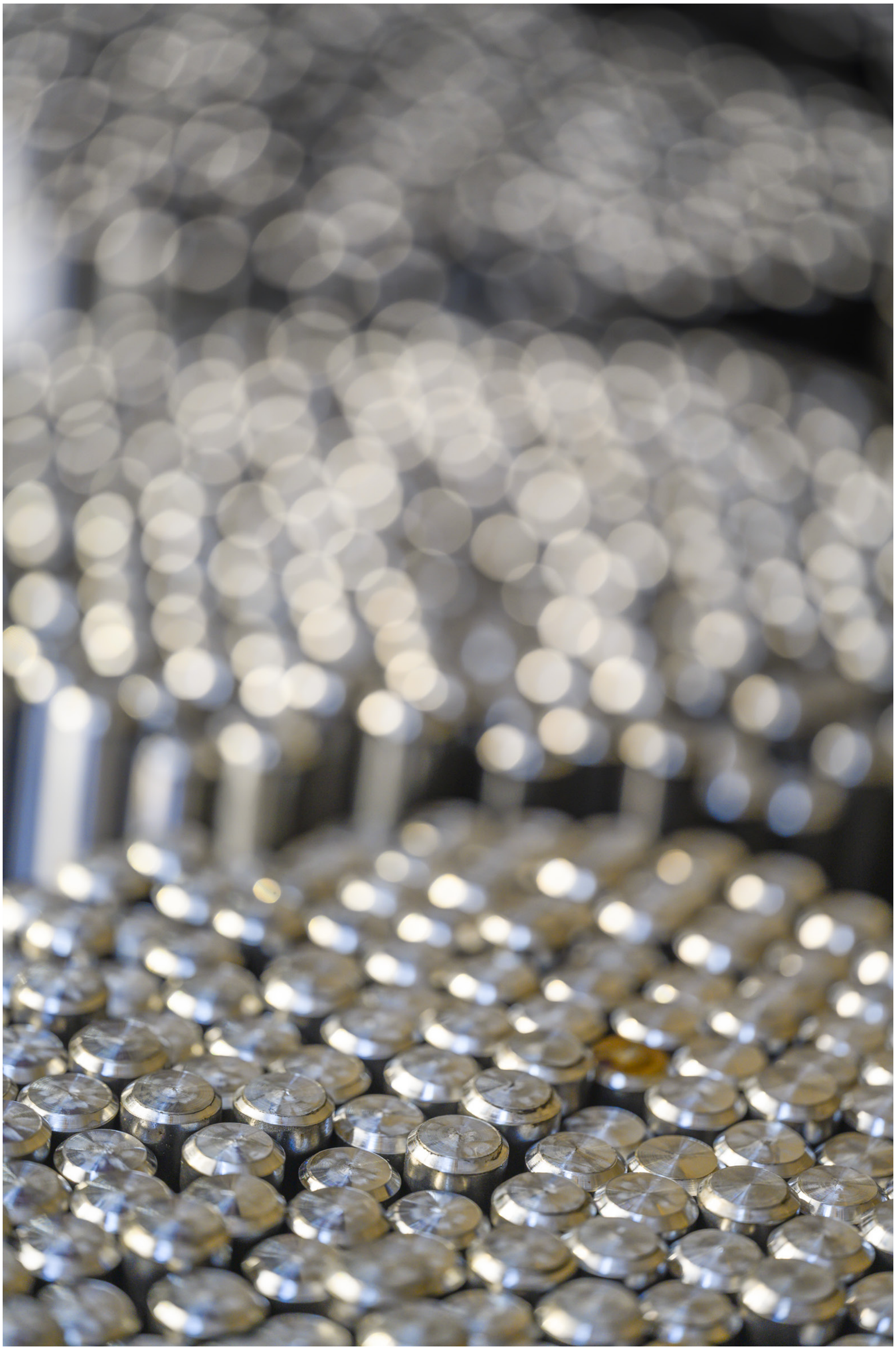
[21] *Ferritic stainless steels used for solenoid valves have specific chemical compositions with 1-1.5% of silicon which makes steel magnetically soft.*



8. AUSTENITIC STAINLESS STEELS

8.1 Metallurgy

If chromium is increased to at least 17-18% and nickel is added to 8-9%, the steel will have an austenitic structure with face-centered cubic lattice at room temperature: due to austenitizing effect of nickel that prevails over the ferritising action of chromium (diagram in figure 8 and Schaeffler diagram in figure 11). Carbon is fixed at very low values (C = 0.02-0.06%) to limit chromium carbides formation as far as possible. Grade EN X5CrNi18-10 (similar to AISI 304) is the ancestor of austenitic chromium-nickel stainless steel family. This stainless steel is highly resistant to atmosphere corrosion and water based solutions[22].

Grade EN X5CrNiMo17-12-2 (similar to AISI 316) is another widely used stainless steel with 11-12% of nickel and 2-3% of molybdenum in addition to chromium. Grade EN X5CrNiMo17-12-2 is the ancestor of the second family of austenitic stainless steels, i.e. chromium-nickel-molybdenum[23].

There is also a third way of making austenitic stainless steel: replace nickel with manganese[24]. This solution was developed in 1950s in order to reduce production costs; grade EN X12CrMnNiN17-7-5 (similar to AISI 201) is the ancestor of austenitic stainless steel family with chromium, manganese and nickel.

Austenitic stainless steels with manganese - which are not taken into consideration - did not have the distribution that was hoped for, due to limited corrosion resistance in contact with water-based solutions, more similar to ferritic stainless steel grade EN X6Cr17, or austenitic stainless steel grade EN X5CrNi18-10.

Figure 34 illustrates the two main types of austenitic stainless steels available on market: one is chromium-nickel stainless steels such as EN X5CrNi18-10 and the other is chromium-nickel-molybdenum such as EN X5CrNi17-12-2.

A further distinction divides these two families into "austenitic" if nickel is less than or equal to 20% and "super-austenitic" if greater.

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[22] *The corrosion resistance in air and water-based solutions, even partially contaminated by chlorides (generally up to 500ppm of ions* Cl^-*), of austenitic stainless steel EN X5CrNi18-10 is higher than martensitic and ferritic types such as EN X30Cr13 and EN X6Cr17.*

[23] *The austenitic chromium-nickel-molybdenum stainless steel EN X5CrNiMo17-12-2 (similar to AISI 316) is suitable for applications in contact with water-based solutions strongly contaminated by chlorides (*$Cl^- \cong$ *2,000ppm).*

[24] *Both manganese and nickel have austenitizing effect to Fe-C alloys, but the effect of manganese is equal to half of nickel (Every 1% nickel must be replaced with 2% manganese).*

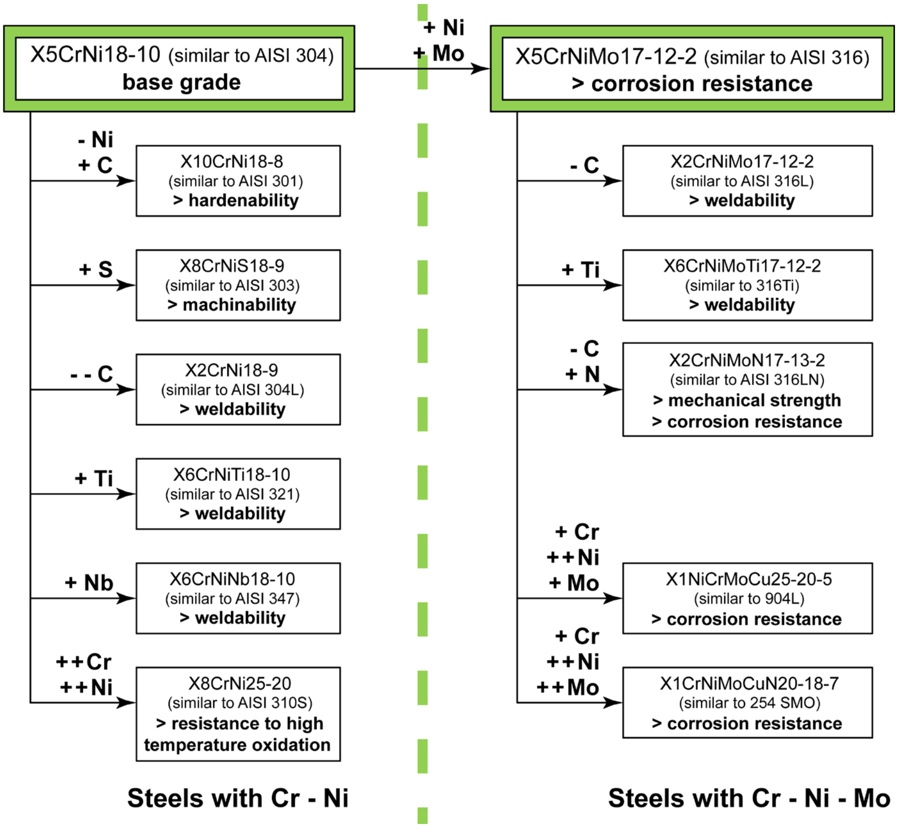

Figure 34 – Main types of chromium-nickel and chromium-nickel-molybdenum austenitic stainless steels starting from EN X5CrNi18-10 (similar to AISI 304) and EN X5CrNiMo17-12-2 (similar to AISI 316).

Table 10 shows chemical composition of the most commonly used austenitic stainless steels and relative designation according to standard EN 10088.

As in the previous cases, it is useful to consider a phase diagram for full understanding the metallurgical problems of austenitic stainless steels: figure 35 shows the simplified phase diagram of a steel with 18% chromium and 8% nickel as the carbon changes.

The phase diagram of austenitic stainless steels doesn't have critical points, i.e. no transformation γ-phase$\rightarrow\alpha$-phase. After initial solidification in $\gamma+\delta$ phase, stainless steel becomes completely austenitic (γ-phase) without any other transformationdown to room temperature.

EN Designation	%C	%Si	%Mn	%P	%S	%Cr	%Ni	%Mo	Other	AISI approximate correspondence
X10CrNi18-8 (1.4310)	0.05-0.15	≤ 2.00	≤ 2.00	≤ 0.045	≤ 0.015	16.0-19.0	6.0-9.5	≤ 0.80	1	AISI 301
X8CrNiS18-9 (1.4305)	≤ 0.10	≤ 1.00	≤ 2.00	≤ 0.045	0.15-0.35	17.0-19.0	8.0-10.0	---	1, 2	AISI 303
X5CrNi18-10 (1.4301)	≤ 0.07	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	17.5-19.5	8.0-10.5	---	1	AISI 304
X2CrNi18-9 (1.4307)	≤ 0.03	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	17.5-19.5	8.0-10.5	---	1	AISI 304L
X6CrNiTi18-10 (1.4541)	≤ 0.08	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	17.0-19.0	9.0-12.0	---	3	AISI 321
X6CrNiNb18-10 (1.4550)	≤ 0.08	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	17.0-19.0	9.0-12.0	---	4	AISI 347
X8CrNi25-21 (1.4845)	≤ 0.10	≤ 1.50	≤ 2.00	≤ 0.045	≤ 0.015	24.0-26.0	19.0-22.0	---	1	AISI 310S
X5CrNiMo17-12-2 (1.4401)	≤ 0.07	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	16.5-18.5	10.0-13.0	2.00-2.50	1	AISI 316
X2CrNiMo17-12-2 (1.4404)	≤ 0.03	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	16.5-18.5	10.0-13.0	2.00-2.50	1	AISI 316L
X2CrNiMoN17-13-3 (1.4429)	≤ 0.03	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	16.5-18.5	11.0-14.0	2.50-3.00	5	AISI 316LN
X6CrNiMoTi17-12-2 (1.4571)	≤ 0.08	≤ 1.00	≤ 2.00	≤ 0.045	≤ 0.015	16.5-18.5	10.5-13.5	2.00-2.50	3	316Ti (*)
X1NiCrMoCu25-20-5 (1.4539)	≤ 0.02	≤ 0.70	≤ 2.00	≤ 0.030	≤ 0.010	19.0-21.0	24.0-26.0	4.00-5.00	6	904 L (*)
X1CrNiMoCuN20-18-7 (1.4547)	≤ 0.02	≤ 0.70	≤ 1.00	≤ 0.030	≤ 0.010	19.5-20.5	17.5-18.5	6.00-7.00	7	254 SMO (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 904 L).
1: %N ≤ 0.11.
2: %Cu ≤ 1.0.
3: %Ti = 5 x C-0.70.
4: %Nb = 10 x C-1.00.
5: %N = 0.12-0.22.
6: %N ≤ 0.15; %Cu = 1.20-2.00.
7: %N = 0.18-0.25; %Cu = 0.50-1.00.

Table 10 – Chemical composition of the main types of austenitic stainless steels [from EN 10088].

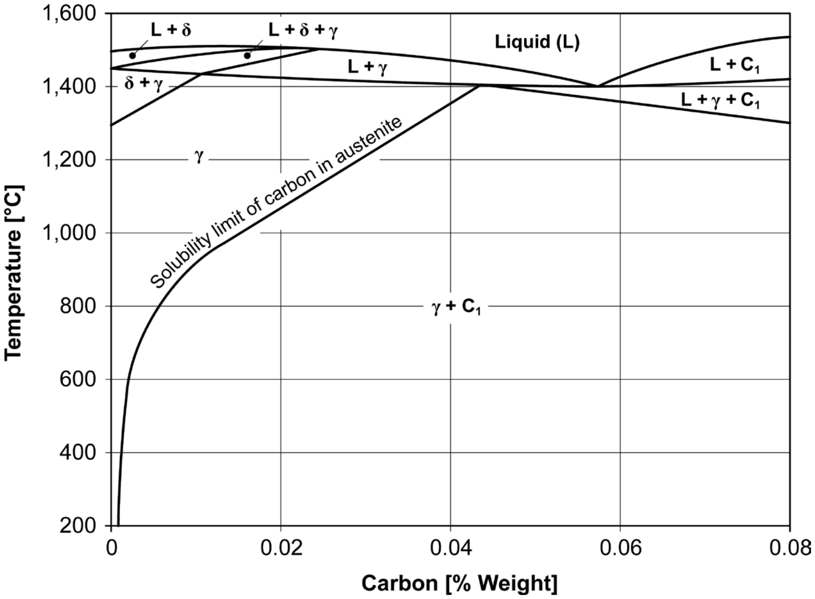

Figure 35 – Two-dimensional section of *Fe-Cr-Ni-C* quaternary phase diagram, isopleth for %Fe-18%Cr-8%Ni-%C alloys. C_1 carbides type $(Cr,Fe)_{23}C_6$ [from Sedriks 1996].

The austenitizing elements, such as carbon, nitrogen, nickel and manganese, have shifted the austenite-martensite transformation well below room temperature. Therefore, hardening heat treatment, such as quenching, cannot be carried out on austenitic stainless steels.

Figure 35 also highlights the extremely limited carbon solubility in γ-phase[25]. Chromium carbides type $(Cr,Fe)_{23}C_6$ are formed at room temperature even if the amount of carbon is very low (austenitic stainless steels have normally 0.04-0.06% of carbon).

The phenomena of carbide precipitation, also known as "sensitization", is quite complex. It occurs for different exposure times at temperatures between 450°C and 900°C: the most critical conditions are found at around 700°C for just few minutes.

Sensitization of austenitic stainless reduces the chromium level near grain boundaries, where carbides are formed. In these areas the chromium level drops below the passivation limit leading to intergranular corrosion (figure 10b).

---

[25] *The carbon solubility limit in γ-phase is equal to 0.03% for austenitic stainless steels with 18% chromium and 8% nickel.*

The chromium carbide problem can be solved by two methods: chemical composition modification or heat treatment.

A first method is to add titanium or niobium as alloying elements: titanium and niobium form very stable carbides, preventing carbon from engaging chromium to form chromium carbides (the mechanism is the same as described for ferritic stainless steels).

Thanks to these metallurgical considerations, "stabilized" austenitic stainless steels have been developed, such as EN X6CrNiTi18-10 (similar to AISI 321), EN X6CrNiNb18-10 (similar to AISI 347) or EN X6CrNiMoTi17-12-2 (similar to AISI 316Ti): in brief, these are steels identical to EN X5CrNi18-10 and EN X5CrNiMo17-12-2 but with addition of titanium or niobium[26].

The semi-finished products should undergo a "stabilization" heat treatment in order to form carbides of the stabilizing elements (*Ti* and *Nb*).

A second method consists to minimise carbon down 0.02-0.03%. As a consequence the time required to form chromium carbides changes from few minutes to several hours.

Figure 36 is helpful to understand this concept. The diagram shows the minimum precipitation time of chromium carbides for each temperature. The curves shown on the diagram are also known as "*C* curves". As can be seen, the time required to sensitize austenitic stainless steel depends on carbon level: for example, if carbon is 0.08%, the time for carbide precipitation is around one minute, while this can extend to several hours if carbon is reduced to 0.02%.

Thanks to "*C* curves" austenitic steels with low carbon have been developed, such as EN X2CrNi18-9 (similar to AISI 304L[27]) or EN X2CrNiMo17-12-2 (similar to AISI 316L) which are not affected by chromium carbide precipitation.

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[26] Traditional and stabilized stainless steels are very similar, the only difference is due to the stabilizing elements which inhibit the chromium carbide formation. Instead, their corrosion resistance is approximately equal.

[27] The L series indicates very low carbon content, normally C = 0.03%. L stands for low carbon.

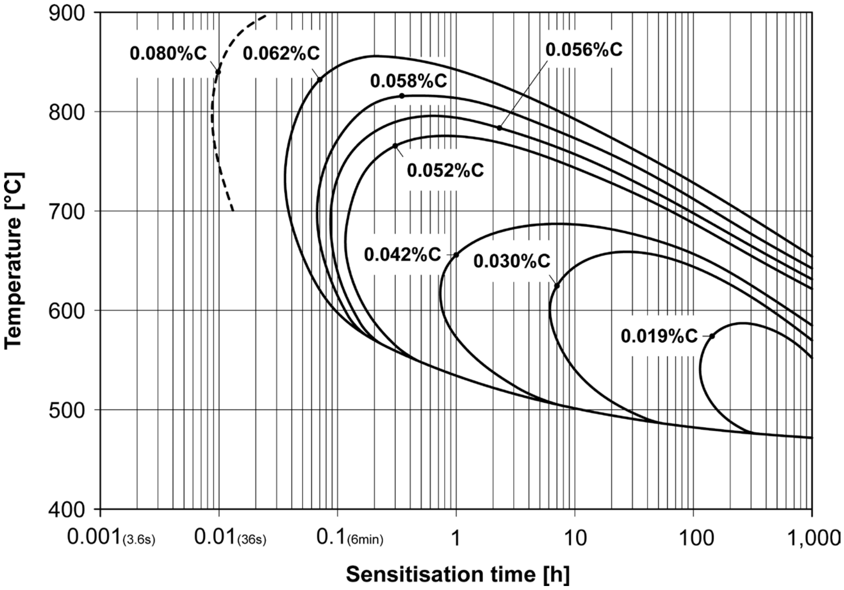

Figure 36 – T.T.T. diagram ("*C* curve") for austenitic stainless steels with 18% chromium and 9% nickel. The diagram shows the precipitation time of chromium carbides as the carbon level changes [from McGuire 2008].

There is always another option to avoid intergranular corrosion. If chromium carbide precipitation has occurred a solution annealing heat treatment can be performed at 1040°-1050°C[28]: this would dissolve any carbides.

There are also metallurgical problems related to holding at high temperatures an austenitic stainless steel.

σ-phase, χ-phase or *Laves* phase can be formed for alloys with high level of chromium or chromium-molybdenum. This phenomenon occurs for prolonged holding times (more than 100 hours) at temperatures between 550°C and 900°C (figure 37).

However the precipitation of phases rich in chromium or chromium-molybdenum is secondary to chromium carbide precipitation, which occurs at same temperatures but for shorter time intervals.

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[28] The dissolution effect also depends on semi-finished product or component dimensions. Small components are easily managed, while for plant parts or large welded structures a final heat treatment is impossible. In these cases the stabilized or low carbon steels should be used.

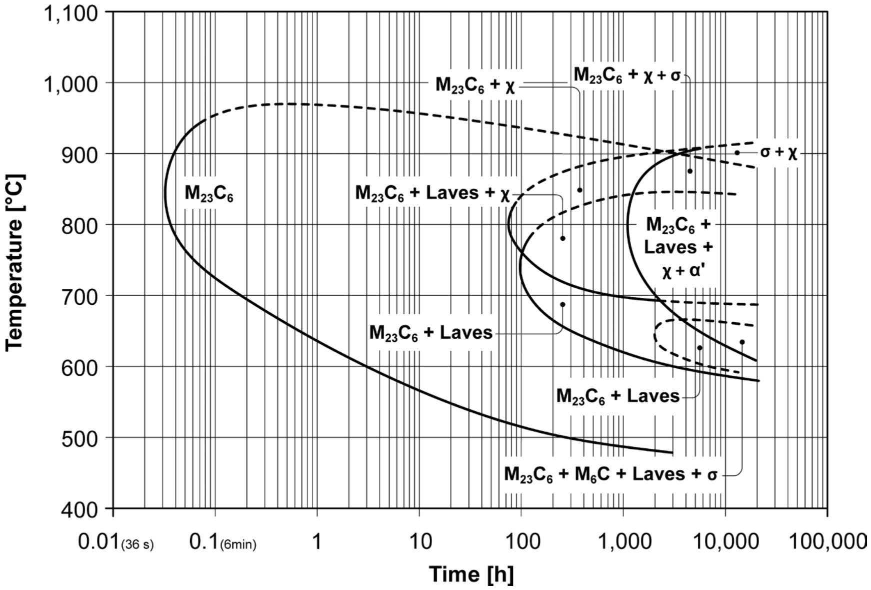

Figure 37 – T.T.T. diagram for austenitic stainless steel grade EN X5CrNiMo17-12-2. The diagram shows the precipitation time of chromium carbides, and σ, χ and *Laves* phases [from Khatak and Baldev 2002].

Other alloying elements are sometimes added to austenitic stainless steels, the most common are sulphur, nitrogen and copper.

Sulphur improves machinability thanks to the formation of iron sulphides and iron-chromium sulphides (as occurs on martensitic and ferritic stainless steels).

Nitrogen is added due to the strongly austenitizing effect and to improve corrosion resistance and mechanical strength, instead copper is used to improve cold deformability.

Lastly, the Schaeffler diagram[29] shows how common austenitic stainless steels (such as EN X5CrNi18-10 and EN X5CrNiMo17-12-2) form small amount of ferrite at room temperature (between 1% and 5%). The ferrite formation occurs if the material undergoes rapid cooling from melting point, as during welding operations[30].

A complete austenitic structure can be obteined by adding nickel (from 12% upwards) and/or nitrogen (0.10%-0.25%). This condition is important when the final application requires only asutenitic structure, for example for specific corrosive environments (strongly reducing acid solutions) or in nuclear applications (magnetic confinement systems operating at 0-5K) or due to problems of hot deformation.

---

[29] *Figure 35 shows a similar situation: the phase diagram highlights the phase structure of $\gamma+\delta$ which can remain unchanged after rapid cooling down to room temperature.*

[30] *Small quantities of ferrite in austenitic stainless steels can be positive: it can improve material weldability as it reduces the risk of hot cracks in weld metal and limits grain growth during heat treatments.*

8.2 Heat treatments

Austenitic stainless steels cannot be hardened by quenching, as their microstructure remains unchanged from the melting point through to room temperature.

The only feasible heat treatment is solution annealing that is normally performed on semi-finished and finished products in austenitic stainless steel downstream of the manufacturing process.

Solution annealing is performed at high temperatures (approximately between 1,000°C and 1,100°C) for a holding time that ensure homogenisation of the chemical composition.

The heat treatment also homogenises the microstructure and, above all, dissolves the chromium carbides.

Table 11 shows precise information on the heat treatment temperatures for the most common austenitic stainless steels.

Before the heat treatment, the workpieces must be cleaned to remove all residue from previous processes (oil, grease, etc.); in many cases solution annealing is performed in controlled atmosphere (nitrogen or nitrogen + hydrogen) so that the steel can maintain its typical metal grey shine, avoiding oxidation or carburisation.

To ensure the effectiveness of solution annealing, austenitic stainless steels must be cooled rapidly in water. Cooling must be rapid to avoid the carbide precipitation on the grain boundary for temperatures between 450°C and 900°C[31]. A high pressure flow of nitrogen can also be used for thin components, although cooling in water is recommended[32].

On the other hand a special heat treatment is used on stabilized austenitic stainless steels. For grades EN X6CrNiTi18-10, EN X6CrNiNb18-10 and EN X6CrNiMoTi17-12-2 stabilization must be performed after solution annealing.

During stabilization the steel is mainteined between 850°C and 950°C for times between 1 to 4 hours depending on dimensions of semi-finished product. During heat treatment, titanium and niobium carbides precipitate to prevent the formation of harmful chromium carbides. The cooling phase is in air.

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[31] *Cooling in water does not produce any structural transformation or hardening, as austenitic stainless steels have no critical points. Normally hardness at the end of the process is less than the initial value.*

[32] *Cooling in nitrogen (combined with heat treatment in controlled atmosphere) does not cause surface oxidation, so that surface maintains a pleasant shine. This treatment is also known as bright annealing.*

EN Designation	Solution annealing	Cooling medium	Stabilzation	AISI approximate correspondence
X10CrNi18-8 (1.4310) X8CrNiS18-9 (1.4305) X5CrNi18-10 (1.4301) X2CrNi18-9 (1.4307)	1,010°-1,120°C	water, air	No	AISI 301 AISI 303 AISI 304 AISI 304L
X6CrNiTi18-10 (1.4541)	955°-1,065°C	water, air	850°-950°C	AISI 321
X6CrNiNb18-10 (1.4550)	980°-1,065°C			AISI 347
X8CrNi25-21 (1.4845)		water	No	AISI 310S
X5CrNiMo17-12-2 (1.4401) X2CrNiMo17-12-2 (1.4404) X2CrNiMoN17-13-3 (1.4429)	1,020°-1,120°C	water, air	No	AISI 316 AISI 316L AISI 316LN
X6CrNiMoTi17-12-2 (1.4571)	1,020°-1,120°C	water, air	850°-950°C	316Ti (*)
X1NiCrMoCu25-20-5 (1.4539)	1,050°-1,150°C	water, air	No	904 L (*)
X1CrNiMoCuN20-18-7 (1.4547)	1,140°-1,200°C	water, air	No	254 SMO (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term “type” (for example type 904 L).

Table 11 – Characteristics of heat treatments on the main types of austenitic stainless steels.

8.3 Physical and mechanical properties

Table 12 shows the physical properties of the most common austenitic stainless steels. Their physical properties are very different from those of ferritic and martensitic stainless steels, since they depend on face-centred cubic lattice of austenite.

The linear thermal expansion of austenitic stainless steels, for example, is 50-60% greater than those of ferritic or martensitic stainless steels, as well as the thermal conductivity, which on the contrary is 40-50% lower. These differences must be taken into account during the heating and cooling phases of heat treatment. The dimensional variation of austenitic stainless steel components will be greater than that of carbon steel (as well as martensitic or ferritic stainless steel) but heat exchange will be less[33].

Austenitic stainless steels have nonmagnetic behaviour, which makes them suitable for some military applications; finally, the semi-finished products become slightly ferromagnetic due to cold deformation.

The mechanical properties of austenitic stainless steels are rather limited, due to the high deformability of austenite. In solution annealed condition, these steels provide an ultimate tensile strength (UTS) of 550-650MPa and yield strength (YS) of 220-280MPa; conversely, the austenitic microstructure has high ductility, with percentage elongation after fracture of 40-50% and hardness of 160-200HB.

Table 13 shows the mechanical properties of the main types of austenitic stainless steel.

The only way to increase the tensile strength of austenitic stainless steels is work hardening: by cold deformation (rolling, cold drawing etc.) it is possible to obtain an UTS of 1,500-1,800MPa and YS of 1,300-1,600MPa, greater than those of a work hardened low carbon steel (Figure 38).

The high increase of tensile strength (UTS can triple and YS can increase up to six times compared to fully annealed state!) is due to the great work hardening capacity of austenite and the transformation of austenite into martensite, triggered by mechanical energy transferred to steel during cold deformation.

Low nickel austenitic stainless steels, as in the case of EN X10CrNi18-8 (similar to AISI 301), can be hardened more easily thanks to their unstable austenitic structure, more prone to turn into martensite due to cold deformation.

Steels with high nitrogen and nickel have more stable austenite and therefore they are more difficult to work harden, such as for example EN X8CrNi25-21 (similar to AISI 310S) or EN X2CrNiMoN17-13-3 (similar to AISI 316LN). To this regard see Figure 39.

---

[33] *Austenitic stainless steel cookware has low thermal conductivity which can be improved applying heat diffuser bases (usually in aluminium).*

EN Designation	Density [kg/dm^3]	Specific heat at 20°C [J·kg^{-1}·K^{-1}]	Electrical resistance at 20°C [W·mm^2·m^{-1}]	Thermal conductivity [W·m^{-1}·K^{-1}]	Mean coefficient of thermal expansion [10^{-6}·K^{-1}]		Elastic modulus [GPa]		AISI approximate correspondence
					between 20°C and 100°C	between 20°C and 200°C	to 20°C	to 200°C	
X10CrNi18-8 (1.4310)	7.9	500	0.73	15	16.0	17.0	200	186	AISI 301
X8CrNiS18-9 (1.4305)	7.9	500	0.73	15	16.0	16.5	200	186	AISI 303
X5CrNi18-10 (1.4301)	7.9	500	0.73	15	16.0	16.5	200	186	AISI 304
X2CrNi18-9 (1.4307)	7.9	500	0.73	15	16.0	16.5	200	186	AISI 304L
X6CrNiTi18-10 (1.4541)	7.9	500	0.73	15	16.0	16.5	200	186	AISI 321
X6CrNiNb18-10 (1.4550)	7.9	500	0.73	15	16.0	16.5	200	186	AISI 347
X8CrNi25-21 (1.4845)	7.9	500	0.85	15	---	15.5	---	---	AISI 310S
X5CrNiMo17-12-2 (1.4401)	8.0	500	0.75	15	16.0	16.5	200	186	AISI 316
X2CrNiMo17-12-2 (1.4404)	8.0	500	0.75	15	16.0	16.5	200	186	AISI 316L
X2CrNiMoN17-13-3 (1.4429)	8.0	500	0.75	15	16.0	16.5	200	186	AISI 316LN
X6CrNiMoTi17-12-2 (1.4571)	8.0	500	0.75	15	16.5	17.5	200	186	316Ti (*)
X1NiCrMoCu25-20-5 (1.4539)	8.0	450	1.00	12	15.8	16.1	195	182	904 L (*)
X1CrNiMoCuN20-18-7 (1.4547)	8.0	500	0.85	14	16.5	17.0	195	182	254 SMO (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term "type" (for example type 904 L).

Table 12 – Physical properties of the main types of austenitic stainless steels [from EN 10088].

EN Designation	Heat treatment condition	YS [MPa]	UTS [MPa]	A [%]	Hardness [HB]	AISI approximate correspondence
X10CrNi18-8 (1.4310)	solution annealed	250-300	600-750	40-50	170-220	AISI 301
X5CrNi18-10 (1.4301)	solution annealed	220-270	550-650	45-55	160-210	AISI 304
X8CrNiS18-9 (1.4305)	solution annealed	200-250	520-630	35-45	170-220	AISI 303
X2CrNi18-9 (1.4307)	solution annealed	200-250	520-630	45-55	160-210	AISI 304L
X6CrNiTi18-10 (1.4541) X6CrNiNb18-10 (1.4550)	solution annealed + stabilized	230-280	550-650	40-50	170-220	AISI 321 AISI 347
X8CrNi25-21 (1.4845)	solution annealed	250-300	550-650	40-50	150-200	AISI 310S
X5CrNiMo17-12-2 (1.4401) X2CrNiMo17-12-2 (1.4404)	solution annealed	250-300	550-650	40-50	160-210	AISI 316 AISI 316L
X6CrNiMoTi17-12-2 (1.4571)	solution annealed + stabilized	250-300	550-650	40-50	160-210	316Ti (*)
X2CrNiMoN17-13-3 (1.4429)	solution annealed	290-340	600-700	40-50	190-240	AISI 316LN
X1NiCrMoCu25-20-5 (1.4539)	solution annealed	230-280	550-650	35-45	170-220	904 L (*)
X1CrNiMoCuN20-18-7 (1.4547)	solution annealed	300-350	700-800	35-45	200-250	254 SMO (*)

(*) This designation is not used in the AISI standard but, nevertheless, is commonly used together with term “type” (for example type 904 L).

Table 13 – Mechanical properties of the main types of austenitic stainless steels.

Figure 38 – Effect of cold work on ultimate tensile strength (UTS) of two austenitic stainless steels compared to a low carbon steel [from Atlas Speciality Metals 2003].

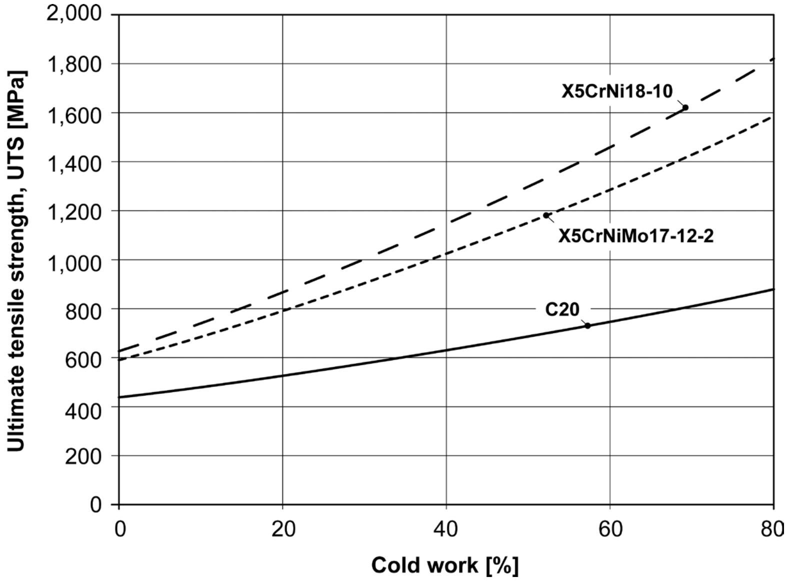
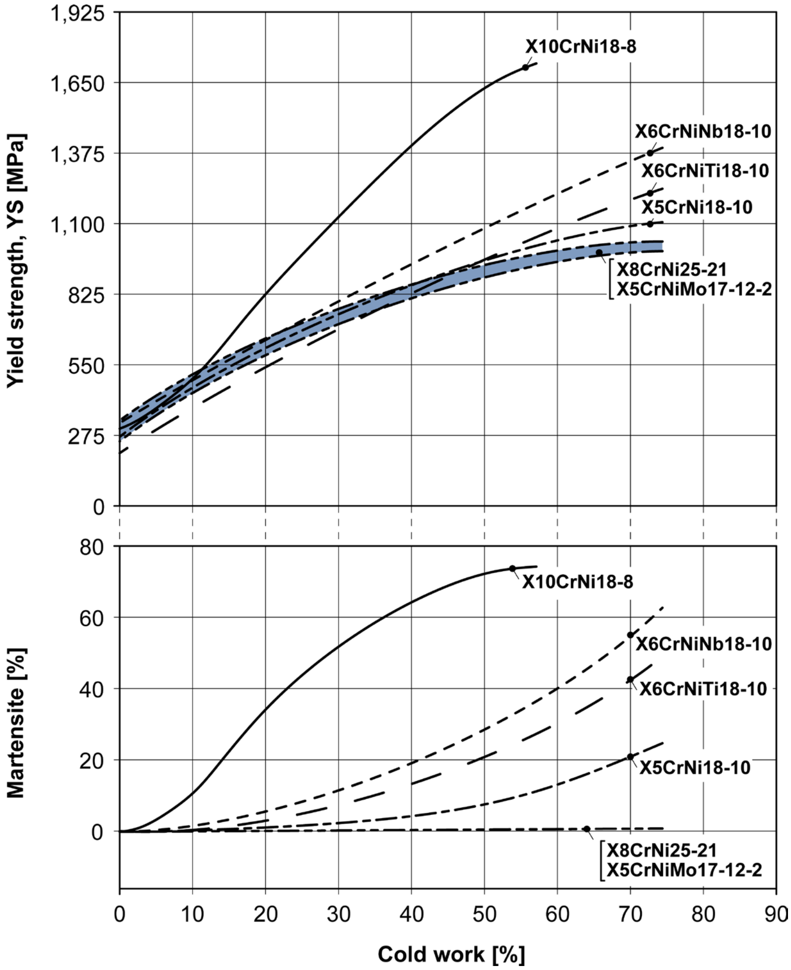


Figure 39 – Effect of cold work on yield strength (YS) and on austenite/ martensite transformation for various austenitic stainless steels [from Llewellyn and Hudd 2003].



Austenitic stainless steels have high fracture toughness and are widely uesd in cryogenic applications. This family of steels never shows the ductile to brittle transition temperature but has high impact strength up to temperatures close to absolute zero (Figure 40).

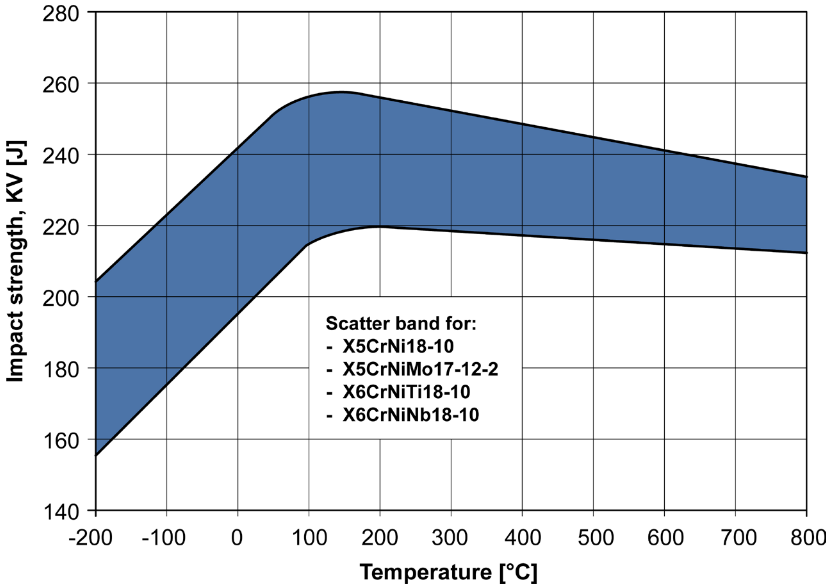


Figure 40 – Trend of impact strength for various austenitic stainless steels as the temperature changes [from Llewellyn and Hudd 2003].

8.4 Types and applications

Stainless steel grade EN X5CrNi18-10 (similar to AISI 304) was the first of austenitic stainless steel with chromium and nickel: it is the single most produced and used material among all the stainless steels.

This steel grade has high corrosion resistance, much greater than martensitic and ferritic stainless steels. Grade EN X5CrNi18-10 does not have high tensile strength and can be easily cold deformed and welded using suitable electrodes.

It is widely used in various applications: boilers, autoclaves, vessels, heat exchangers, pipes, plumbing, elevators and signs. It is also used in building and urban furnishings, in domestic utensils (cookware, cutlery, appliances), in sinks and cabinets, as well as in chemical, petrochemical, nuclear and pharmaceutical industries as well as for production of milk, beer, canned food, paper and pulp, colorants and explosives. Due to its high fracture toughness at low temperatures, it is also widely used in cryogenics sector for storage and transport of liquefied gases.

The stainless steel grades EN X6CrNiTi18-10 (similar to AISI 321) and EN X6CrNiNb18-10 (similar to AISI 347) are the stabilized versions of EN X5CrNi18-10 with titanium and niobium. These materials have a corrosion resistance similar to EN X5CrNi18-10, and for this reason, they are used in the same applications, especially for production of very thick items that are subjected to welding. The stabilized types are not suitable for decorative applications as the presence of titanium or niobium carbides does not allow an optimum surface finish.

EN X6CrNiTi18-10 and EN X6CrNiNb18-10 have greater tensile strength at high temperature than EN X5CrNi18-10: in addition to traditional applications, they are also used for making exhaust systems, boilers, chemical reactors, pressure vessels and tubular sheathed heaters.

EN X2CrNi18-9 (similar to AISI 304L) is the low carbon version of EN X5CrNi18-10: this steel is a good alternative to the stabilized grades and it is also used to solve the problem of chromium carbide precipitation during welding. Tensile strength, both at room and high temperaure, is lower than that of stabilized stainless steels but the surface finish is excellent. EN X2CrNi18-9 is widely used to perform weld overlay cladding, for the construction of large-scale tanks, for very thick wall reactors, as well as in all applications where the surface finish is very important.

The steel EN X10CrNi18-8 (similar to AISI 301) is the most used austenitic stainless steel in work hardened condition: since it has very high tensile strength after cold deformation. It is commonly used for making chains for conveyor belts, springs, mechanical components for the automotive sector and, sometimes, also for manufacturing knives. It is not suitable for drawing or deep drawing operations.

The type EN X8CrNiS18-9 (similar to AISI 303) is the version of EN X5CrNi18-10 with improved machinability: sulphur improves machinability but worsen corrosion resistance. EN X8CrNiS18-9 is widely used for production of screws, nuts, pins and bushings.

Finally, there is grade EN X8CrNi25-20 (similar to AISI 310S), an austenitic stainless steel resistant to high temperature oxidation. It is used for components or parts of plant in contact with oxidizing non sulphurous atmospheres at temperatures up to 1,100°C. In the case of sulphurous or carbon oxidizing atmospheres, the maximum operating temperatures are usually 1,000°C; in reducing atmospheres, the temperature is limited to 750°C. This material is used to make crucibles for salt baths, carburizing boxes, proteciotn tubes for thermocouples, pateting furnaces and piping for cracking and reforming plants.

The first steel of chromium-nickel-molybdenum stainless steel family is grade EN X5CrNiMo17-12-2 (similar to AISI 316) containing 2-2.5% of molybdenum. It is the reference material for manufacturing components or parts of plants operating in marine atmospheres or subject to serious corrosion issues: it is usually used when chromium-nickel stainless steels (such as EN X5CrNi18-10) are not able to meet the operating conditions.

EN X5CrNiMo17-12-2 has good deformability, good weldability and mechanical properties similar to those of EN X5CrNi18-10. This stainless steel has high corrosion resistance in contact with waters contaminated with halides (Cl^-, I^-, F^-), acid condensates and waste water; it has excellent behaviour in contact with organic acids or alkaline solutions, also showing small corrosion resistance in dilute sulphuric, hydrochloric or phosphoric acid solutions.

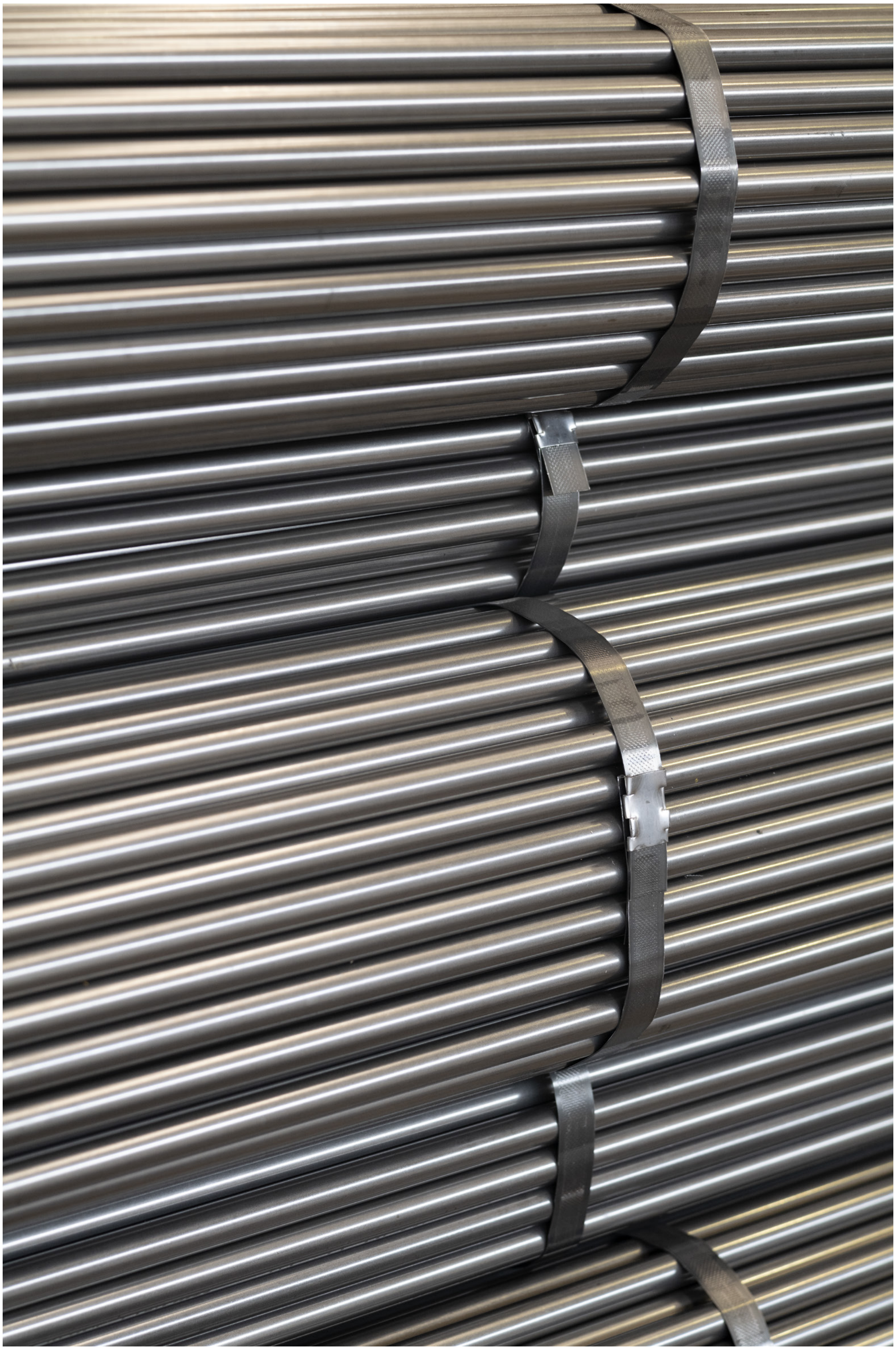
Stainless steel grade EN X5CrNiMo17-12-2 is widely used in chemical and petrochemical plants and in off-shore structures, as well as in food and pharmaceutical industry and dyeing industry. Due to its nonmagnetic behaviour, it is used in some military applications.

The stabilized grade containing titanium, EN X6CrNiMoTi17-12-2 (similar to AISI 316Ti), and the low carbon grade, EN X2CrNiMo17-12-2 (similar to AISI 316L) are ideal in welding operations.

To further increase corrosion resistance, the stainless steels EN X1NiCrMoCu25-20-5 (similar to 904L) and EN X1CrNiMoCuN20-18-7 (similar to 254 SMO) are used.

The type EN X1NiCrMoCu25-20-5, due to its high nickel content, is very resistance to solutions of sulphuric and phosphoric acids (both dilute and concentrate) and is used in storage and transport systems.

The grade EN X1CrNiMoCuN20-18-7 has very high resistance to chlorides due to its high chromium and molybdenum content. It is used in desalination plants, in the chemical sector and in pulp bleaching systems.



9. AUSTENITIC-FERRITIC STAINLESS STEELS

9.1 Metallurgy

Austenitic-ferritic stainless steels (also called duplex) owe their name to a mixed structure of austenite and ferrite at room temperature. This result is due to balanced combination of chromium and nickel in chemical composition: typically, duplex stainless steels have a chromium content between 22% and 25%, nickel content between 4% and 7%, with added molybdenum (3-4%) and nitrogen (0.1-0.25%) in many cases.

Table 14 shows the chemical composition of the most used austenitic-ferritic stainless steels and their designation according to standard EN 10088. The trade name originally developed by Sandvik is also commonly used: it includes two pairs of numbers which indicates the chromium content (the first part of number) and the nickel content (the second part of number). For example 2205 indicates a duplex stainless steel containing 22% chromium and 5% nickel.

The phase diagram of duplex stainless steels (figure 9) shows an initial solidification in α-phase followed by a transformation into $\alpha+\gamma$ phases which remain practically unchanged up to room temperature. The optimal ratio between austenite and ferrite is reached between 1,050°C and 1,150°C (the two phases vary between 40% and 60%), and guarantees high mechanical properties and corrosion resistance, especially against stress corrosion cracking in chloride-rich solutions.

Duplex stainless steels combines the specific properties of corrosion resistance of austenitic and ferritic stainless steels; however, they also share a number of specific problems typical of both, such as precipitation of chromium carbides, formation of harmful phases at around 800°C and 475°C embrittlement.

The formation of carbides/nitrides and σ, χ and *Laves* phases, even for short exposure periods between 550°C and 900°C, can cause considerably reductions of fracture toughness and corrosion resistance. Great attention must be placed on technological processes that cause thermal alteration, as for example welding operations or the cooling phase after forging of medium-large sized components.

Similar changes to fracture toughness and corrosion resistance occur at temperatures around 475°C due to the spinodal decomposition of ferrite. This phenomenon, together with the previous at around 800°C, limits the use of duplex stainless steels only at temperatures up to 300°C.

Figure 41 shows the holding times and temperatures that allow the formation of detrimental phases for some types of duplex stainless steels.

EN Designation	%C	%Si	%Mn	%P	%S	%Cr	%Ni	%Mo	%N	Sandvik trade name
X2CrNiN23-4 (1.4362)	≤ 0.03	≤ 1.00	≤ 2.00	≤ 0.035	≤ 0.015	22.0-24.0	3.50-5.50	0.10-0.60	0.05-0.20	2304
X2CrNiMoN22-5-3 (1.4462)	≤ 0.03	≤ 1.00	≤ 2.00	≤ 0.035	≤ 0.015	21.0-23.0	4.50-6.50	2.50-3.50	0.10-0.22	2205
X2CrNiMoN25-7-4 (1.4410)	≤ 0.03	≤ 1.00	≤ 2.00	≤ 0.035	≤ 0.015	24.0-26.0	6.00-8.00	3.00-4.50	0.24-0.35	2507

Table 14 – Chemical composition of the main types of austenitic-ferritic stainless steels [from EN 10088].

EN Designation	Solution annealing	Cooling medium	Sandvik trade name
X2CrNiN23-4 (1.4362)	950°-1,050°C	water, air	2304
X2CrNiMoN22-5-3 (1.4462)	1,020°-1,100°C	water	2205
X2CrNiMoN25-7-4 (1.4410)	1,040°-1,120°C	water	2507

Table 15 – Characteristics of full annealing heat treatment of the main types of austenitic-ferritic stainless steels.

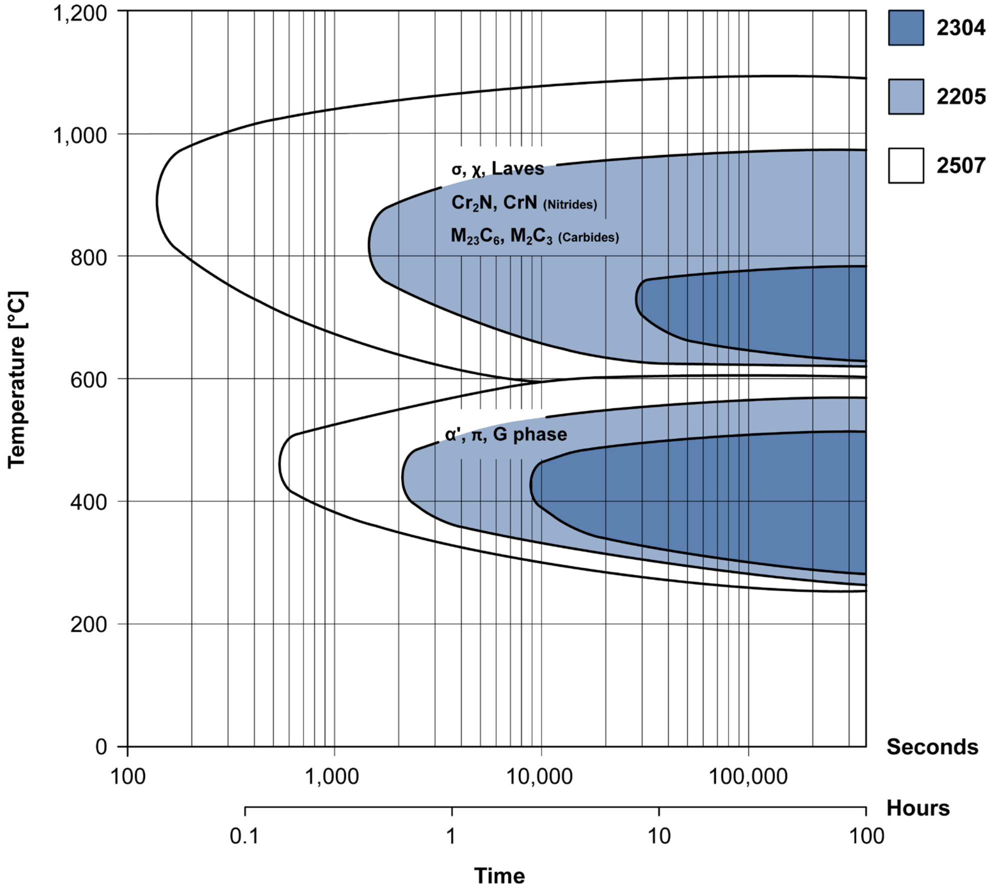


Figure 41 – T.T.T. diagram for three widely used duplex stainless steels. The diagram shows the formation or precipitation time of the main detrimental phases.

9.2 Heat treatments

Semi-finished products made of duplex stainless steels must be solution annealed before being put into operation. The heat treatment is performed by holding the steel between 1,050°-1,150°C; it is then rapidly cooled in water[34] to optimise the austenite-ferrite ratio (close to unity) and to dissolve the detrimental phases possibly formed during manufacturing.

Table 15 shows the heat treatment parameters adopted for the most common types of duplex stainless steel. Solution annealing is often carried out in controlled atmosphere to avoid surface oxidation.

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[34] *Only small sized components can be cooled in air.*

EN Designation	Density [kg/dm^3]	Specific heat at 20°C [J·kg^{-1}·K^{-1}]	Electrical resistance at 20°C [W·mm^2·m^{-1}]	Thermal conductivity [W·m^{-1}·K^{-1}]	Mean coefficient of thermal expansion [10^{-6}·K^{-1}]		Elastic modulus [GPa]		Sandvik trade name
					between 20°C and 100°C	between 20°C and 200°C	at 20°C	at 200°C	
X2CrNiN23-4 (1.4362)	7.8	500	0.80	15	13.0	13.5	200	186	2304
X2CrNiMoN22-5-3 (1.4462)	7.8	500	0.80	15	13.0	13.5	200	186	2205
X2CrNiMoN25-7-4 (1.4410)	7.8	500	0.80	15	13.0	13.5	200	186	2507

Table 16 – Physical properties of the main types of austenitic-ferritic stainless steels [from EN 10088].

EN Designation	Heat treatment condition	YS [MPa]	UTS [MPa]	A [%]	Hardness [HB]	Sandvik trade name
X2CrNiN23-4 (1.4362)	Solution annealed	420-480	650-750	25-35	200-250	2304
X2CrNiMoN22-5-3 (1.4462)	Solution annealed	460-520	700-800	25-35	200-250	2205
X2CrNiMoN25-7-4 (1.4410)	Solution annealed	520-580	750-850	25-35	230-280	2507

Table 17 – Mechanical properties of the main types of austenitic-ferritic stainless steels.

9.3 Physical and mechanical properties

Table 16 shows the physical properties of the most common biphasic stainless steels. The physical properties are similar to those of austenitic stainless steels (specific heat, thermal conductivity, electrical resistance and elastic modulus); the only exception is thermal expansion which is among those of austenitic and ferritic stainless steels. Duplex stainless steels are ferromagnetic, like ferritic stainless steels.

Duplex stainless steels have high yield strength, YS, and ultimate tensile strength, UTS. Table 17 shows the mechanical properties of the main types of austentic-ferritic stainless steels.

The high tensile strength of duplex stainless steels is very important during the design phase because it allows to reduce the component dimensions.

Furthermore, duplex stainless steels have an excellent impact strength: their ductile to brittle transition temperature is around -80°C. Figure 42 shows a comparison between the impact strength of duplex ($\alpha+\gamma$), austenitic (γ) and ferritic (α) stainless steels.

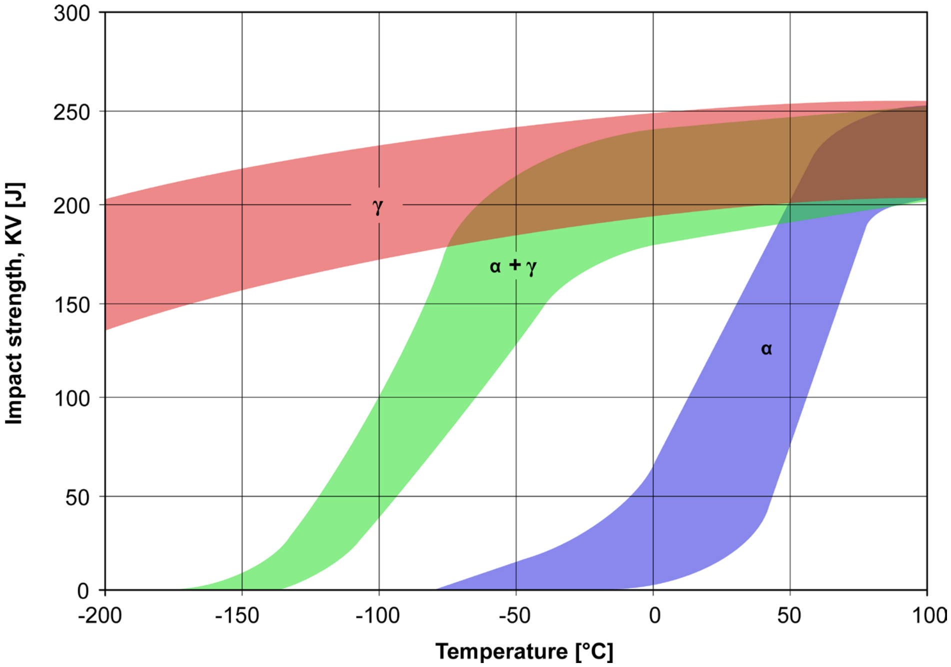

Figure 42 – Comparison between the impact strength of duplex ($\alpha+\gamma$), austenitic (γ) and ferritic (α) stainless steels [from Nicodemi 2002].

9.4 Types and applications

Stainless steel grade EN X2CrNiN23-4 (Sandvik trade name: 2304) was the first duplex stainless steels: it was developed to compete with traditional austenitic stainless steels EN X5CrNi18-10 and EN X5CrNiMo17-12-2 when mechanical strength and corrosion resistance in chloride-rich environments are essential. It is used for production plants of nitric acid and for plants in contact with caustic substances (concentrations < 30%), with organic acids or chloride-rich aqueous solutions.

Stainless steel grade EN X2CrNiMoN22-5-3 (Sandvik trade name: 2205) is definitely the most widespread duplex stainless steels: it has high mechanical strength and excellent corrosion resistance, especially in marine environments where its corrosion resistance is much greater than EN X5CrNiMo17-12-2. It is largely used in petrochemical and chemical field, in environments contaminated by chlorides and in contact with solution contaminated by carbon dioxide CO_2 or hydrogen sulphide H_2S [35]; it is widely used in desalinisation plants and plants in contact with dilute and concentrate solutions of sulphuric, phosphoric, acetic and formic acid.

Finally, stainless steel grade EN X2CrNiMoN25-7-4 (Sandvik trade name: 2507) is the evolution of type 2205 and was created to ensure further increase of tensile strength and corrosion resistance. It has niche use compared to the previous grade, but it is an alternative to titanium alloys and asutenitic stainless steels with high chromium and nickel; it is used in oil wells and in subsea pipelines where high resistance to corrosion and fatigue phenomena, as well as erosive wear, is required.

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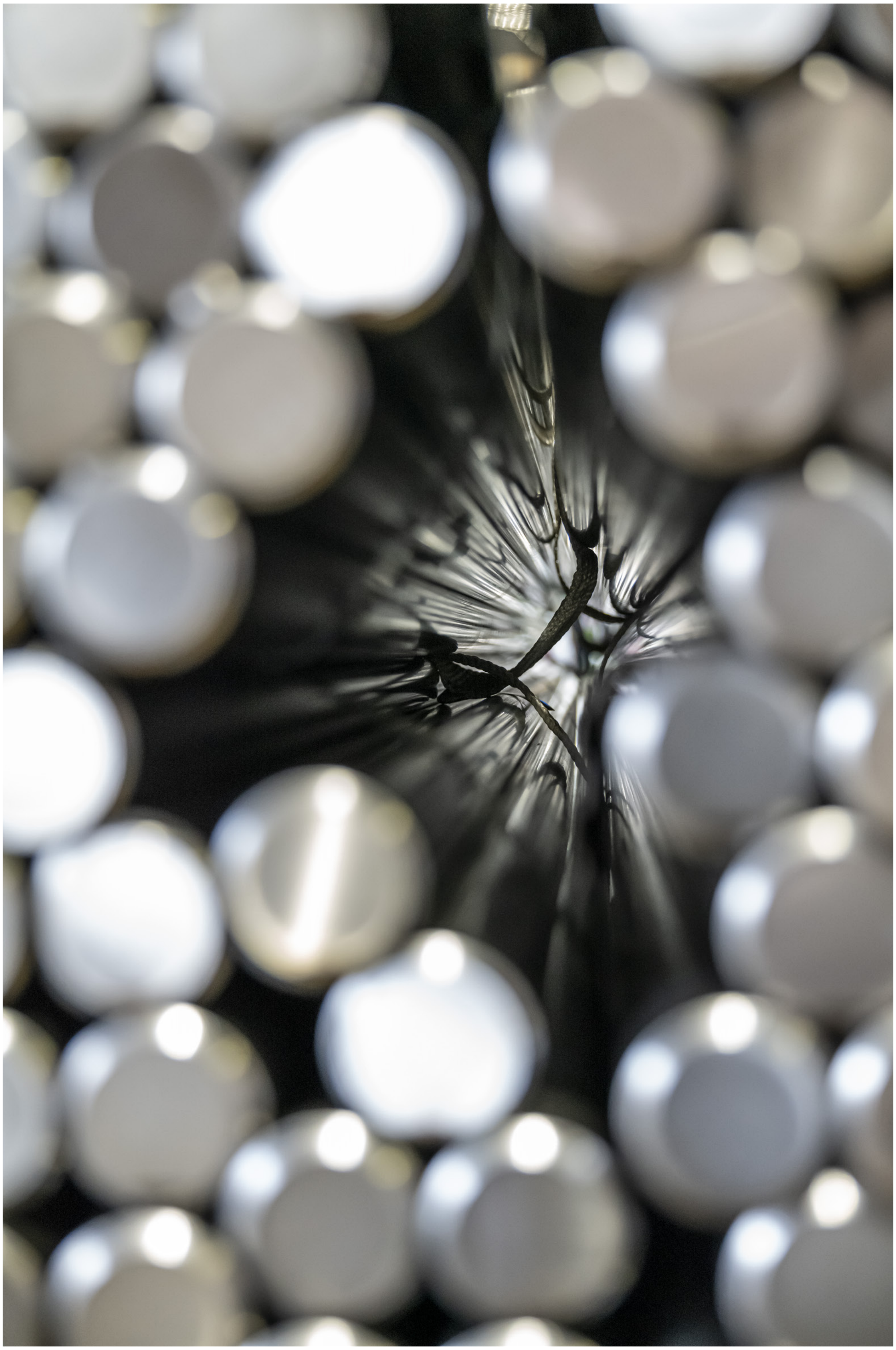
[35] *Hydrogene sulfide is the most dangerous element which exists in oil and gas reservoir.* H_2S *acidifies water which causes pitting corrosion to carbon steel pipelines and decrease the corrosion resistance of stainless steels.*



10. PRECIPITATION HARDENING STAINLESS STEELS

10.1 Metallurgy

Precipitation hardening (or *PH*) stainless steels were created to improve both mechanical properties (especially the fracture toughness) and corrosion resistance of martensitic stainless steels.

They are classified according to their microstructure after the solution annealing heat treatment: they are divided into martensitic, semi-austenitic and austenitic[36]. Hardening is due to an aging heat treatment which causes the precipitation of finely dispersed compounds. For this purpose, alloying elements such as aluminium, copper, titanium and niobium are added in order to form compounds such as type $Ni_3(Al, Ti)$, Ni_3Ti and $NiAl$ or $Fe_2(Mo, Nb)$ or even carbonitrides type $M(C, N)$ with $M = Nb$, Ti, Cr ; copper does not form compounds but creates very small metal particles that strengthen the steel.

Nickel is always added to precipitation hardening stainless steels, in order to improve both corrosion resistance and fracture toughess; molybdenum is also often added in order to improve corrosion resistance. Finally, carbon is usually very low ($C \leq 0.1\%$). Table 18 shows the chemical composition of the main types of precipitation hardening stainless steels.

10.2 Heat treatments, physical and mechanical properties

Semi-finished products are supplied in solution annealed state with fair cold deformability and good machinability: the work piece is then thermally aged to obtain the mechanical properties expected during operation.

Martensitic *PH* stainless steels, such as for example EN X5CrNiCuNb16-4 (also called 17-4 PH), are usually solution annealed at 1,030°-1,060°C and then cooled in air; after solution annealing, steel has low carbon martensitic structure with low hardness and fair cold deformability.

At the end of forming and machining, the semi-finished product is thermally aged at temperatures between 480°C and 630°C for times from 1 to 4 hours[37].

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[36] *Martensitic and austenitic PH stainless steels maintain their microstructure until the end of the hardening heat treatment, whereas semi-austensitic PH undergo a further heat teatment that induces the transformation of the initial microstructure into martensite.*

[37] *Solution annealing is indicated with letter A (Annealing) whereas hardening treatment is indicated by the letter H (Hardening) followed by the aging temperature in degrees Fahrenheit. For example A + H925 indicates that the steel was solution annealed and aged at 495°C (925°F).*

EN Designation	Trade name	%C	%Si	%Mn	%P	%S	%Cr	%Ni	%Mo	Other	AISI approximate correspondence
X5CrNiCuNb16-4 (1.4542)	17-4 PH	≤ 0.07	≤ 0.70	≤ 1.50	≤ 0.040	≤ 0.015	15.0-17.0	3.50-5.00	≤ 0.60	1	AISI 630
X7CrNiAl17-7 (1.4568)	17-7 PH	≤ 0.09	≤ 0.70	≤ 1.00	≤ 0.040	≤ 0.015	16.0-18.0	6.50-7.80	---	2	AISI 631
X5NiCrTiMoVB25-15-2 (1.4606)	A-286	≤ 0.08	≤ 1.00	1.00-2.00	≤ 0.025	≤ 0.015	13.0-16.0	24.00-27.00	1.00-1.50	3	AISI 600

1: %Cu = 3.00-5.00; %Nb = 5 x C-0.45.
2: %Al = 0.70-1.50.
3: %B = 0.001-0.010; %Ti = 1.90-2.30; %V = 0.10-0.50; %Al ≤ 0.35.

Table 18 – Chemical composition of the main types of precipitation hardening stainless steels [from EN 10088].

After the aging heat treatment, the ultimate tensile strength, UTS, can reach values between 850MPa and 1,400MPa; instead, the elongation after fracture varies from 25% to 12% (figure 23). The impact strength at room temperature is below 40J (if UTS = 1,400MPa) and 100J (if UTS = 850MPa).

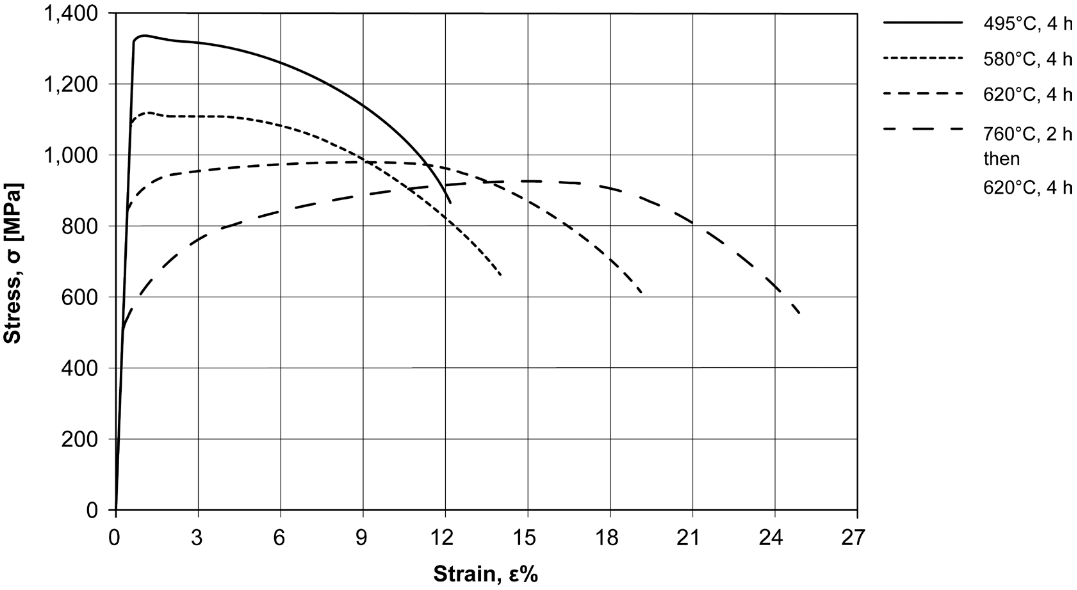

Figure 43 – *PH* stainless steel grade EN X5CrNiCuNb16-4 (also called 17-4 PH) solution annealed at 1,050°C in air, then aged according to various methods: stress-strain curves. [Laboratories of the Department of Mechanical Engineering, Politecnico di Milano - Milano].

Semi-austenitic *PH* stainless steels, such as for example EN X7CrNiAl17-7 (also called 17-7 PH), have a predominantly austenitic structure at room temperature after solution annealing[38]. Cold deformation in thin strips or sheets is therefore very easy. However, due to the special chemical composition, austenite is unstable and can be transformed into martensite by cold deformation and adequate heat treatments[39]. The aging heat treatment will be performed on the martensitic structure similarly to what happens in martensitic *PH* stainless steels.

Figure 44 shows a schematic representation of the principal technological processes performed on semi-austenitic *PH* stainless steel grade EN X7CrNiAl17-7. UTS is between 1,300MPa and 1,700MPa, while YS is between 1,100 and 1,500MPa; hardness is around 42-48HRC.

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[38] Semi-austenetic PH stainless steels has always little amount of ferrite after solution annealing.

[39] The name "semi-austenitic" stainless steels derives from the austenite instability at room temperature.

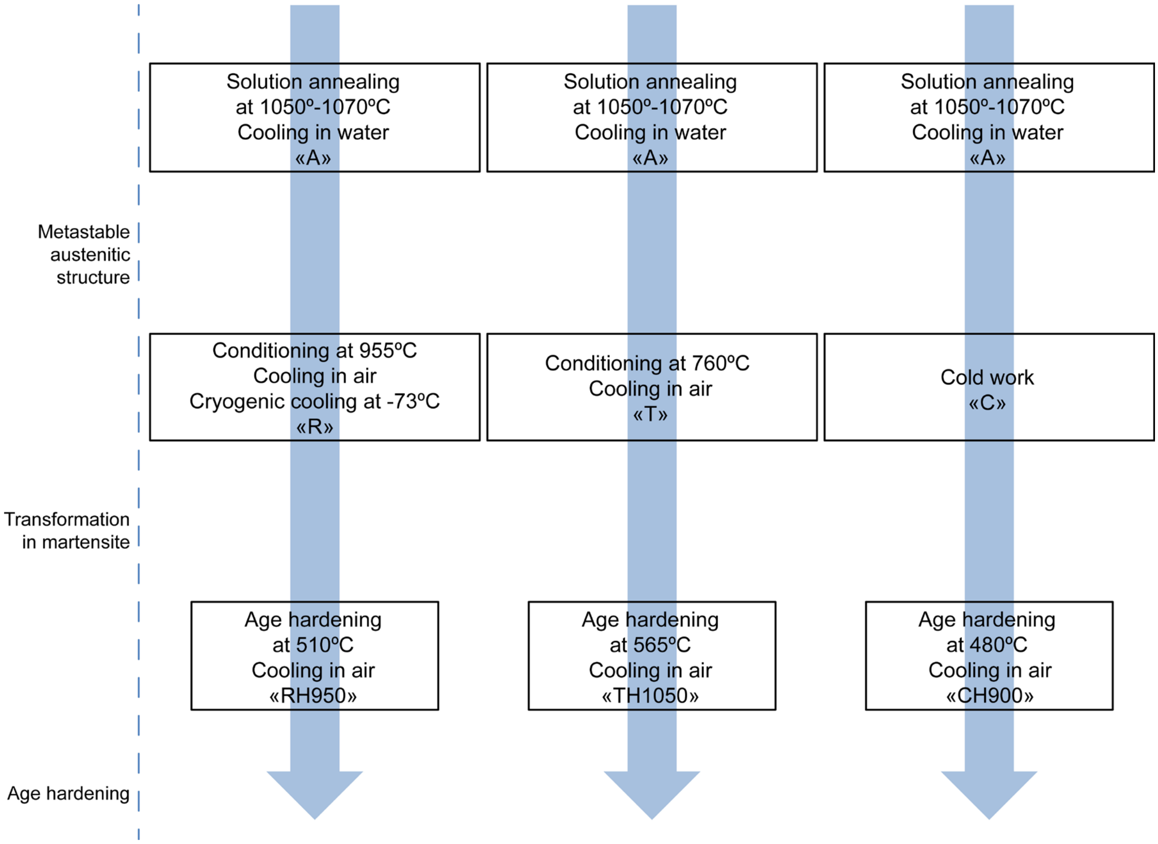

Figure 44 – *PH* stainless steel grade EN X7CrNiAl17-7 (also called 17-7PH): technological processes performed to cause precipitation hardening.

Finally, austenitic *PH* stainless steels, such as EN X5NiCrTiMoVB25-15-2 (also called A-286[40]).
Due to the high level of nickel, the microstructure is completely austenitic and is very stable even after cold deformation. Solution annealing is performed between 970°C and 1,050°C with cooling in water or in oil; aging is performed between 650°C and 750°C.
Figure 45 shows the hardness of EN X5NiCrTiMoVB25-15-2 after solution annealing, cold working and aging at different temperatures, while table 19 shows the physical properties of the main types of precipitation hardening stainless steel.

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[40] *This steel is also called Incoloy A-286: Incoloy is the trade name that American Special Metal Corporation assigns to its own Fe-Ni-Cr superalloys.*

10.3 Types and applications

Precipitation hardening stainless steels are generally available on market in form of round or hexagonal bars; plates and sheets are less widespread.

They are used in aeronautical and aerospace industries, in naval field, in chemical and petrochemical industry and in the energy sector for components characterised by high mechanical strength and excellent corrosion resistance, such as valves, shafts, bearings and turbine and compressor blades.

They are also used in applications for load cells, gears, firearms, utensils, springs and surgical instruments.

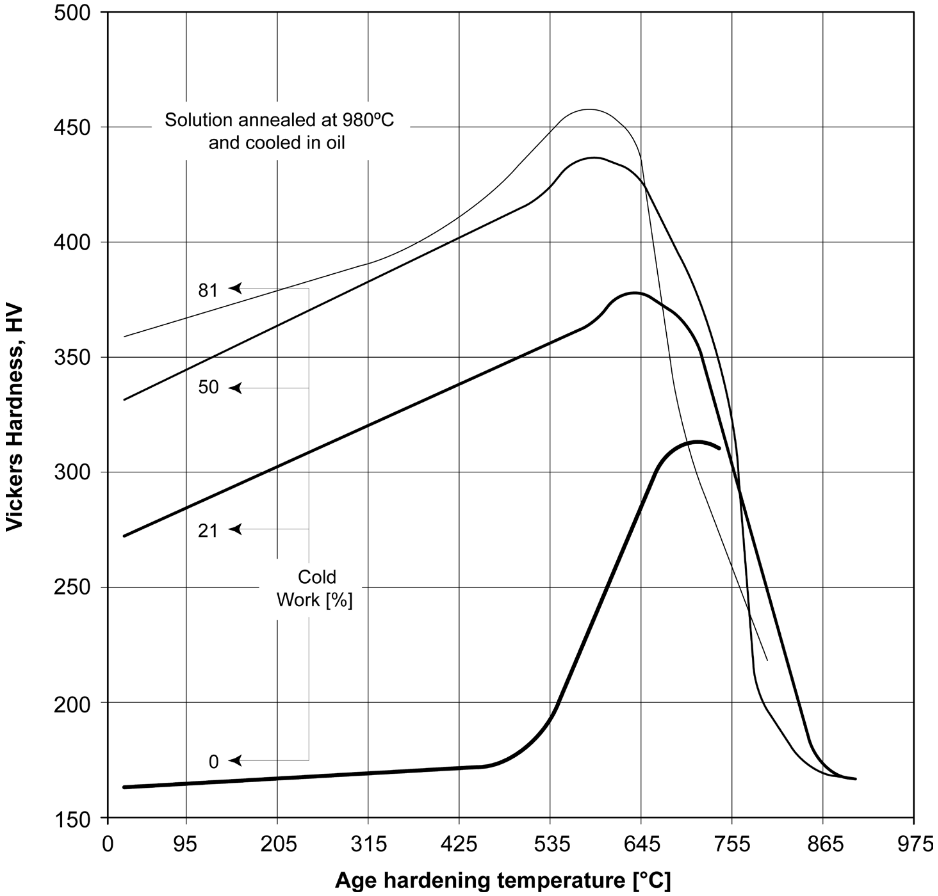
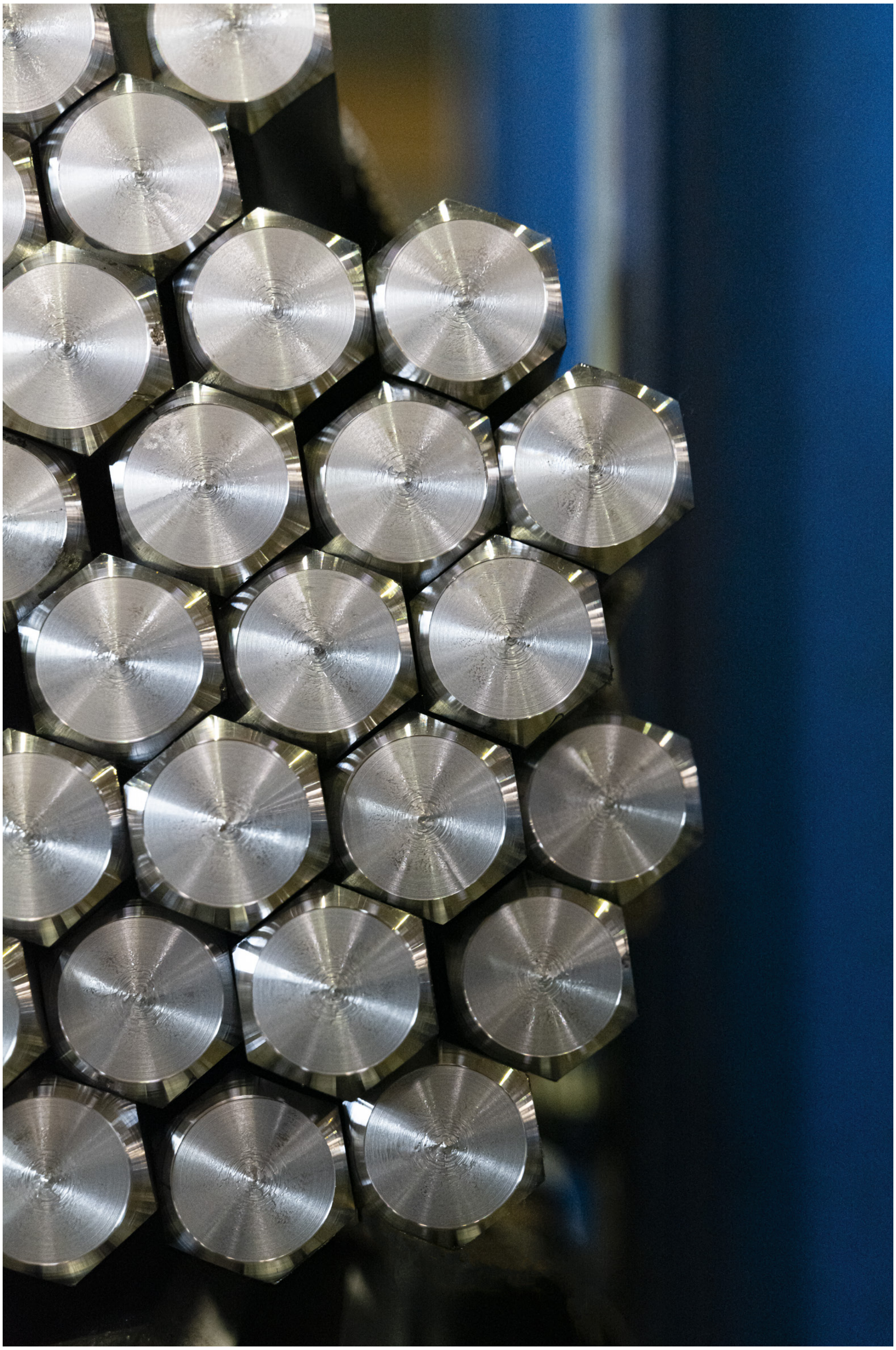


Figure 45 – Hardness of *PH* stainless steel grade EN X5NiCrTiMoVB25-15-2 (also called A-286) after solution annealing, cold rolling and aging at different temperature [from McGuire 2008].

EN Designation	Trade name	Density $[kg/dm^3]$	Specific heat at 20°C $[J\cdot kg^{-1}\cdot K^{-1}]$	Electrical resistance at 20°C $[W\cdot mm^2\cdot m^{-1}]$	Thermal conductivity $[W\cdot m^{-1}\cdot K^{-1}]$	Mean coefficient of thermal expansion $[10^{-6}\cdot K^{-1}]$		Elastic modulus [GPa]		AISI approximate correspondence
						fbetween 20°C and 100°C	between 20°C and 200°C	at 20°C	at 200°C	
X5CrNiCuNb16-4 (1.4542)	17-4 PH	7.8	500	0.71	16	10.9	---	200	185	AISI 630
X7CrNiAl17-7 (1.4568)	17-7 PH	7.8	500	0.80	16	13.0	13.5	200	185	AISI 631
X5NiCrTiMoVB25-15-2 (1.4606)	A-286	7.9	460	0.91	14	16.5	16.8	211	200	AISI 600

Table 19 – Physical characteristics of the main types of precipitation hardening stainless steels [from EN 10088].



11. THE CORROSION OF STAINLESS STEELS

11.1 Introduction[41]

Stainless steels are mainly used because of their excellent corrosion resistance and it is perhaps for this reason that corrosion is their typical form of failure. This problem therefore needs to be investigated further, because only through understanding the mechanisms of damage will it be possible to identify the proper criteria of choice and use of stainless steels.

Corrosion is a form of degradation caused by chemical and electrochemical reactions that take place at the interface between environment and material surface: the result is a gradual decay of stainless steel properties occurring when the alloying elements (*Fe*, *C*, *Cr*, *Ni*, etc.) combine with the harmful elements in the environment, forming corrosion products.

The corrosion of stainless steels can cause several problems. In case of piping and tanks, corrosion can form small punctures that lead to fluid leakage, while in structural elements corrosion can cause loss of the load capacity. Other problems are linked to the formation of corrosion products, which can worsen the surfaces finish or contaminate the contained substances (for example, corrosion can alterate the food organoleptic characteristics)[42]. The corrosion of stainless steels can be divided into two basic forms:

- wet corrosion, when the metal alloy undergoes an oxidation reaction in contact with an electrolyte (usually water); the oxidation reaction is coupled with a reduction reaction of the substances in the environment (usually oxygen): the combination of the two reactions, anodic (oxidation) and cathodic (reduction), involve both chemical species (ions and molecules) and electrons;
- high temperature oxidation, when the metal alloy undergoes an oxidation reaction upon contact with a gaseous atmosphere (usually air); the phenomenon usually occurs at temperatures well above room temperature (> 300°C); the corrosion products are oxides and salts with low melting points.

---

[41] *Paragraphs 11, 12 and 13 were partially taken from the article by Boniardi M., Casaroli A., Tagliabue C., Fenomeni di danneggiamento dei materiali metallici dovuti all'esercizio (Failure Analysis). The article is part of the book by Various Authors, Le Prove non Distruttive, Vol. 1, Associazione Italiana di Metallurgia, Milano 2013.*

[42] *The reader should consider that corrosion is not limited to just iron based alloys (carbon steels, stainless steels, cast iron, etc.) but regards several types of metal materials (alluminium, magnesium, copper, titanium, nickel and their alloys). Corrosion has significant financial impact: the damage due to corrosion is equal to 4-5% of the GDP of the most industrialised countries, both in form of direct damage (restoring the corroded structures) and indirect damage (lack of production).*

Most corrosion problems of stainless steels (~95%) are due to wet corrosion, whereas only few cases (~5%) are due to high temperature oxidation.

11.2 Wet corrosion

Wet corrosion of stainless steels can be described using the electrochemical model: the phenomenon depends on an anodic process, i.e. the oxidation of metal/metal alloy subject to corrosion, and a cathodic process or reduction of a chemical species in the environment (reduction of oxygen or development of hydrogen). The anodic reaction (oxidation) and the cathodic reaction (reduction) must occur at the same time and at the same speed on metal surfaces.

The redox reactions needs an ionic conductor, the so-called electrolyte, to take place. The electrolyte allows current to pass between anodic and cathodic zone: in most of the corrosive processes, the electrolyte is water (freshwater, sea water, condensation of aqueous steam and atmospheric moisture).

To understand the problem further, refer to figure 46, in which an iron plate is placed in contact with a copper plate and the electrolyte is a drop of water.

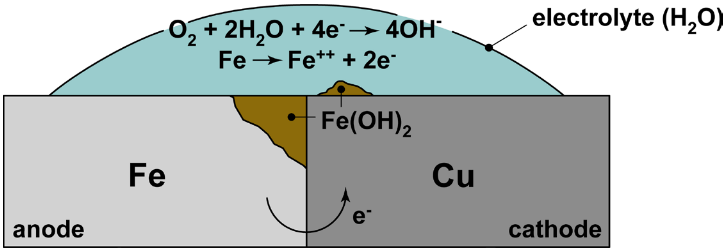


Figure 46 – Schematic representation of the electrochemical phenomenon involved in the corrosion of an ironplate in contact with a copper plate.

As the copper is a nobler metal than iron (copper has a greater electrochemical potential than iron), an electric potential difference is established between copper and iron, i.e. an electromotive force that creates the current circulation. The analogy using the galvanic cell is clear[43]: the iron behaves as an anode and the copper as a cathode and the electric potential difference between the two metals creates the current circulation. The oxidation reaction occurs to the anode (iron) and the reduction reaction of oxygen occurs to the cathode (copper) at the same time.

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[43] *The corrosion phenomenon caused by contact between different metals is called galvanic corrosion for this reason.*

The two reactions are:

$Fe \longrightarrow Fe^{+2} + 2e^{-}$ (anodic reaction of oxidation)

$½\, O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-}$ (cathodic reaction of reduction)

and overall:

$$½\, O_2 + H_2O + Fe \longrightarrow Fe(OH)_2$$

In summary: iron gradually corrodes in Fe^{+2} and passes into solution while oxygen reduction takes place at the copper cathode.

In the previously example, the anodic and cathodic zones are distinct: the corrosive phenomenon occurs due to galvanic couple,[44] that creates an electric potential difference E.

However, corrosion does not occur only in these conditions: corrosion of metal alloys not in contact with different metals is much more common.

To better undestand the problem, let's consider the Evans[45] drop experiment (figure 47).

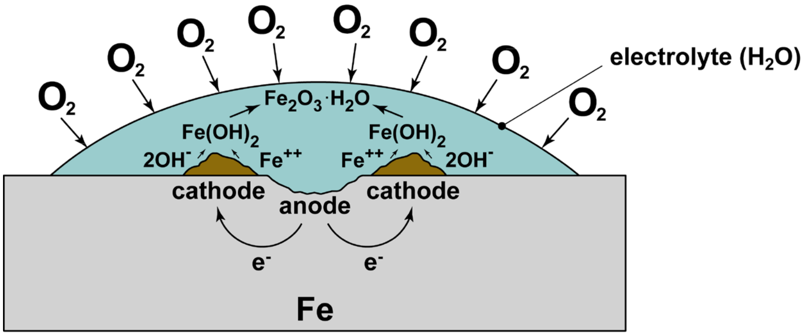

Figure 47 – Schematic representation of the Evans drop experiment which explains wet corrosion of homogeneous metal materials [from Pedeferri 2010].

Evans placed a drop of deaerated water on an iron plate. After a short time, corrosion appeared only near the central area of the drop. The phenomenon can be explained by the oxygen diffusion process in the water drop, also called differential aeration corrosion.

Initially, the chemical composition of the drop is homogeneous and oxygen free: over the time, the outer surface of the water drop absorbs oxygen from the sorrounding air. Therefore, the outer part of the drop becomes richer in oxygen whose concentration becomes uneven.

---

[44] *Galvanic corrosion occurs when stainless steel is placed in contact with a nobler metal (such as graphite), or with a less noble metal (such as aluminium).*

[45] *Ulick Richardson Evans (1889-1980) was one of the founding fathers of modern corrosion science.*

The different O_2 concentration in the water drop will create an anodic zone, i.e. the zone lacking in oxygen in the drop centre, and a cathodic zone, i.e. the zone rich in oxygen on the outside of the drop[46]. Therefore, a local anode-cathode couple can trigger the corrosion process.

The electric potential difference E between anode and cathode is a kind of electromotive force that allows corrosion to happen: it is called *free corrosion potential*.

The anodic and cathodic reactions are the same observed for galvanic corrosion:

$Fe \longrightarrow Fe^{+2} + 2e^-$ (anodic reaction of oxidation)

$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (cathodic reaction of reduction)

and overall:

$$\frac{1}{2} O_2 + H_2O + Fe \longrightarrow Fe(OH)_2$$

with iron oxides/hydroxides formation.

If the iron oxidation occurs in an acid environment (such as when an iron plate is immersed in chloride acid), the cathodic process will be the reduction of hydrogen ion to hydrogen gas, i.e.:

$Fe \longrightarrow Fe^{+2} + 2e^-$ (anodic reaction of oxidation)

$2H^+ + 2e^- \longrightarrow H_2$ (cathodic reaction of reduction)

and overall:

$$2H^+ + Fe \longrightarrow Fe^{+2} + H_2$$

The anodic and cathodic reactions must happen at the same time: the electrons created by oxidation reaction on anode are consumed by reduction reaction on cathode.

The above reactions are very common in all metal materials subject to corrosion: any anodic-cathodic couple provides the electromotive force required to trigger corrosion.

However, the differential aeration corrosion is not the only phenomenon able to trigger corrosion: often the metal materials have already local areas with different electrical potential.

The problem arises for various reasons: heterogeneity of chemical composition, inhomogeneity of the microstructure (inclusions, carbides, etc.), high residual stresses, local defects (micro cavities, blowholes, high roughness etc.). All these areas act as an anode to the surrounding metal which acts as a cathode.

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[46] *Anode and cathode are areas of the metal mass in contact with liquid: the area rich in oxygen is cathode, while the area lacking in oxygen is anode.*

Similar situations also arise due to inhomogenities of the corrosive environment, such as, for example, different concentration of harmfull chemical species, greater or smaller stagnation level or uneven temperatures.

11.3 Potentiodynamic polarisation curves

Corrosion produces always metal ions in solution in the electrolyte and electrons moving in the metal, i.e. a circulation of electrical current, as occurs in a cell.

The higher the quantity of metal ions, which will dissolve in the solution, the greater the number of electrons. Therefore, the corrosion rate V_{corr} of a material in a given environment increases with increasing current density[47] i_c.

corrosion rate, $V_{corr} \propto i_c = i_{anodica} = i_{catodica}$[48]

It should be repeated that corrosion occurs when there is an anodic zone and a cathodic zone[49]: an electrical potential difference E is established between these two zones and causes the circulation of current density i proportional to the corrosion rate V_{corr}. Both electrical potential difference E and current density i are correlated with the electrochemical properties of the anodic process (i.e. "how quickly" metal dissolves) and the cathodic process (i.e. "how quickly" oxygen or hydrogen ions are reduced). If the contribution to the E-i correlation of the anodic reaction is separate from that of the cathodic reaction, it is possible to estimate the current density i, as the electromotive force E[50] changes.

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[47] *The parameter that best describes corrosion is the current density (current per surface unit). Therefore the current intensity produced by corrosion must be divided by the size of the corroded surface.*

[48] *The correlation between current density and corrosion rate can be estimated by simple calculation based on Faraday's Law: for every 1μA/cm^2 there is a corrosion penetration equal to 10-12μm/year. This value is valid for most of iron, copper, aluminium and nickel alloys.*

[49] *The anodic and cathodic areas can be in two different materials (case of figure 46) or be in different areas of the same material (case of figure 47).*

[50] *The correlation between electrical potential E and current density i is similar to what is looked for when you want to establish the electrical resistance of a conductor: the potential V continuously changes and the variations of current I are measured, obtaining the Ohm's Law ($V = R \cdot I$).*

This is exactly what Evans did and which is still possibly to recreate in laboratory: to trace the curves that describe the correlation between the set voltage E and the current density i both in anodic and in cathodic area. Figure 48 shows the experimental curves: they are called potentiodynamic polarisation curves (or Evans diagrams) for the anodic process (metal corrosion) and the cathodic process (oxygen or hydrogen ion reduction). Figure 48a shows a carbon steel in aerated aqueous solution (the cathodic process is oxygen reduction) whereas figure 48b shows a stainless steel in the same enviroment[51].

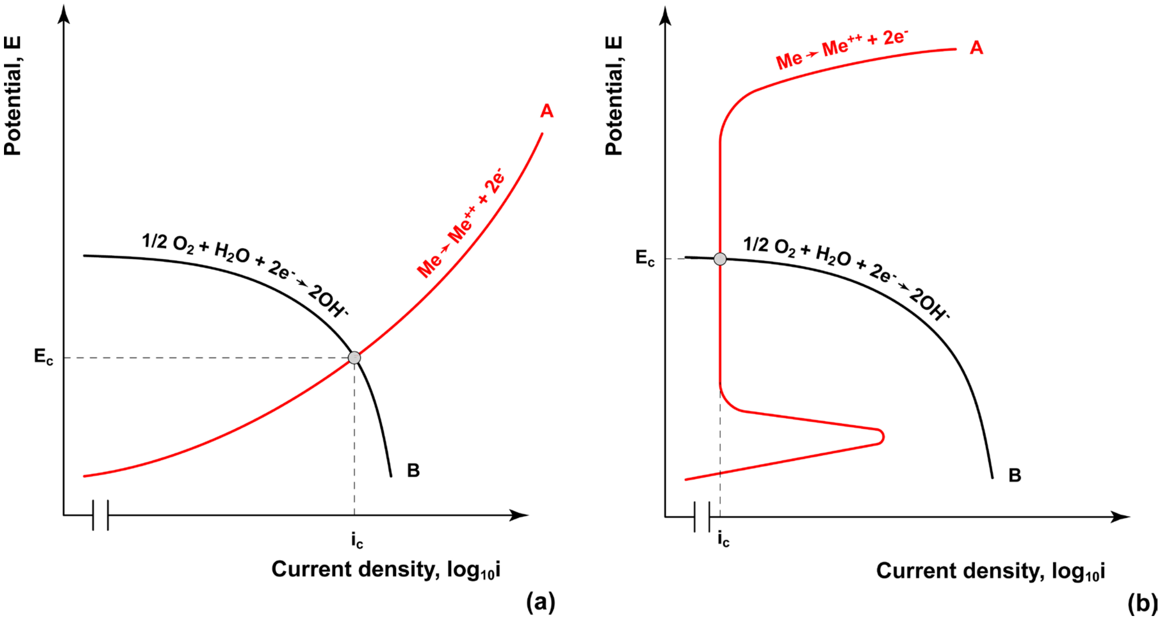

Figure 48 – Schematic representation of potentiodynamic polarisation curves (anodic characteristic *A*: material - cathodic characteristic *B*: environment) in aqueous solution 0.05M of H_2SO_4: (a) material with active behavior, (b) material with active-passive behavior.

The intersection point of the two curves is the operating point of the material-environment system and therefore defines the free corrosion potential E_c and the current density i_c, as well as the material corrosion rate in that environment ($W_{corr} \propto i_c$).

In the case of carbon steels, the anodic curve (curve *A* - figure 48a) increases monotonically: the current density increases with increasing voltage and with it the corrosion rate increases.

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[51] *A small amount of acid must be added to the solution to observe the active-passive behavior of stainless steel: in this case ~4.9g/litre of sulphuric acid were added to obtain an aqueous solution 0.05molar = 0.05M of* H_2SO_4.

Instead stainless steels have a typical active-passive behaviour (curve *A* - figure 48b). The two cathodic curves indicated by letter *B* in figure 48 have the same trend because they represent the same environment for both materials.

The comparison between these two conditions (figure 48a and figure 48b) shows the behaviour of the two materials: the corrosion rate of carbon steel, in that environment, will be greater than that of stainless steel[52], since the current density i_c of case (a) is higher than that of case (b).

11.4 Wet corrosion of stainless steels

We will now describe the anodic curve of stainless steels in more depth, indicating the parameters that characterize the material behavior (figure 49).

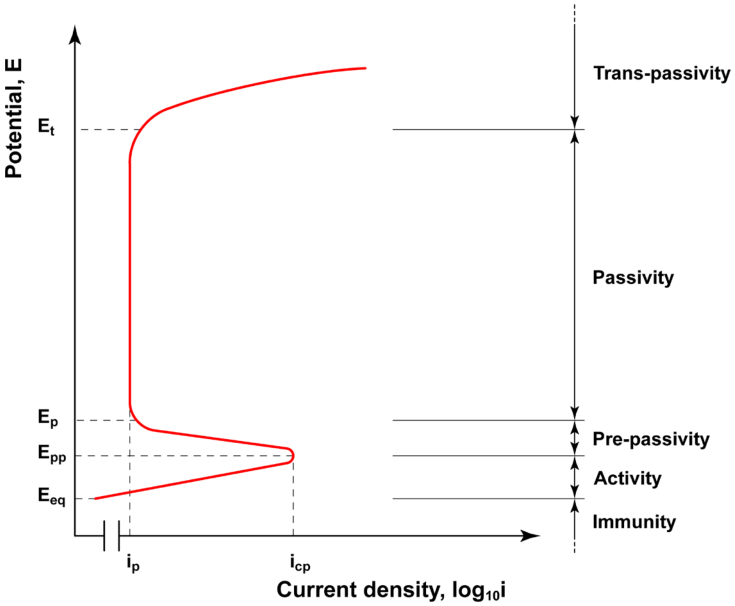

Figure 49 – Schematic representation of the anodic curve of a generic stainless steel.

The stainless steel is immune from corrosion below the equilibrium potential E_{eq} : it is thermodynamically stable and the oxidation reaction cannot take place.

The anodic curve shows an active behaviour (from E_{eq} up to point E_{pp} - i_{cp} , primary passivation potential-critical passivation current density): in this area the stainless steel acts like a carbon steel with increasing corrosion rate with the increase of voltage.

---

[52] *The x-axis shows the current density in logarithmic scale with base 10 (not in linear scale!): a linear variation on the axis leads to a variation of several order of magnitude of current density and, therefore, of corrosion rate.*

Passivation starts from point E_{pp}- i_{cp} with the formation of the passive film of chromium oxide. After passivation the electrochemical characteristic of the stainless steel is radically modified: the increase of set voltage E causes a gradual decrease of the current density i which is stabilized around the i_p value (passivation current density). At i_p the corrosion rate is extremely low and can be considered as practically zero[53]: in this field the chromium oxide/hydroxide film is formed which begins to protect the stainless steel. i_p is constant for a wide potential interval (from E_p, passivation potential, up to E_t, transpassivation potential): beyond this value the stainless steel returns to an active behavior due to the dissolution of the chromium oxide film. When E_t is exceeded, localised forms of corrosion occur where the passive film has been damaged by the environment.

The high corrosion resistance of stainless steels is due to the low i_p values in the passivation field, i.e. in the E_p- E_t interval.

The passive film forms only in oxidizing enviroments such as in air or in aerated aqueous solutions.

However, how does a stainless steel behave when it comes into contact with other environments?

To answer this question, it is useful to consider figure 50 which shows the effect of four different cathodic processes (*B1*, *B2*, *B3* and *B4*) on the anodic behaviour of a generic stainless steel (*A*).

The cathodic polarisation curves *B1*, *B2*, *B3* and *B4* represent four different cathodic processes (i.e. four different environments) characterised by increasing oxidizing power.

Curve *B1* is typical of an acid environment without oxygen (or other oxidizing species): therefore the only possible reaction is hydrogen ions reduction. This situation would occur for example for a stainless steel immersed in 50% sulphuric acid solution. The operating point is X_1 and the stainless steel has an active behavior. Passivation cannot take place and therefore corrosion will be general over the entire surface.

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[53] *The passivation current density i_p of stainless steels is very low (10^{-5} - 10^{-7} A/cm^2), therefore it can be assumed that the corrosion rate is practically zero.*

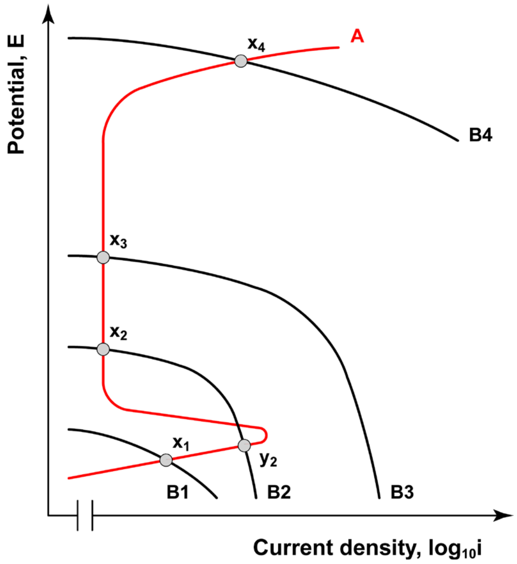

Figure 50 – Cathodic polarisation curve of four environments with increasing oxidizing power (*B1*, *B2*, *B3* and *B4*) and relative “operating points” on the anodic polarisation curve of a generic stainless steel.

Curves *B2* and *B3* represent two cathodic processes characterised by oxygen reduction; the difference is related to the oxygen concentration: lower for *B2* and greater for *B3* . This is what would happen in a stagnant (*B2* curve) or agitated (*B3* curve) aqueous solution.

The two situations described by the cathodic polarisation curve *B2* and *B3* are very different from each other. In the case of *B2* curve, there are two operating points of the anodic-cathodic system: X_2 and Y_2. If stainless steel is immersed in the aqueous solution and is already in passive conditions[54], it will remain in this condition and preserve its typical corrosion resistance (operating point X_2). However, if passive film is mechanically damaged stainless steel works in an active way (point Y_2), thus giving rise to localised corrosive phenomena. If the agitation level or the oxygen concentration in aqueous solution are increased, the cathodic polarisation curve will move towards high potentials (*B3* curve), giving rise to a single operating point X_3: in this case the passive film will be stable and will reform if mechanically damaged.

Finally, the condition defined by the cathodic polarisation curve *B4* which represents the cathodic behaviour of a strongly oxidizing electrolyte, thus an aqueous solution with chromate.

In this environment the passive film will be unstable: in some points localised corrosion attacks would occur due to damage of the chromium oxide layer.

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[54] *Usually, stainless steels are put in operation after pickling and passivation (using nitric acid solution): these chemical treatments aim to form a stable passive film on the stainless steel surface.*

11.5 Corrosion resistance of stainless steels

The previous paragraphs should have clarified that corrosion resistance of stainless steel depends not only on their chemical composition but also on the environment in which they are used[55].

Therefore, we will now examine the anodic behaviour of the stainless steel with the variation of their chemical composition and the corrosive solutions they are in contact with.

First of all, in order to improve the corrosion resistance of a stainless steel (with the same environment) it is important to:

- increase the transpassivation potential, E_t , in order to extend the passivation interval E_p - E_t ;
- decrease the critical passivation current density, i_{cp} , in order to reduce the current density level which allows steel passivation;
- reduce the passivation current density, i_p , in order to decrease the corrosion rate under passive condition.

In this regard, figure 51clarifies because stainless steel is the best choice to prevent corrosion in aggressive environment, while figure 52 highlights that iron-chromium-nickel alloys show relevant passivation phenomenon only for high level of chromium.

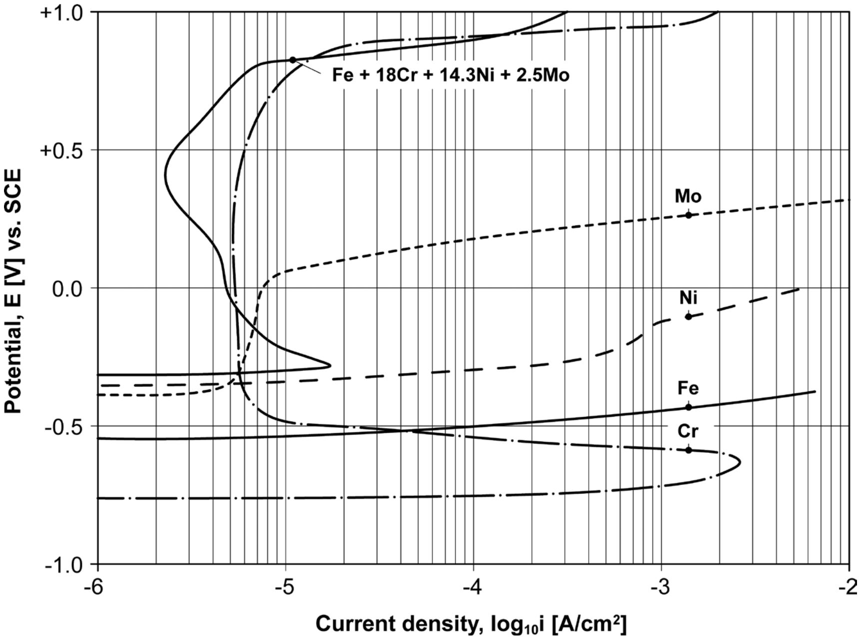

Figure 51 – Potentiodynamic polarisation curves for chromium, iron, nickel, molybdenum and stainless steel with 18% chromium, 14.3% nickel and 2.5% molybdenum; aqueous solution 0.1M of *HCl* + 0.4M of *NaCl* at 25°C [from Olefjord et al. 1985].

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[55] *This statement is true for all metal materials that suffer corrosion phenomena. Corrosion resistance always depends on surrounding environments as well: to understand corrosion phenomena it is never possible to separate material from environment.*

A chromium content of around 11.7%, forms a wide passivation interval (E_p - E_t), with passivation current density of around 10μA/cm^2 (corrosion penetration: 100-120μm/year); the passive film becomes more stable with increasing of chromium level, as can be observed from the decrease of passivation current density, equal to approx. 0.1μA/cm^2 (1-1.2μm/year), and the further enlargement of the interval E_p - E_t.

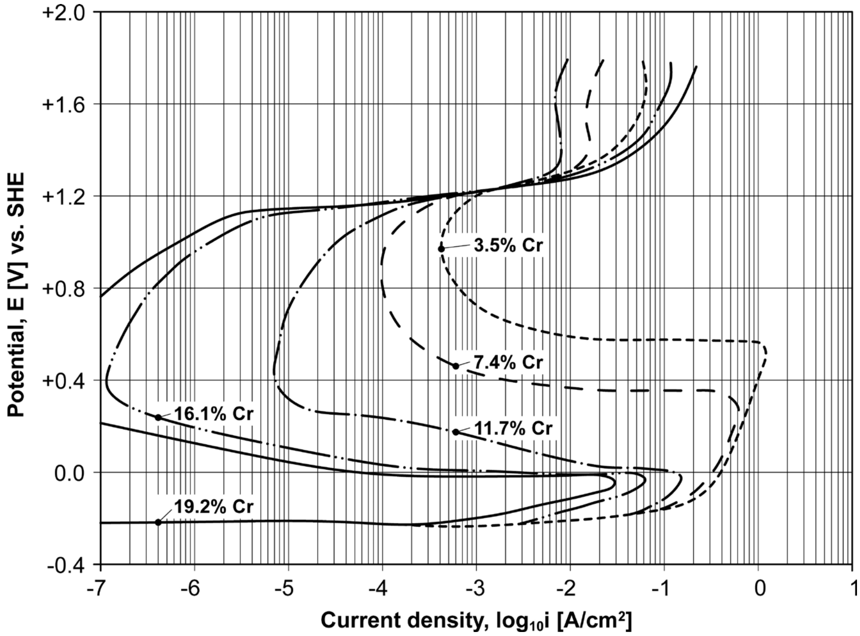

Figure 52 – Effect of chromium on the anodic polarisation curves of iron-chromium alloys with 8.3-9.6% nickel; 1M aqueous solution of H_2SO_4 at 90°C [from Osozawa and Engell 1966].

The anodic polarisation curve also explains how alloying elements affect the corrosion resistance of stainless steels (figure 53).

Nickel and molybdenum slightly improve the ability of stainless steel to passivate (decrease of the critical passivation current density, i_{cp}) and extend the passivation interval E_p - E_t (increase of transpassivation potential, E_t).

By contrast, the reduction of the passivation current density, i_p, is only slightly affected by alloying elements. The corrosion rate of stainless steel in passive condition is very low and therefore is not significantly affected by chemical composition (figure 54).

In a similar way, the effect of similar environments on the same material can be evalueted. In this regard, figure 55 shows for example the anodic polarisation curve of stainless steel grade EN X5CrNi18-10 in aqueous solution with different concentrations of chlorides. Similar effects are produced by the increase in temperature and/or the decrease in *pH* (figure 56).

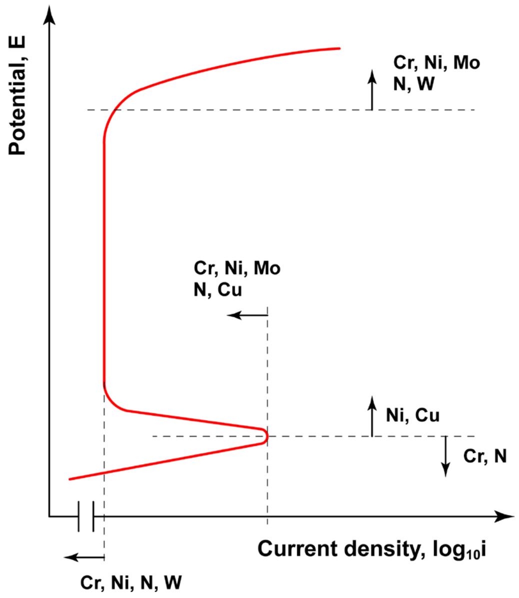

Figure 53 – Effect of various alloying elements on an anodic polarisation curve of a generic stainless steel [from Sedriks 1986].

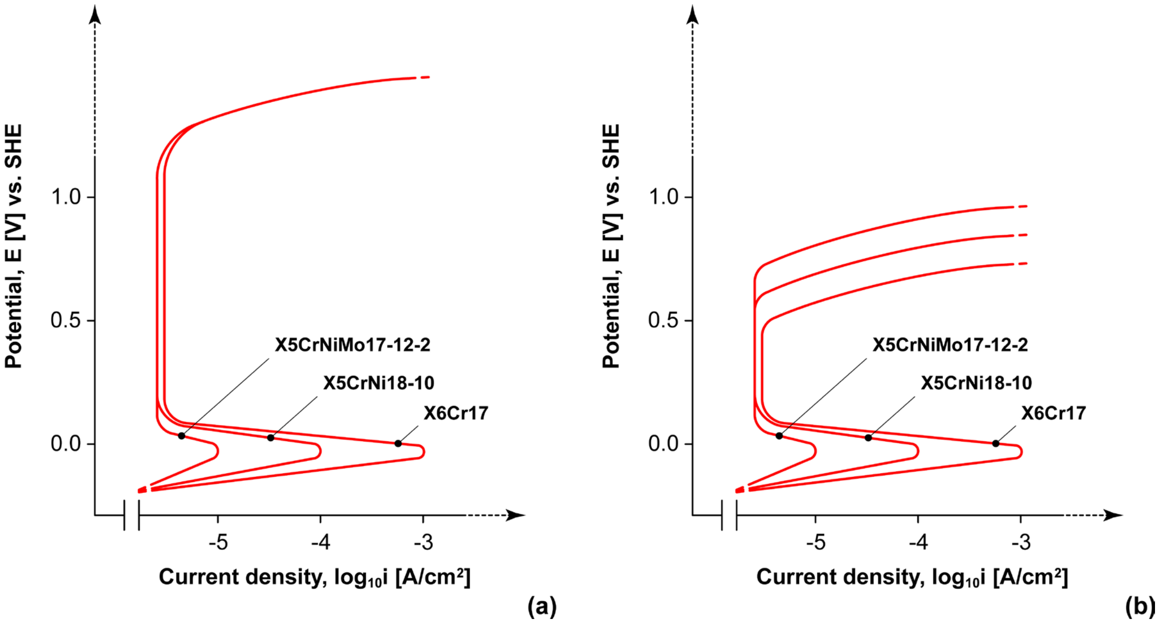

Figure 54 – Schematic representation of potentiodynamic polarisation curves for three stainless steels in acid solutions contamintaed with chlorides: (a) 0.05M solution of sulphuric acid, (b) 0.05M solution of sulphuric acid and 0.1M solution of sodium chloride [from Talbot and Talbot 1998].

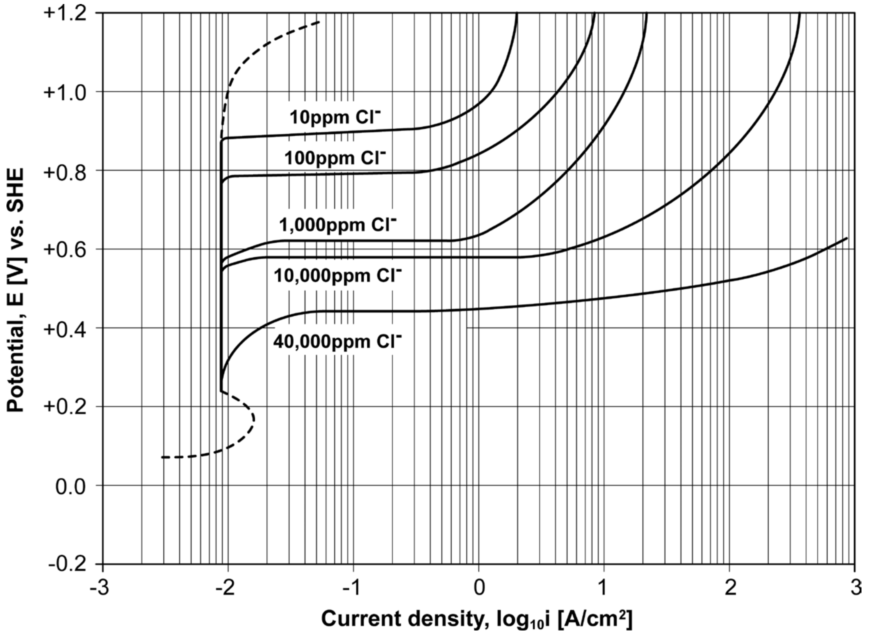

Figure 55 – Potentiodynamic polarisation curves for stainless steel grade EN X5CrNi18-10 in water at 25°C contaminated with different levels of chlorides, Cl^- [from Stansbury and Buchanan 2000].

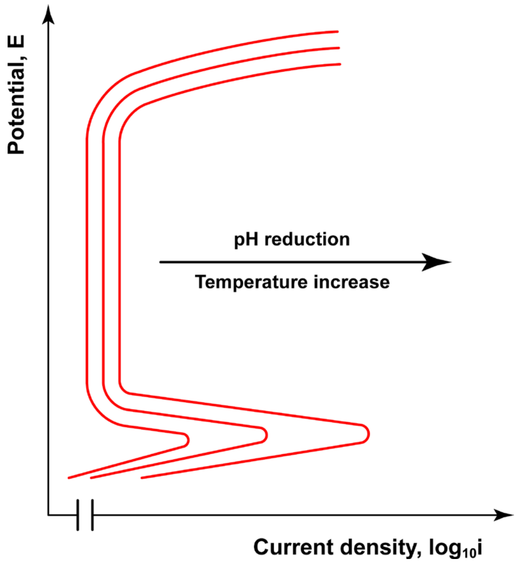

Figure 56 – Effect of temperature and *pH* on the anodic polarisation curve of a generic stainless steel.

12. CORROSION MORPHOLOGY OF STAINLESS STEELS

12.1 Introduction[56]

Corrosion can also be classified according to the morphology of the degradation phenomenon as it appears upon visual observation or using low magnification microscopy.

An initial distinction can be made between "general or uniform corrosion" and "localised corrosion":

- in the first case the whole material surface is subject to corrosion (general), with constant penetration along the whole component section (uniform);
- in the second case corrosion is limited on some areas of the surfaces (localised), with pits, craters or cracks.

Many types of corrosion belong to this second category: including the most significant for stainless steels, i.e. galvanic corrosion, pitting corrosion, crevice corrosion, intergranular corrosion and stress corrosion cracking.

12.2 Uniform or general corrosion

General corrosion affects the whole surface of the metal material exposed to the aggressive environment, with limited local variations of the damage penetration. A typical example is represented by stainless steels in contact with acid solutions (aqueous solutions of hydrochloric acid, sulphuric acid, phosphoric acid, oxalic acid, formic acid, citric acid, etc.).

From an electrochemical point of view, the general corrosion of stainless steels takes place when the system "functions" in the active zone of the anodic polarisation curve, i.e. in the interval between the equilibrium potential, E_q, and the primary passivation potential, E_{pp} (figure 50 - case B1).

The corrosion rate V_{corr} can be expressed in terms of mass loss (Δm) per surface unit (A) over time (t):

$$V_{corr} = \Delta m/A \cdot t$$

usually measured in mg per day per dm^2 or 1mdd.

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[56] *Paragraphs 11, 12 and 13 were partially taken from the article by Boniardi M., Casaroli A., Tagliabue C., Fenomeni di danneggiamento dei materiali metallici dovuti all'esercizio (Failure Analysis). The article is part of the book by Various Authors, Le Prove non Distruttive, Vol. 1, Associazione Italiana di Metallurgia, Milano 2013.*

In industrial applications it is often more interesting to talk about penetration or thinning rate V_{thin} of the corrosive phenomenon. Corrosion rate can be converted to thinning rate by adding material density (ρ), according to the formula:

$$V_{ass} = V_{corr}/\rho = \Delta m/\rho \cdot A \cdot t$$

The unit of measurement of V_{thin} is μm/year; for stainless steel and for other metals and metal alloys (carbon steel, copper, brass, zinc etc.) the equivalence between thinning and corrosion rate is around:

$$1 \text{ mdd} \approx 5\mu\text{m/year}$$

There are several methods to preserve the componet from general corrosion. A commonly used method is to predict the so-called "corrosion allowance", i.e. the thickness that the designer has allowed for degradation during the component life.

Usually, iso-corrosion diagrams are used to ensure the correct choice of stainless steel. These graphs indicate the condition with constant corrosion rate (0.1mm/year) for various stainless steels in different environments. Figures 57 and 58 show some typical examples.

12.3 Galvanic corrosion

An early form of localised corrosion is galvanic corrosion[57]. It occurs when a metal (or a metal alloy) is in electrical contact with another metal/metal alloy with greater or lower nobility[58]: a significant potential difference causes a redox reaction with consequent corrosion phenomena, even in a mildly aggressive environment. Figure 46 shows a very similar mechanism.

Every metal or metal alloy has its own potential that depends on its nature, its chemical composition and on the surrounding environment (temperature, *pH* , agitation rate, level of harmful species, etc.).

A significant movement of electrons is created between the anode (less noble metal) and the cathode (nobler metal) only if the difference between the potentials exceeds a certain threshold. The intensity of the electron movement (actually an electric current) will be greater as the potential difference increases: as a consequence, the corrosion rate will also be higher as the distance between the two materials on the standard electrode potential increases.

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[57] *This form of corrosion is also called bimetallic corrosion.*

[58] *The standard electrode potential is the scale of electrode potential measured with regards to the standard hydrogen electrode (E_0= 0.00V) at 298K and 100kPa of pressure, when all the chemical species involved in the electrochemical process have unitary activities.*

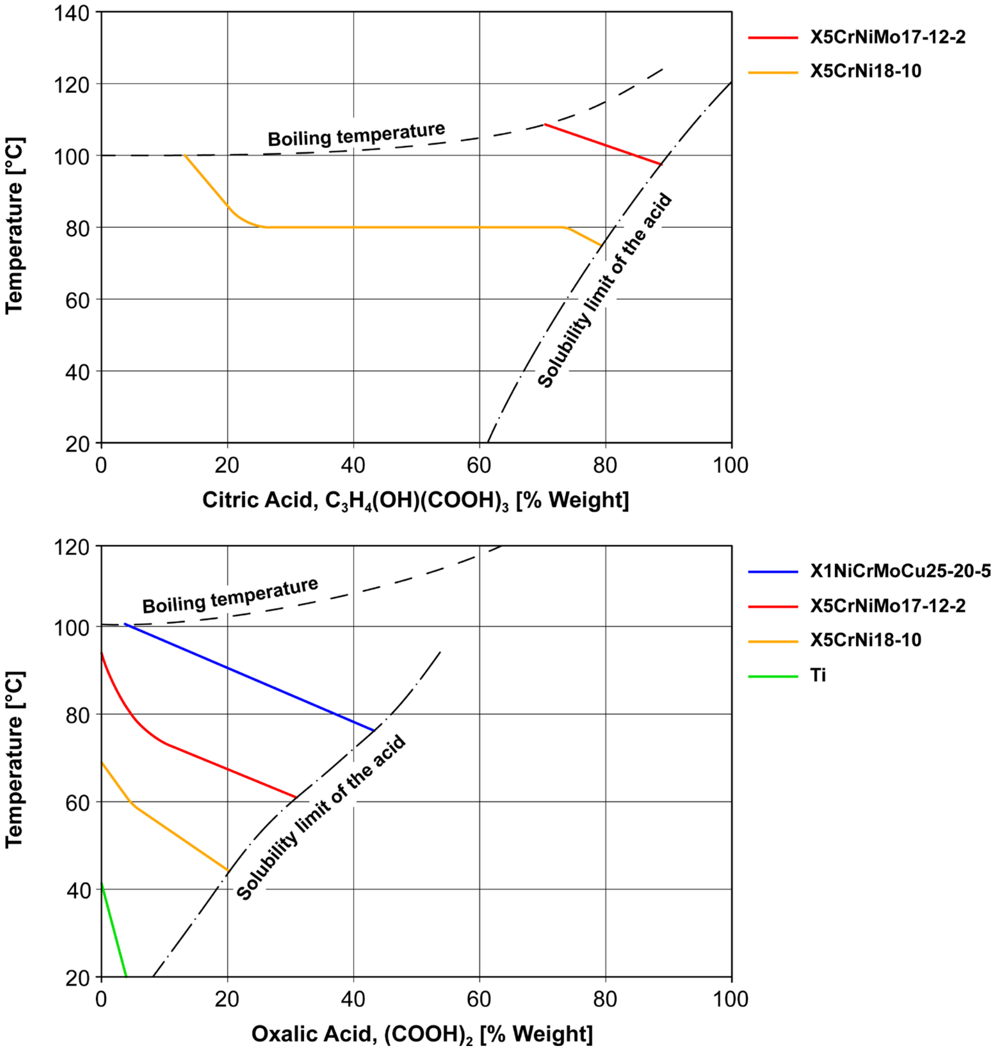

Figure 57 – Iso-corrosion diagram (0.1mm/year) for some stainless steels in citric acid and oxalic acid; the dashed curve indicates the boiling temperature [from Outokumpu 2009].

Another relevant parameter that governs galvanic corrosion is the relationship between areas of the two materials in contact: the rate of degradation increases with the increase of the ratio between the areas of the cathodic zone (nobler) and the anodic zone (less noble) exposed to the environment.

In order to assess whether galvanic corrosion can cause problems practically, it is better not to refer to the standard electrode potential: as a matter of fact, there is a great variability in the behaviour of the same material between one corrosive environment and another. Therefore the galvanic series in saltwater scale of nobility is used (figure 59), which is a scale of potentials measured under conditions close to actual operation.

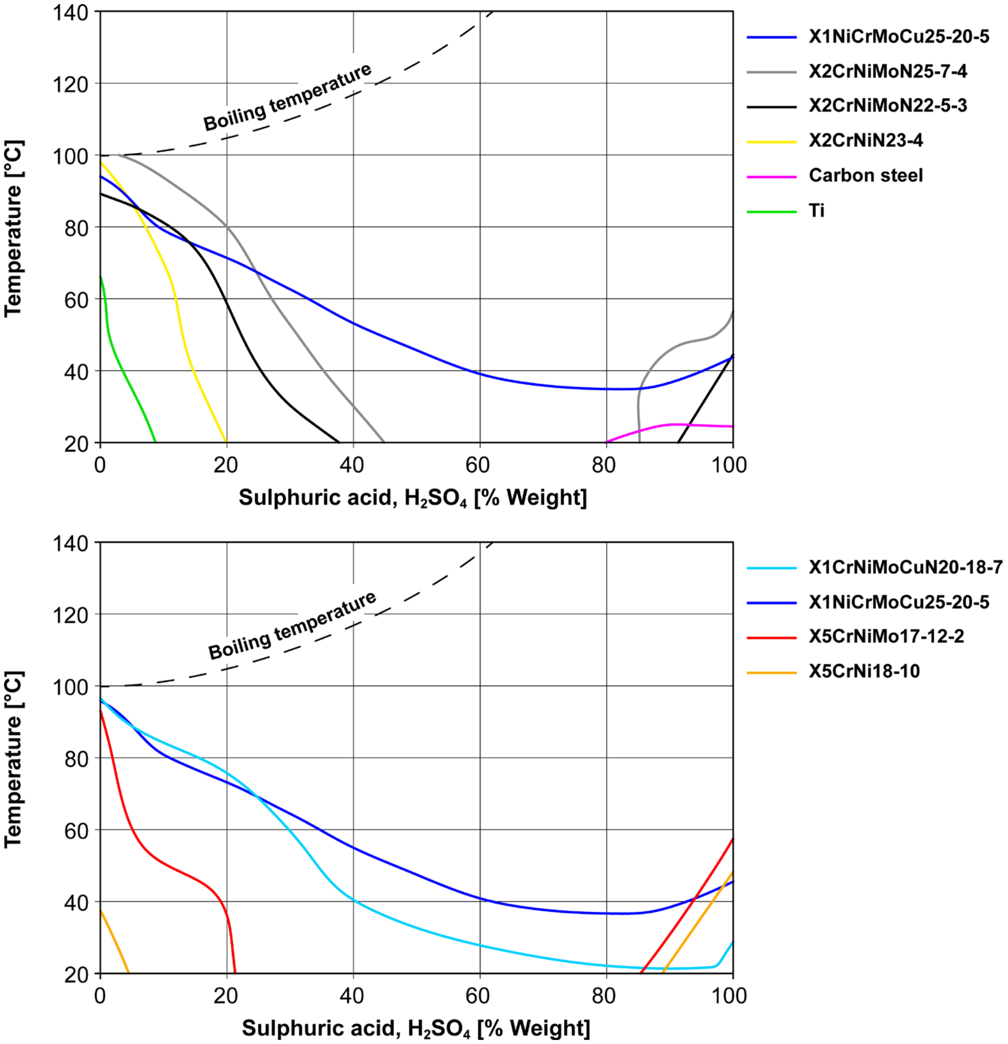

Figure 58 – Iso-corrosion diagrams (0.1mm/year) for some stainless steels in sulphuric acid; the dashed curve indicates the boiling temperature [from Outokumpu 2009].

A typical example of galvanic corrosion occurs on carbon steel sheets (also galvanised) or on aluminium alloy sheets in contact with stainless steel fasteners, placed in marine environments, in aerate aqueous solutions or in mildly aggressive environments (figure 60).

The opposite situation would be much more serious, i.e. stainless steel sheets fastened with carbon steel or galvanised steel rivets; in this case, the relationship between areas is also very negative, because the stainless steel surface is much higher than carbon steel one.

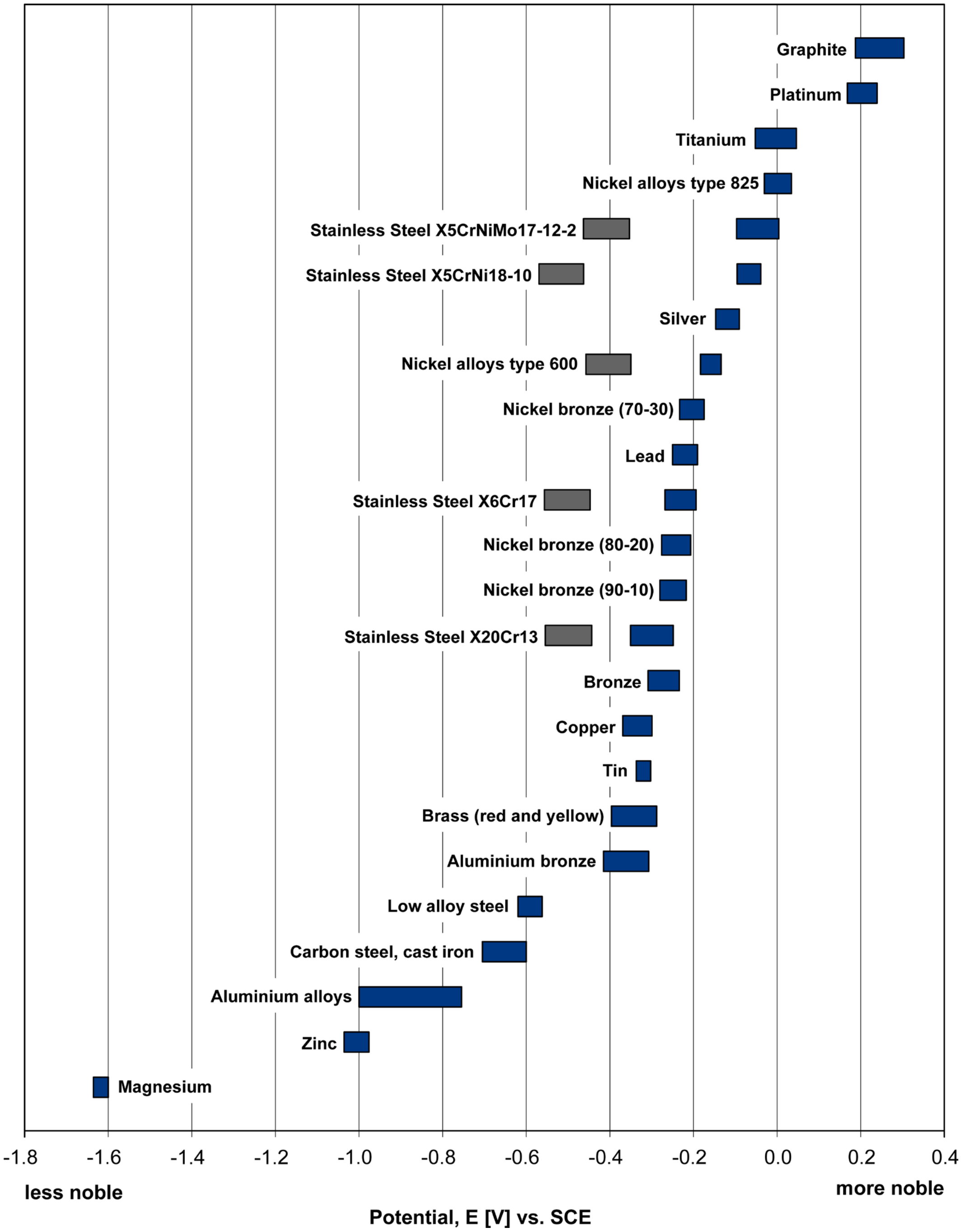

Figure 59 – Galvanic series in seawater [from ASM-H.13 1992].

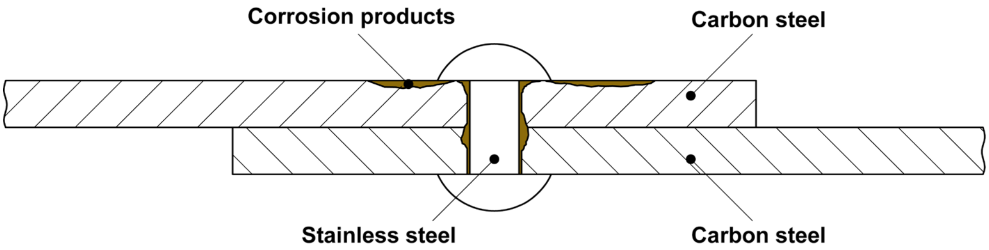

Figure 60 – Galvanic corrosion of carbon steel sheets with stainless steel fasteners.

The most correct solution to eliminate galvanic corrosion is to avoid contact between metals with different nobility or, if impossible, providing for electrical insulation of the components (figure 61).

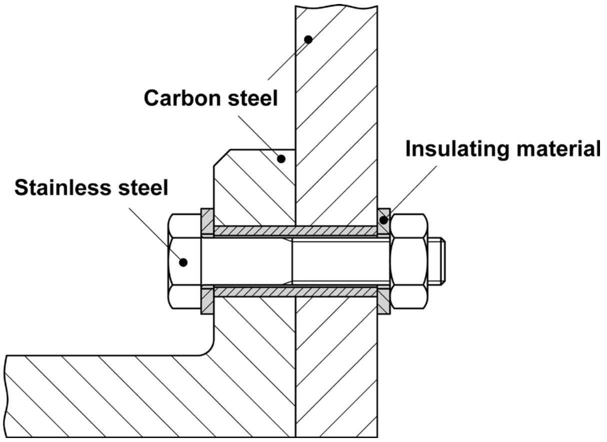

Figure 61 – Electric insulation between two plates and the relative connection bolt.

A particular type of galvanic corrosion is corrosion by superficial contamination.
This type of degradation occurs when foreign particles of ferrous or non ferrous metals are deposited on the stainless steel surface. These particles are often generated during grinding operation of carbon steel. The particles deposited on the surface can create conditions for localised corrosion, even in not very aggressive environments. Marks appear on the surface (rust-coloured in case of ferrous contamination, whitish in case of contamination from aluminium or zinc) as a consequence of the rapid oxidation of the contaminant (carbon steel, aluminium or zinc) and not, as wrongly believed, of stainless steel. In the most extreme case, particles can also damage stainless steel, as it can hinder the passivation phenomenon, as well as form a preferential trigger zone for other types of corrosion.

To work around the problem, greater attention has to be made during all the machining/cutting/handling operations of stainless steel semi-finished or finished products. The working tools and packaging methods (winders, unwinders, cutting systems, shears, benders, chains, ropes, etc.) must be appropriate for contact with only stainless steel; tools used in the machining of other materials must be strictly avoided.

If surface contamination is suspected, the foreign particles must be removed using pickling and passivation chemical treatments.

12.4 Pitting corrosion

Pitting is a phenomenon of localised corrosion of stainless steel that produces dangerous holes in the components during operation.

Pitting causes multiple small pits on the component surface. Holes are very deep but have small surface size, between 0.1mm and 2mm; therefore the corrosion products are very limited.

The greatest problem related to this form of corrosion is not the loss of mass, but rather the damage caused by the penetration of pits through the component section. For example, consider the case of a stainless steel tank affected by pitting that could lead to the creation of holes, the spilling of the process fluid and the overall system disruption.

Figure 62 shows some typical morphologies of pitting corrosion, as classified by the American standard ASTM G46.

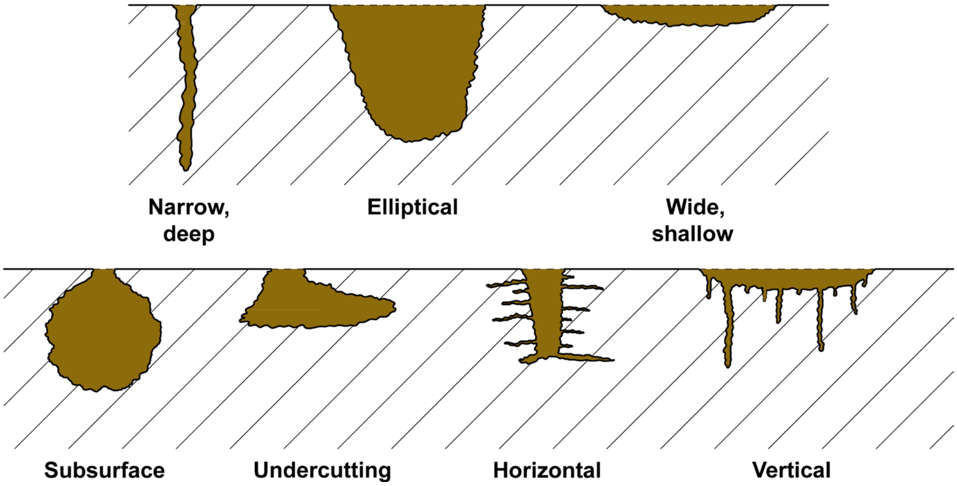

Figure 62 – Typical morphologies of pitting corrosion [from ASTM G46].

Pitting occurs both on metals with active behaviour, such as carbon steels, and on metals with active-passive behavior, such as stainless steels[59]. Corrosion is caused by neutral or oxidizing environments able to chemically attack the passive film. Pitting corrosion of stainless steels occurs typically in aqueous solutions containing chlorides[60], such as in marine environments (wet-dry areas or areas exposed to sea spray).

The other parameters that influence pitting are the increase of temperature, the acidification of the electrolyte and the level of other aggressive substances (such as in industrial atmospheres or in the contaminated process fluids). Once triggered, pitting corrosion tends to be self-sustaining: the cavity of the pit gradually recalls chloride ions due to the electrophoresis effect[61] and an increase of the *pH* occurs due to the acid hydrolysis of the water[62] (figure 63).

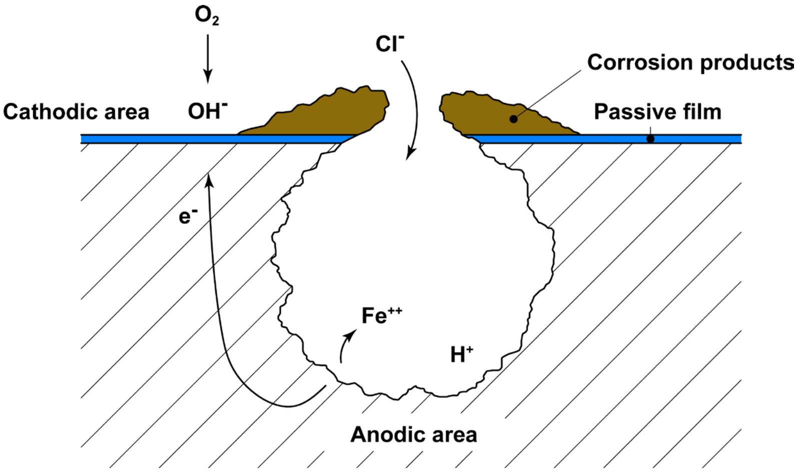

Figure 63 – Schematic representation of the damage mechanism caused by pitting.

Pitting occurs when the passivation conditions in the active-passive polarisation curve of the stainless steel are exceeded, i.e. when the potential of the cathodic reaction is greater than the transpassivation potential, E_t, of the anodic reaction (figure 50 - case *B4*). Therefore, the transpassivation potential, E_t, also known as pitting potential, is an excellent parameter for classifying the stainless steel resistance to pitting corrosion.

---

[59] *Pitting corrosion is also common in other metals with active-passive behavior, such as aluminium and its alloys or titanium and its alloys.*

[60] *Pitting occurs not only upon contact with aqueous solutions contaminated by chlorides, but also due to the effect of other halides, such as fluorides (F^-) and iodides (I^-).*

[61] *The electrophoresis effect causes the movement of electrically charged particles (ions) immersed in a fluid, as the result of an electric field induced by the anode-cathode micro-couple. The ions move towards the cathode if they have positive charge and towards the anode if they have negative charge. In the case of pitting, Cl^- ions are attracted to the anodic zone of the pit cavity.*

[62] *Acid hydrolysis can occur with variation of pH of the water solution, according to the reaction:* $Fe^{+2} + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+$.

E_t can also be used to assess the effects of various environment on the same stainless steel: the higher the pitting potential, the higher the resistance to pitting corrosion.

For example figures 64-66 show the pitting potential according to temperature, chloride concentration and *pH* for two commonly used stainless steels.

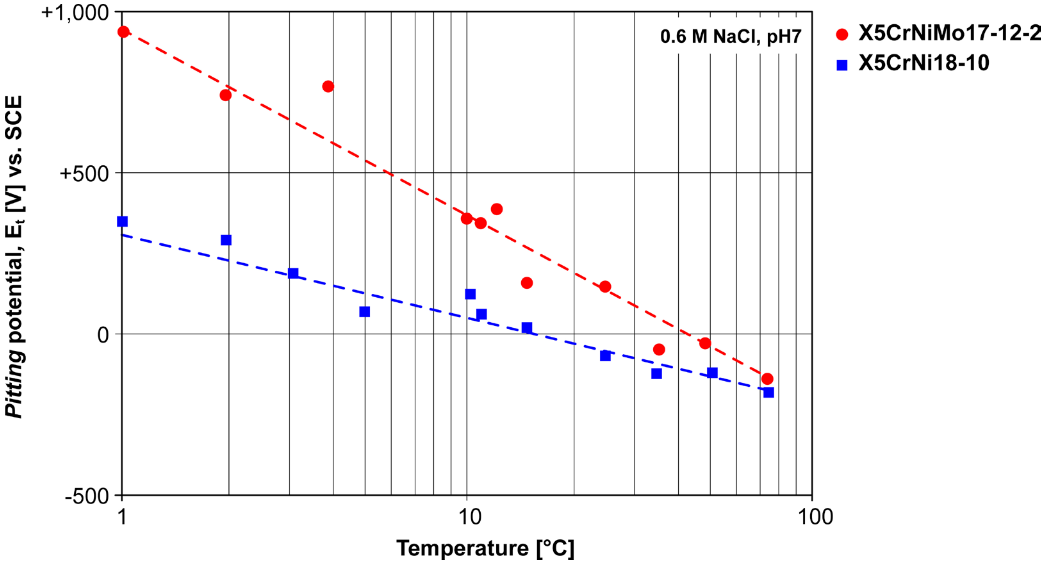

Figure 64 – Pitting potential according to temperature for austenitic stainless steel grades EN X5CrNi18-10 and EN X5CrNi17-12-2; aqueous solution 0.6M of *NaCl* at *pH* 7 [from Shirer 1994].

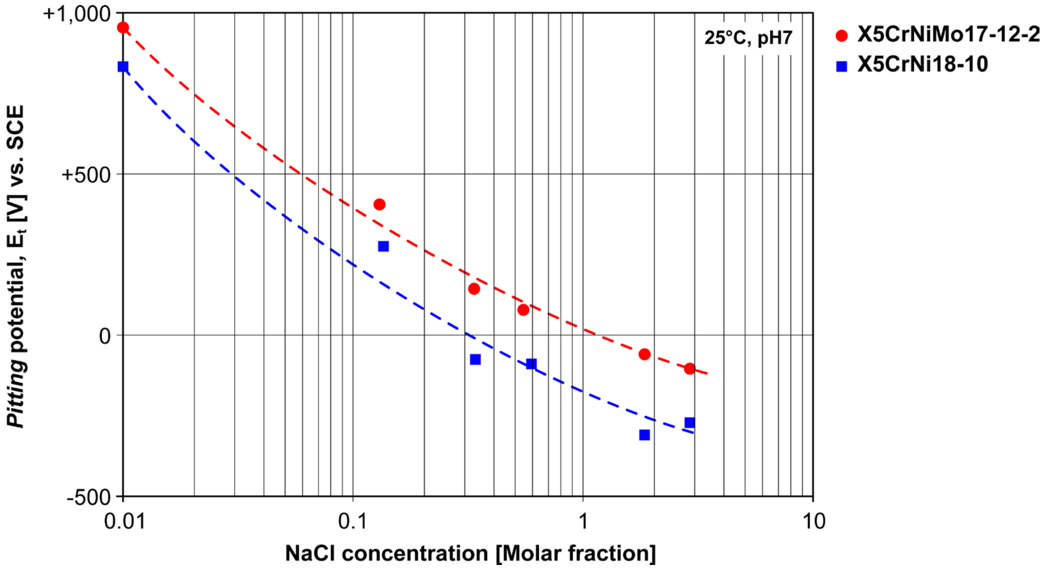

Figure 65 – Pitting potential according to chloride concentration for austenitic stainless steel grades EN X5CrNi18-10 and EN X5CrNi17-12-2; aqueous solution with *pH* 7 at 25°C [from Shirer 1994].

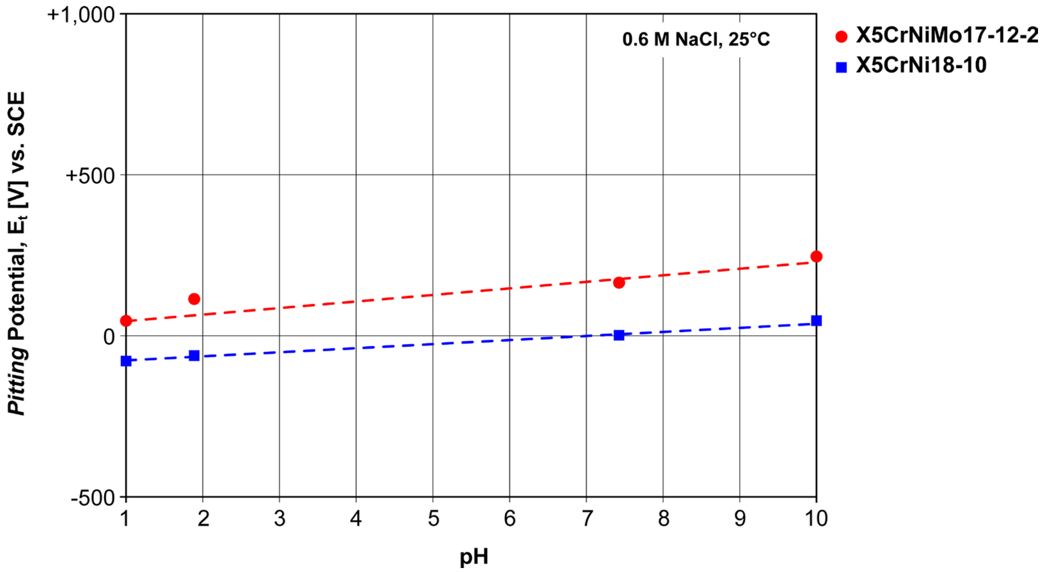

Figure 66 – Pitting potential according to *pH* for austenitic stainless steel grades EN X5CrNi18-10 and EN X5CrNi17-12-2 in aqueous solution 0.6M of *NaCl* at 25°C [from Shirer 1994].

Resistance to pitting corrosion can be estimated from the chemical composition of stainless steel: in fact, it is well known that elements such as chromium, molybdenum and nitrogen promote the expansion of the passive field (they raise the transpassivation potential, E_t).

To this end the most important parameter used to correlate chemical composition to pitting resistance is *PREN* (Pitting Resistance Equivalent Number), which is defined by the formula [63]:

$$PREN = \%Cr + 3.3 \cdot \%Mo + 16 \cdot \%N$$

This index allows to classify the various type of stainless steels with regards to pitting resistance (figure 67): the higher the *PREN*, the higher the resistance to pitting corrosion.

In addition to figure 67, it also useful to consider figure 68, which shows the great variability in the correlation between *PREN* and pitting potential, especially for *PREN* values > 30. Albeit easy to determine, the *PREN* index allows only a qualitative classification of stainless steels and can only be used for pitting corrosion.

---

[63] The PREN formula is not unambiguous: various coefficient for molybdenum and nitrogen are available. In the case of molybdenum both 3 and 3.3 can be used, while for nitrogen a coefficient equal to 13, 16, 27 or 30 can be used. The equation proposed is the most common.

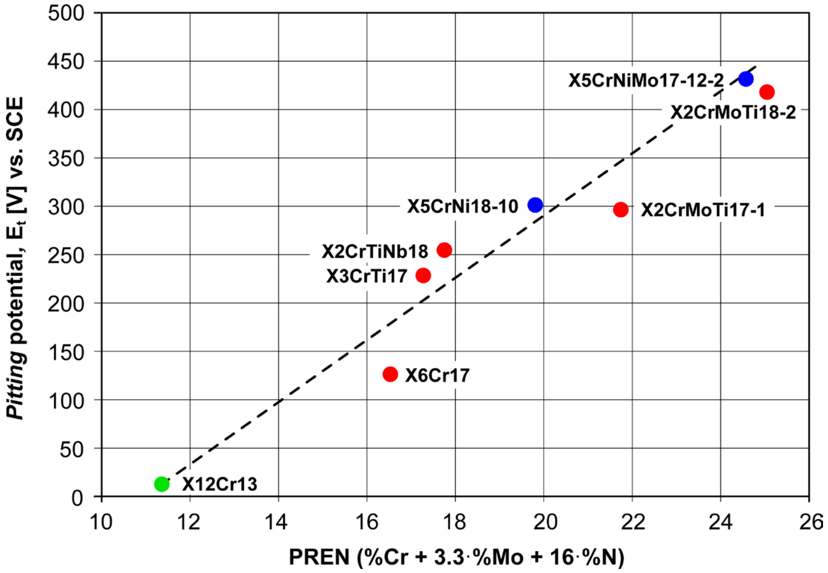

Figure 67 – Pitting potential according to *PREN* for some stainless steels in aqueous solution 0.5M of *NaCl* at 50°C with *pH* 6.6 [from ArcelorMittal 2010].

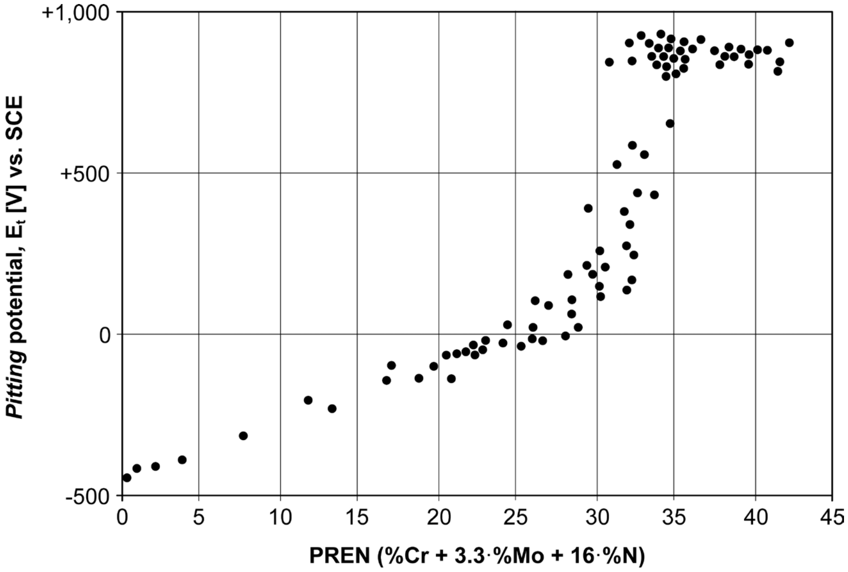

Figure 68 – Pitting potential according to *PREN* in aqueous solution 0.5M of *NaCl* at 50°C with *pH* 6.6; iron based alloys with %Cr = 0.021-28, %Ni = 0.22-20.39, %Mo = 0.01-4.23, %N = 0.01-0.45, %Mn = 0.22-4.53, %Si = 0.13-0.71 [from Shirer 1994].

The resistance to pitting corrosion can also be evaluated through standard laboratory tests. A typical example is given by standard ASTM G48 - 2003 (*Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution*) which allows to classify materials according to temperature at which pitting corrosion occurs.

Test includes the sample immersion in aqueous solution of ferric chloride[64]. Pitting corrosion threshold can be evalueted experimentally by gradually increasing temperature: this threshold, called *Critical Pitting Temperature* (*CPT*), can be used as an index of resistance to pitting corrosion (figure 69).

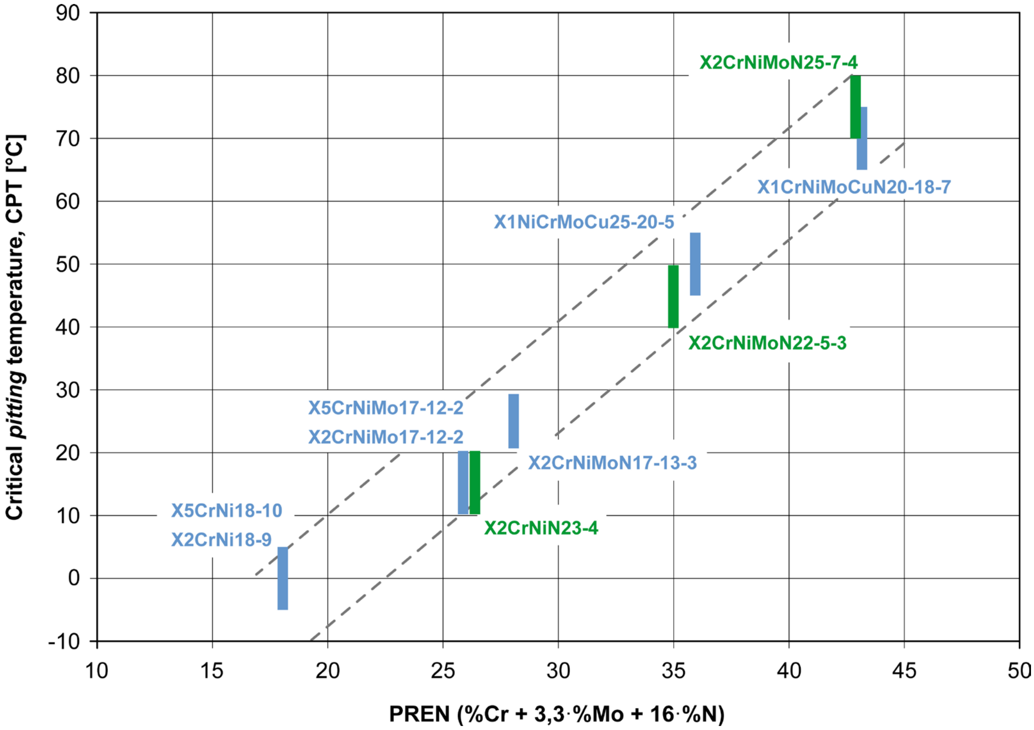

Figure 69 – Correlation between critical pitting temperature (according to ASTM G48) and *PREN* for some austenitic and austenitic-ferritic stainless steels.

Pitting corrosion is a phenomenon that must be prevented rather than hindered: in this regard it is very important to choose the material in relation to the environment and its surrounding conditions (temperature, *pH* , harmful substances, chloride concentration, agitation level, etc.).

---

[64] *Iron chloride, $FeCl_3$, is the iron salt (III) of hydrochloric acid: it is a compound soluble in water (with solubility equal to 920g/litre at 20°C) and is very corrosive to carbon and stainless steels.*

12.5 Crevice corrosion

Crevice corrosion is another common form of localised corrosion: it occurs when the electrolyte (generally water) stagnates inside cracks, crevice, incrustations and geometrical discontinuities that separate it from surrounding enviroment. A typical case of crevice corrosion regards the seals of flanged piping or the contact zones between bolted or riveted plates (figure 70).

Similar situations can occur in spot welding of car unitized bodies, in welding joints with incomplete penetration, between the strands of metal cables, underneath lubricating films such as graphite or molybdenum disulfide and on surfaces coated with Teflon or polyethylene.

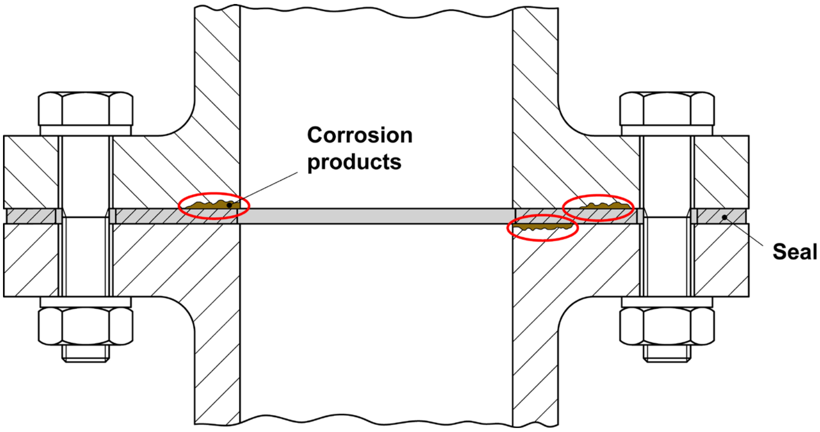

Figure 70 – Schematic representation of flanged pipes which could cause crevice corrosion.

The geometric discontinuities create a differential aeration phenomenon between the interstitial area, i.e. the anodic zone where the diffusion of oxygen is limited, and the surrounding metal mass which represents the cathodic zone where the oxygen saturation is ensured (figure 71). As a matter of fact, the interstices highlight the same critical factor of pitting corrosion, i.e. gradual consumption of oxygen, accumulation of positive metal ions, chloride ions attracted due to the electrophoresis effect and acid hydrolysis with *pH* decrease (compare figure 71 with figure 63).

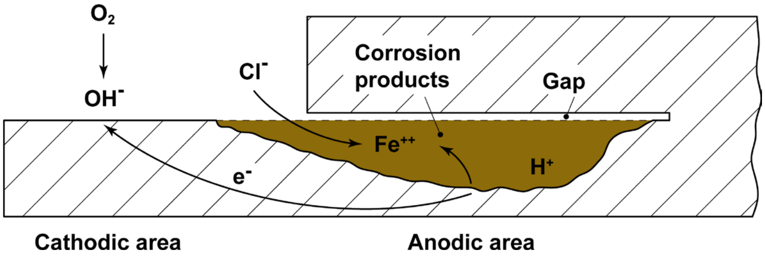

Figure 71 – Schematic representation of crevice corrosion.

The analogy between pitting and crecive leads to an identical classification of stainless steels with regard to these types of phenomena. The better the pitting corrosion behavior, the better the crevice corrosion resistance: therefore the *PREN* index can be also used to choose the correct stainless steel against crevice corrosion. However, if material and environmental conditions are equal, it is much easier to trigger crevice than pitting. As a matter of fact, in case of pitting the cavity must be formed by chemical aggression of the environment, but for crevice the "cavity" is already present in the component due to the geometric discontinuity: therefore crevice is much more critical then pitting!

Another important parameter that governs crevice corrosion is the interstice dimension: above a certain threshold the electrolyte can flow freely, whilst below this threshold stagnation will be promoted and crevice will be triggered (figure 72).

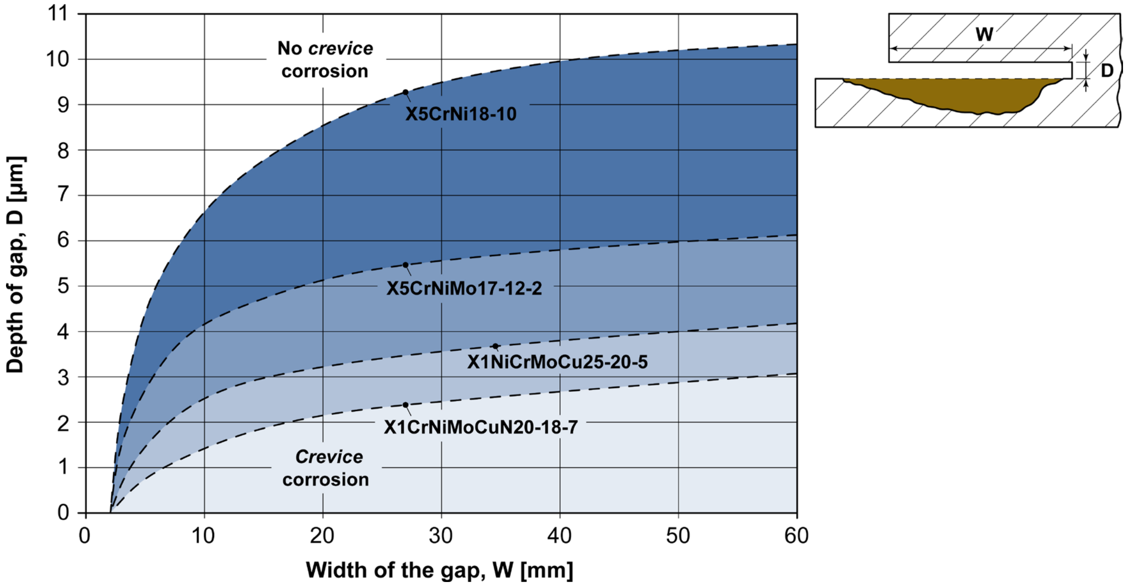

Figure 72 – Interstice dimensions that can cause crevice corrosion in relation to stainless steel grade [from Sedriks 1996].

Therefore, focus must be placed on component design, in order to avoid interstices, cracks, incrustations or, in general, any points of preferential corrosion of stainless steel.

A particular form of crevice corrosion is under deposit corrosion which occurs under limestone deposits with the formation of degradation mechanisms similar to those of crevice corrosion (figure 73). The phenomenon is typical of limestone-rich waters that flow through household pipes.

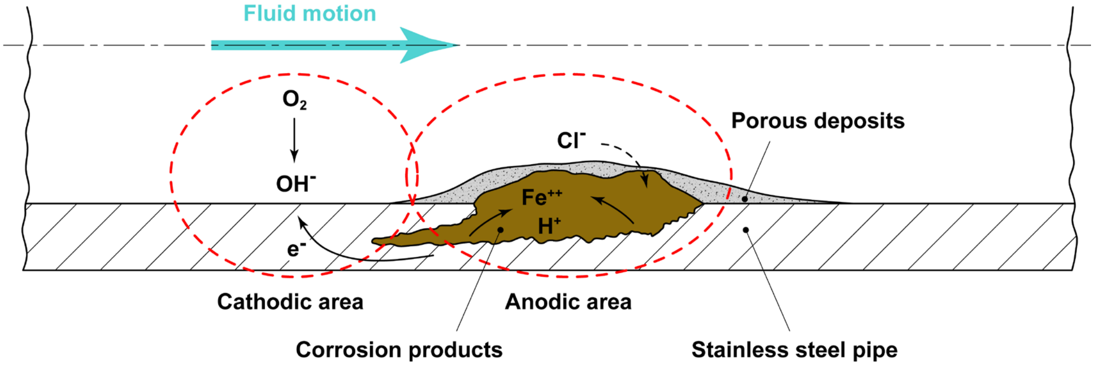

Figure 73 – Schematic representation of under deposit corrosion in a stainless steel pipe.

12.6 Intergranular corrosion

Intergranular corrosion is a form of degradation associated with a chemical composition discontinuity of the material's microstructure: it is a symptom of the formation of a continuous network of carbides or intermetallic phases, rich in chromium or chromium/molybdenum, near to grain boundaries (figure 10).

It is a mechanism of localised corrosion, also called "sensitization", that occurs on many families of stainless steels even in mildly aggressive environments; some authors prefer to classify it as selective corrosion because the aggression occurs only along grain boundaries.

The cause of degradation is the local depletion of chromium or chromium/molybdenum near to grain boundaries: the corrosion is developed in the form of individual or branched cracks that "follow" grain boundaries where the carbide precipitation has occurred.

This issue was discussed in chapter 3: please refer to paragraph 3.4 for further information. However the most important considerations will be repeated below; the list was made starting from the stainless steel families most used industrially.

The sensitization of austenitic stainless steels occurs due to prolonged exposure in the critical temperature interval between 450°C and 900°C. Three factors explain why chromium depletion at the grain boundaries is so deleterious:

- carbon can "bind" an amount of chromium equal to about 16 times its own quantity in weight (carbides type $Cr_{23}C_6$);
- carbon diffuses into austenite much more quickly than chromium and then "captures" a very large quantity of chromium; however, chromium has a much lower diffusivity than carbon and therefore the depletion of chromium only occurs near to grain boundaries;
- carbides preferentially precipitate at grain boundaries, an area with lower atomic density where precipitate nucleation is facilitated.

The austenitic stainless steels with carbon level greater than 0.03% are at risk of integranular corrosion if exposed in the critical temperature interval. This condition can occur, for example, during the heat treatment of semi-finished product, due to the effect of inappropriate operating temperatures, or due to welding operations. In the latter case the phenomenon typically occurs in the areas near to the welding bead (heat affected zone), where the time spent in the critical precipitation interval is longer (figure 74).

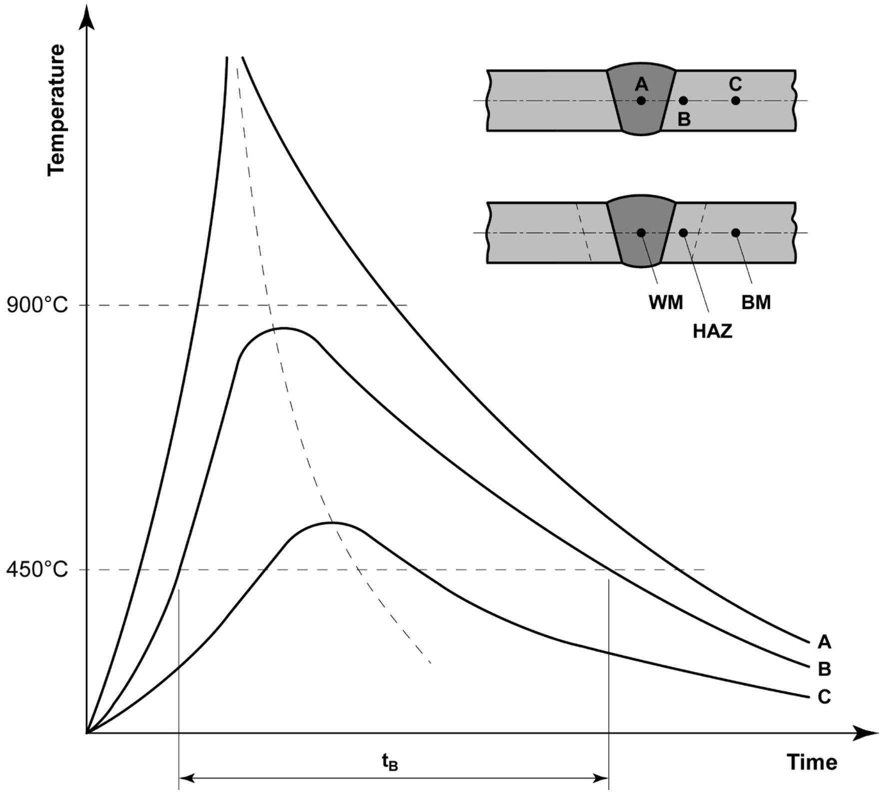

Figure 74 – Temperature distribution along the cross section of welding joints. *WM*: welded metal (*A*); *HAZ*: heat affected zone (*B*); *BM*: base metal (*C*). Intergranular corrosion can occur in zone *B* because it is more exposed to the critical interval compared to *A* and *C*.

In terms of potentiodynamic curves, the carbide precipitation causes an increase in current density with the same applied potential (figure 75): consequently, different problem can arise depending on environment and sensitization level of the steel.

To work around this problem, as already mentioned in chapter 8, the carbon content can be reduced to values lower than 0.03% (low carbon austenitic stainless steels) or alloying elements, such as titanium or niobium, can be added to stabilize chromium (stabilized austenitic stainless steels). Alternatively, if possible, a solution annealing heat treatment can be performed at 1,050°C, followed by rapid cooling in water.

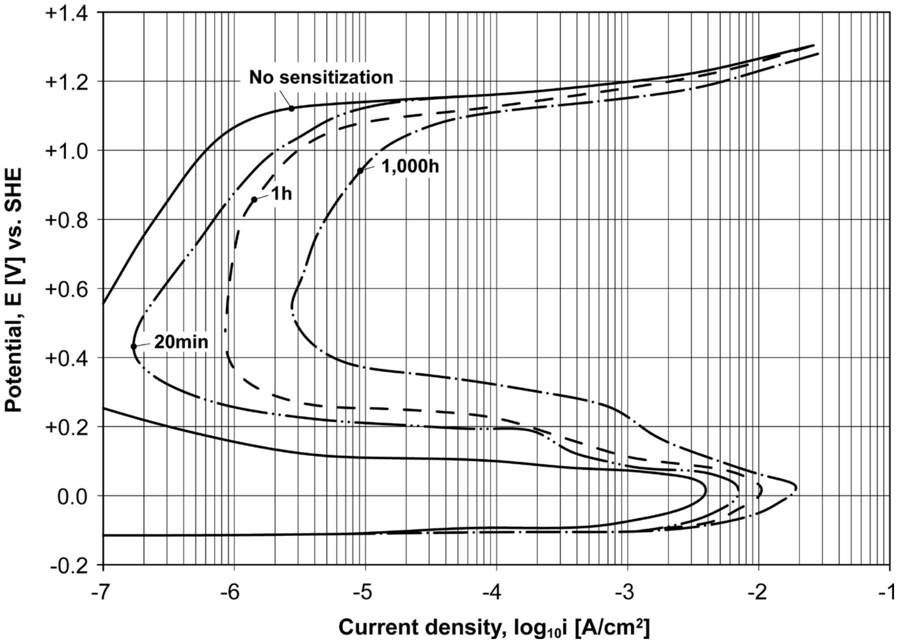

Figure 75 – Potentiodynamic polarisation curves of stainless steel grade EN X5CrNi18-10 in its solution annealed state and after sensitization at 650°C for various times; aqueous solution 1M of H_2SO_4 at 90°C [from Osozawa et al. 1966].

Sensitization problems due to carbide precipitation can also occur for ferritic stainless steels: the critical temperatures are lower than those of austenitic stainless steels and precipitation occurs in very short times (figure 76). To reduce this phenomenon, the semi-finished product must be fully annealed at 800°C, in fact, at this temperature, chromium diffuses towards the depleted zones; alternatively, the material can be stabilized using titanium or niobium. Conversely, it is not possible to reduce carbon to very low level, since its solubility in the body-centred cubic lattice is very limited.

Finally, duplex stainless steels: these materials have greater resistance to intergranular corrosion compared to both the families of austenitic and ferritic stainless steels.

The lower sensitivity is due to the formation of chromium carbides at the interface between the austenite grains and the ferrite grains. As the diffusion rate of chromium in α-phase is 100-150 times greater than in γ-phase the carbides are preferentially enriched with chromium at the expense of ferrite. Therefore, chromium depletation occurs at long-range without a significant chromium reduction at the γ/α interface (similar to what is shown in figure 10a).

The problem of duplex stainless steels is due to the formation of the phases rich in chromium or chromium/molybdenum (phases σ, χ and *Laves*) or to the 475°C embrittlement (figure 41).

Stabilization is not provided for duplex stainless steels, therefore a solution annealed heat treatment followed by water cooling is recommended in case of unwanted phases formation (such as during large section component welding).

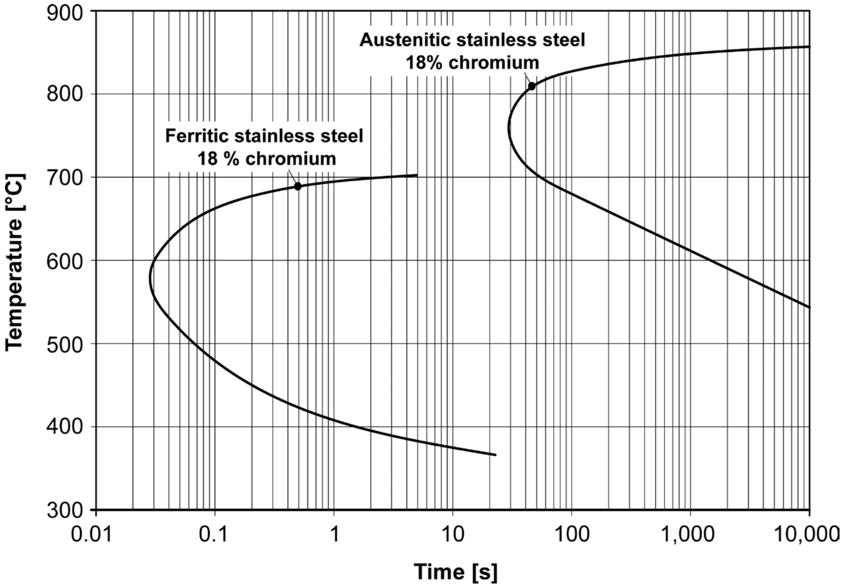

Figure 76 – T.T.T. diagram ("*C* curve") for ferritic and austenitic stainless steels with same chromium content [from Cowan and Tedmon 1973].

12.7 Stress Corrosion Cracking (*SCC*)

Stress Corrosion Cracking (*SCC*) is a very hazardous form of localised corrosion because it occurs in environments not particularly aggressive for stainless steel: it generally has very short incubation and propagation times (from 3 to 12 months) and often leads to malfunction of components or plants as the problem is recognised when the phenomenon is overt[65].

Stress corrosion cracking only occurs if three conditions are simultaneously met:

- a stainless steel with specific chemical composition,
- a specific corrosive environment,
- a tensile stress greater than a specific threshold[66].

---

[65] *This problem is common to many families of materials: for example, copper alloys undergo SCC in ammonia rich environments, aluminium alloys in aqueous solutions with chlorides and high strength steels in distilled water.*

[66] *Tensile stress may derive from external forces or residual stresses induced by previous metalworking process (deep drawing, drawing, stamping, bending, welding etc.).*

Only this combination is critical: when considered individually, mechanical stress and corrosive environment do not cause mechanical or corrosion problems.

Furthermore, the temperature must be greater than room temperature: the most common forms of stress corrosion cracking of stainless steels occur for temperatures of 45°-50°C.

Figure 77 shows a schematic representation of the Stress Corrosion Cracking phenomenon.

SCC causes the formation of simple or multi-branched cracks; propagation of cracks can be both intergranular (i.e. it follows the grain boundary) and transgranular (i.e. it crosses the grains): sometimes the propagation can be mixed.

Usually, corrosion products are not observed, so much so that in some cases the cracks are wrongly attributed exclusively to mechanical problems.

Usually, the prevention of stress corrosion cracking is implemented by changing the material in contact with critical environment. If possible, a further solution is to reduce the mechanical stresses applied to the component, both increasing the component dimensions (with a consequent reduction of the applied stress), and eliminating the residual stresses through suitable heat treatments (stress relieving)[67].

Stress Corrosion Cracking does not occur in all stainless steels in any corrosive environment: in practice there are only two critical "material-environment" couples.

The most common case of *SCC* occurs for the couple austenitic stainless steels in seawater or in chloride solution (even with very low concentrations of Cl^-[68]) as, for example, in seawater heat exchangers.

For austenitic stainless steels in chloride-rich environments the *SCC* cracks are generally transgranular and their trigger is often associated with surface pits. The phenomenon is aided by temperature, chloride concentration and oxygen concentration increase. The critical stress threshold is between 70-90MPa, i.e. one third of the yield stress in the solution annealed state; beyond this value, fracture time gradually reduces with increase of the applied stress.

Stress corrosion cracking of austenitic stainless steels in chloride environments depends on the amount of nickel: the most critical conditions occur when the nickel content is around 8-10%, i.e. the typical percentages of the most common austenitic stainless steels (figure 78).

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[67] *It is possible to perform shot peening that produces a positive effect against SCC, by including a compressive residual stresses in the material.*

[68] *Some authors indicate the maximum chloride concentration to avoid SCC in 10ppm.*

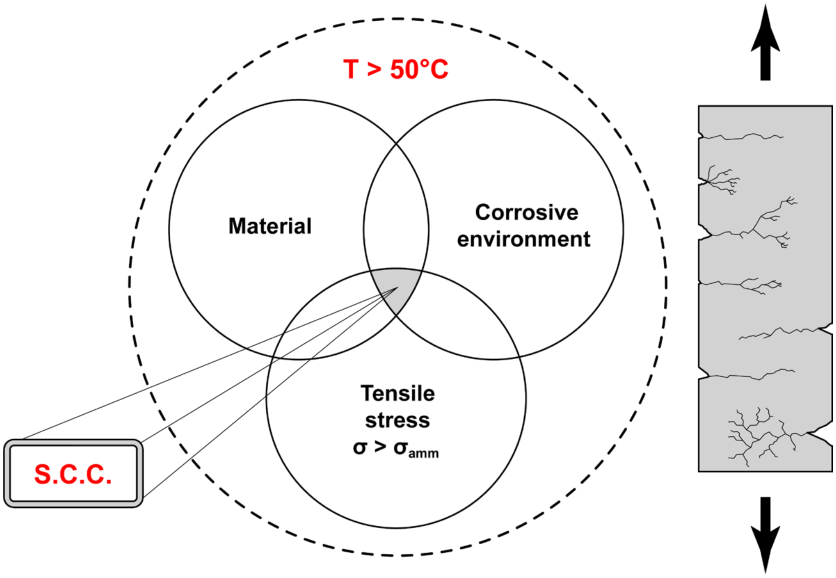

Figure 77 – Schematic representation of the Stress Corrosion Cracking phenomenon.

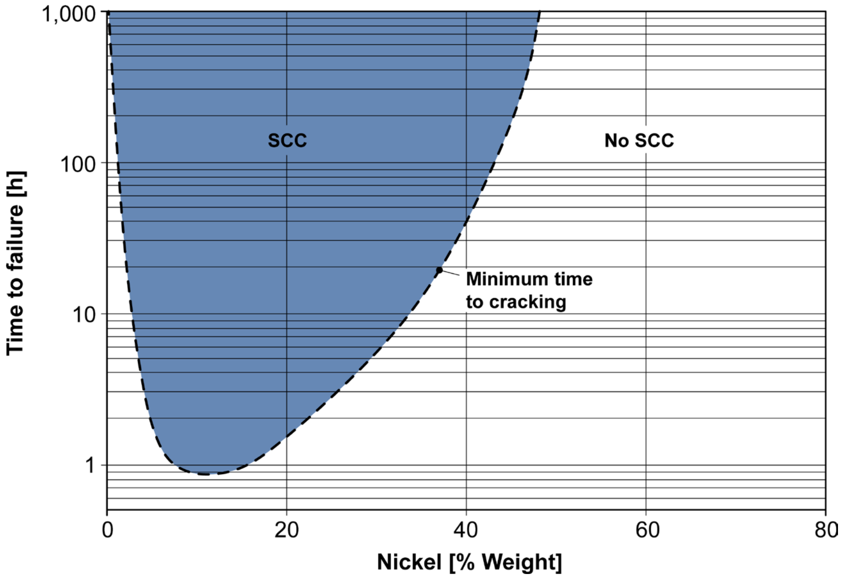

Figure 78 – Stress corrosion cracking of stainless steel wires with 18-20% chromium and variable nickel content; aqueous solution with 42% magnesium chloride at 154°C [from Copson 1956].

If the nickel is greater than 40% or completely absent, the steel will be much less sensitive to *SCC* : this is the reason why nickel based super-alloys or ferritic stainless steels are insensitive to the problem[69].

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[69] *SCC in chloride environments can also occur on ferritic stainless steels if carbide precipitation has occurred, for example on welding joints.*

Duplex stainless steels are a better alternative in seawater to austenitic stainless steels, due to the high resistance to stress corrosion cracking of the ferritic phase (figure 79).
In some cases *SCC* occurs at temperatures lower than the threshold. The problem has occurred since the mid-eighties in indoor swimming pools; failures take place at around 30°C on tie rods for false ceilings or on support structures: *SCC* was favored by the high humidity level and high chloride concentration.

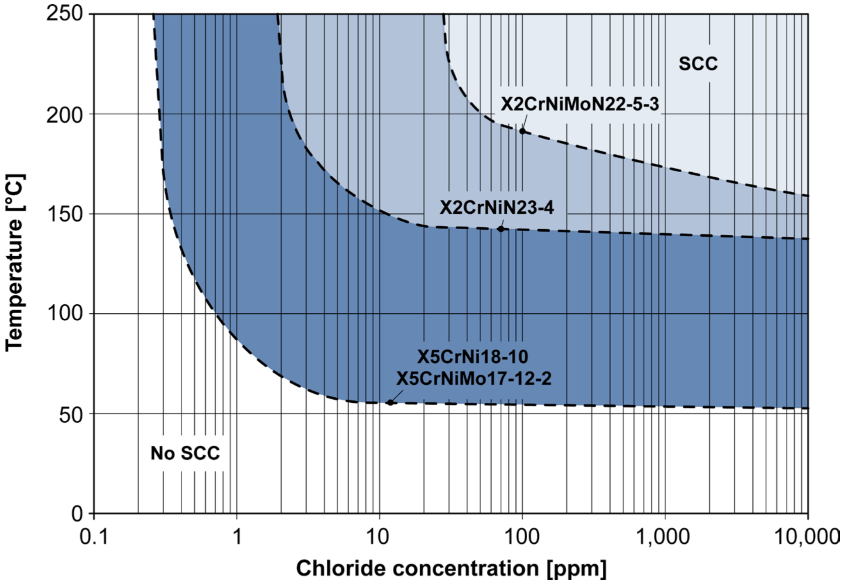

Figure 79 – Effect of temperature and chloride concentration on *SCC* resistance of some austenitic and austenitic-ferritic stainless steels [from Sedriks 1996].

Caustic solutions (solutions rich in sodium or potassium hydroxide) are also critical for stainless steels: stress corrosion cracking, pitting and generalised corrosion can occur in these environments.
The phenomenon is typical of austenitic stainless steels and occurs at temperatures between 80°-100°C, both in aerate and deaerate solutions with various concentrations of *NaOH* (figure 80). In caustic *SCC*, the fracture can be transgranular, intergranular or mixed.
The resistance to caustic *SCC* can be slightly improved with an increase of nickel or using austenitic-ferritic stainless steels, even though, in both cases, it is not possible to guarantee complete immunity.

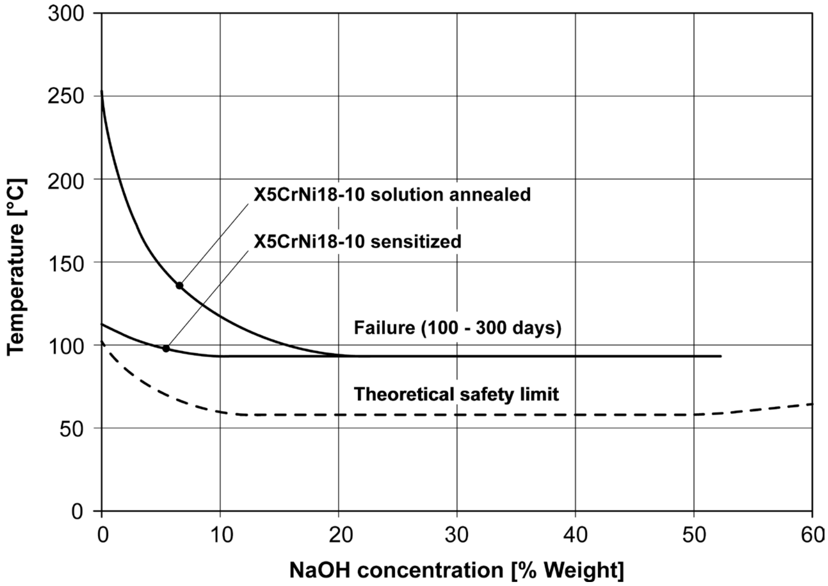

Figure 80 – Effect of temperature and sodium hydroxide concentration (*NaOH*) on caustic *SCC* resistance of austenitic stainless steel grade EN X5CrNi18-10 [from Lacombe 1993].

Stress corrosion cracking of austenitic, duplex or martensitic stainless steels can be caused by contact with hydrogen sulphide (H_2S). This form of corrosion is known as *SSCC* (*Sulphide Stress Corrosion Cracking*) but it is, for all effects and purposes, a phenomenon of hydrogen embrittlement[70] which is very common in the sector of extraction and refining of petroleum products and natural gas. Hydrogen embrittlement is caused by reaction between hydrogen sulphide and iron. This reaction forms sulphurs and atomic hydrogen (H^+) that can easily diffuses into steel, inducing intergranular embrittlement.

The chemical species that promote *SSCC* are also chloride and hydrogen ions (as what occurs in acid environments); the most critical temperature interval is between 60°-100°C.

In the case of austenitic, martensitic or *PH*-martensitic stainless steels, the degradation also depends on their mechanical strength. For example the standard NACE MR0175 / ISO 15156[71] specifies a maximum hardness of 22HRC in order to consider the steel suitable for these uses. To avoid the problem, duplex stainless steels, super-austenitic stainless steels or nickel based alloys are often used.

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[70] *Atomic hydrogen (H^+) is a very small atom which, under appropriate temperature and pressure conditions, diffuses into the crystal lattice, making the steel very brittle.*

[71] *International standard NACE MR0175 / ISO 15156 (Petroleum and Natural Gas Industries - Materials for use in H_2S - containing Environments in Oil and Gas Production).*

13. HIGH TEMPERATURE OXIDATION OF STAINLESS STEELS[72]

High temperature oxidation occurs when stainless steels are in contact with hot gases, such as in the case of components operating at high temperatures in contact with air, oxygen, carbon dioxide and superheated steam. Degradation phenomena with similar morphologies occur in contact with reducing, carburizing, nitriding or sulphurous atmospheres, with salt baths or molten metals ($NaCl$, KCl, Na_2SO_4, KCN, zinc, aluminium, low-melting metals etc.). High temperature oxidation is also named dry corrosion, as it occurs at temperature much higher than room temperatures (T > 300°C).

Turbine or compressor blades, combustion chambers, chemical and nuclear reactors, boilers, vehicle exhaust systems, distillation columns of petroleum products and equipment for industrial furnaces or steel plants are typical components subject to high temperature oxidation.

The degradation derives from the interaction between gas and metal and can be explained as the sum of an oxidation reaction combined with a reduction reaction, in perfect analogy with wet corrosion.

We will now consider the high temperature oxidation phenomenon of a stainless steel component: for example, a chamber of an industrial furnace operating in air at high temperature.

Iron and chromium oxidize whilst oxygen reduces. In this case the formulae are:

$$2Fe \longrightarrow 2Fe^{+2} + 4e^- \qquad 4Cr \longrightarrow 4Cr^{+3} + 12e^-$$

$$O_2 + 4e^- \longrightarrow 2O^{-2} \qquad 3O_2 + 12e^- \longrightarrow 6O^{-2}$$

and overall:

$$2Fe + O_2 \longrightarrow 2FeO \qquad 4Cr + 3O_2 \longrightarrow 2Cr_2O_3$$

The degradation process, due to the oxide-reduction reactions, occurs mainly at the interface between metal and oxygen, as the iron oxide and the chromium oxide are permeable to oxygen. Figure 81 shows a schematic representation of the high temperature oxidation phenomenon. In order to understand the behaviour of a metal material in contact with an oxidizing atmosphere, it is necessary to know whether the oxide will be brittle and porous or adherent and compact.

In the first case, the degradation will happen quickly as the metal is continually exposed to oxidation. However, in the second case, a barrier prevents the contact of oxygen or other harmful chemical species with metal; consequently the damage will be drastically reduced.

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[72] *Paragraphs 11, 12 and 13 were partially taken from the article by Boniardi M., Casaroli A., Tagliabue C., Fenomeni di danneggiamento dei materiali metallici dovuti all'esercizio (Failure Analysis). The article is part of the book by Various Authors, Le Prove non Distruttive, Vol. 1, Associazione Italiana di Metallurgia, Milano 2013.*

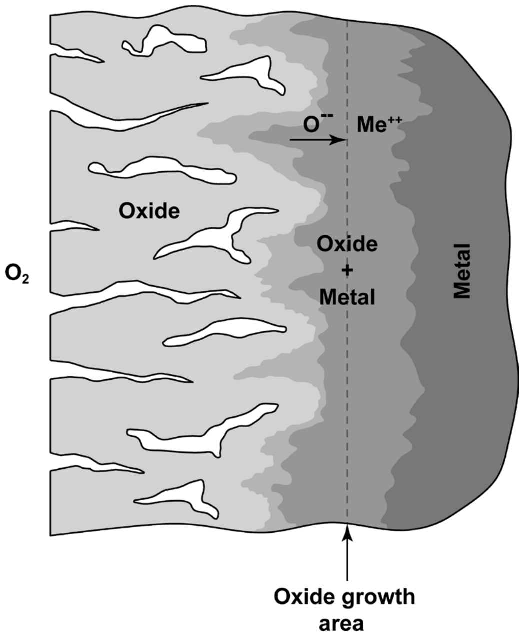

Figure 81 – Schematic representation of the high temperature oxidation phenomenon on a stainless steel in contact with an oxidizing hot gas.

This is what occurs in metal alloys.

In carbon steels only iron oxide will form. At temperatures higher than 570°C, iron oxide (*FeO*) is porous and tends to break away from the component surface: in such conditions high temperature oxidation will continually occur.

In stainless steels, however, the high level of chromium forms a stable and adherent oxide at least up to 900°C: with the increase of chromium the oxide stability and the resistance to high temperature oxidation will also increase. There are also other chemical elements that can improve the stainless steel behavior at high temperatures: i.e. silicon, which forms stable oxides up to 1,200°C (SiO_2), or aluminium, which forms compact oxides up to 1,300°C (Al_2O_3).

It is also useful to highlight the effect of molybdenum and nickel.

Molybdenum, improves the resistance of stainless steel to high temperature oxidation because it forms a stable and adherent oxide on the surface (MoO_3): however, this oxide becomes liquid at 795°C and phenomena of catastrophic corrosion will occur.

Instead, nickel is always beneficial with regards to high temperature oxidation for two reasons:

- it has a low tendency to be oxidized and,
- it improves the adhesion of chromium oxides to the steel surface.

The resistance to high temperature oxidation of the stainless steels does not only depend on their chemical composition. Other factors influence degradation significantly: the temperature of the hot gases, the chemical composition of the atmosphere, the presence of aqueous vapour, as well as the operating conditions of the component, i.e., if the temperature is constant or fluctuates over time[73]. Table 20 shows the maximum operating temperature for the main types of stainless steels.

		Maximum operating temperature [°C]	
EN Designation	**Stainless steel type**	**Fluctuating temperature**	**Constant temperature**
X5CrNi18-10 (1.4301)	austenitic	870	925
X6CrNiTi18-10 (1.4541)	austenitic	870	925
X6CrNiNb18-10 (1.4550)	austenitic	870	925
X5CrNiMo17-12-2 (1.4401)	austenitic	870	925
X8CrNi25-21 (1.4845)	austenitic	1,035	1,150
X12Cr13 (1.4006)	ferritic	815	705
X2CrTi12 (1.4512)	ferritic	815	705
X6Cr17 (1.4016)	ferritic	870	815
X10CrAlSi25 (1.4762)	ferritic	1,175	1,095
X12Cr13 (1.4006)	martensitic	815	705
X12CrS13 (1.4005)	martensitic	760	675
X30Cr13 (1.4028)	martensitic	735	620
X105CrMo17 (1.4125)	martensitic	815	760

Table 20 – Maximum operating temperature for the main types of stainless steels [from Schweitzer 2007].

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[73] *Fluctuating temperatures are more critical than constant ones, because they cause repeated expansions and contractions that facilitate the breakage and detachment of the oxide.*

Martensitic, ferritic and austenitic stainless steels are the three type of stainless steel most used against high temperature oxidation.

In general terms, the resistance to high temperature oxidation increases with the increase of chromium if temperature is constant; stainless steels with 13% chromium are suitable up to 660°-680°C, 17% chromium up to 800°-820°C and 18-20% chromium up to 960°-980°C. In order to reach the upper limit, it is necessary to add 25% chromium: in this case the maximum temperatures are between 1,050°-1,100°C. However, stainless steels with nickel must be used if temperature fluctuates over time. Therefore, an austenitic stainless steel will usually has longer service life compared to martensitic or ferritic stainless steel with the same chromium content[74].

Although stainless steels grades EN X6Cr17, EN X5CrNi18-10 and EN X5CrNiMo17-12-2 are widely used at high temperatures, there are specific stainless steels developed for extreme applications. In this regard, some examples are ferritic stainless steel grade EN X10CrAlSi25 (similar to AISI 446), with aluminium, silicon and high chromium, or austenitic stainless steel grade EN X8CrNi25-21, with high level of chromium and nickel: in both cases the materials are very resistant up to 1,000°-1,100°C.

If high resistance to creep is required, austenitic stainless steels should be used. Thanks to their face-centred cubic lattice, they can be used up to 850°-870°C. Alternatively, martensitic stainless steels can be used, but only up to maximum temperature between 500°-550°C.Conversely, ferritic stainless steels do not have good resistance to creep, as their microstructure becomes brittle and their mechanical strength is drastically reduced beyond 400°C.

---

[74] *Ferritic and martensitic stainless steels have the highest operating temperatures if temperature fluctuates over time, while austenitic stainless steels have the highest operating temperature when the temperature is constant (table 20). This strange result is due to the greater linear thermal expansion of austenite compared to ferrite or martensite. This property causes greater mechanical stress between metal and oxide and, consequently, reduces its compactness.*

BIBLIOGRAPHICAL RECOMMENDATIONS

With regards to stainless steels the bibliography available is very extensive: the number of contributions becomes endless if, in addition to books, scientific journals and conference papers are considered.

In our opinion, there are three basic reference texts.

Firstly, the now unobtainable Peckner D., Bernstein I. M., Handbook of Stainless Steels, McGraw Hill, New York, USA, 1977. This is a collective works with contributions from various authors. Despite being a little dated, it gives an overall framework of the most important issues relative to stainless steels; it also contains very interesting information which is still very relevant.

The second text we recommend is another collective work: Lacombe P., Baroux B., Beranger G., Stainless Steels, Les Edition de Physique, Les Ulis, France, 1993. Initially published in French, it was then translated into English for greater use by an international audience. Both scientific and technological application are addressed in depth.

Last but certainly not least is a reference volume on stainless steel corrosion. It is Sedriks A. J., Corrosion of Stainless Steels, 2nd, John Wiley & Sons, New Jersey, USA, 1996: the text was specifically written to address the issues of stainless and carbon steel corrosion; this book is not, as is usual, a text about corrosion in which the stainless steels are just one of the many topics described.

In Italian, the choice is much more poor: there are only two reference texts on stainless steels.

On one hand there is Di Caprio G., Gli Acciai inossidabili, 4ª ed., Hoepli, Milano, Italia, 2003. The text by Prof. Di Caprio is very good, especially for non-experts: it is a very interesting introduction (the term "introduction" should not be misleading) to stainless steels and their problems; the volume has been translated into various languages. It contains a lot of information on stainless steel application that the author has collected starting from the sixties until his death in 2010.

The other Italian book is Nicodemi W., Introduzione agli acciai inossidabili, 2ª Ed., Associazione Italiana di Metallurgia, Milano, Italia 2002. First published in the late eighties and nineties of the last century in a single volume; it suffers a little as it has never been re-published in a composite way. It is a very interesting book that also includes some practical cases of failure due to stainless steel corrosion; it is the metallurgic counterpart to the text by Prof. Di Caprio.

Unfortunately, there is nothing specific in Italian on the subject of corrosion of stainless steels. We refer the reader who wishes to improve their knowledge to the volume Pedeferri P., Corrosione e protezione dei materiali metallici, Polipress, Milano, Italia 2010 which contains many references to stainless steels.

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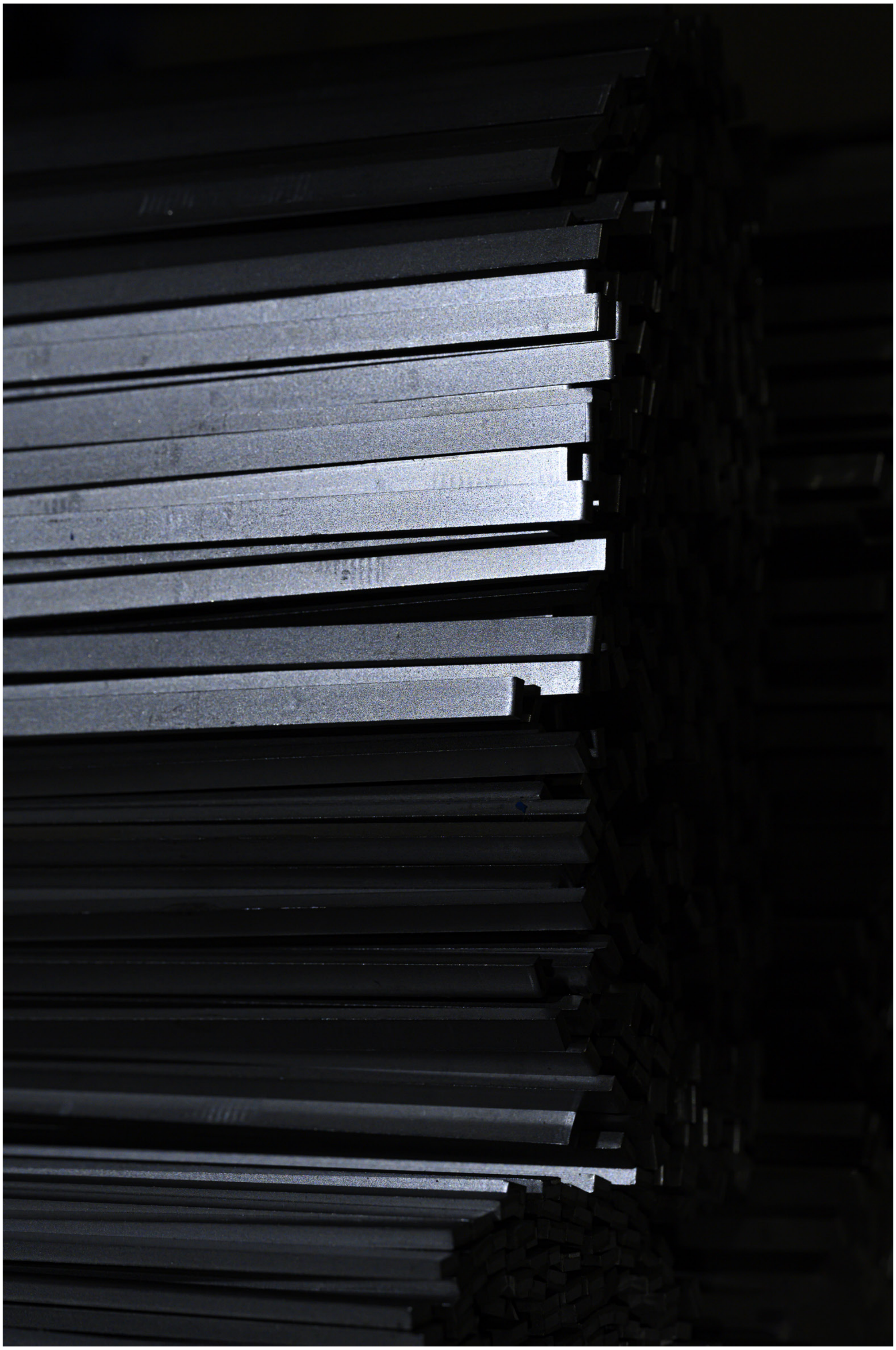


APPENDIX

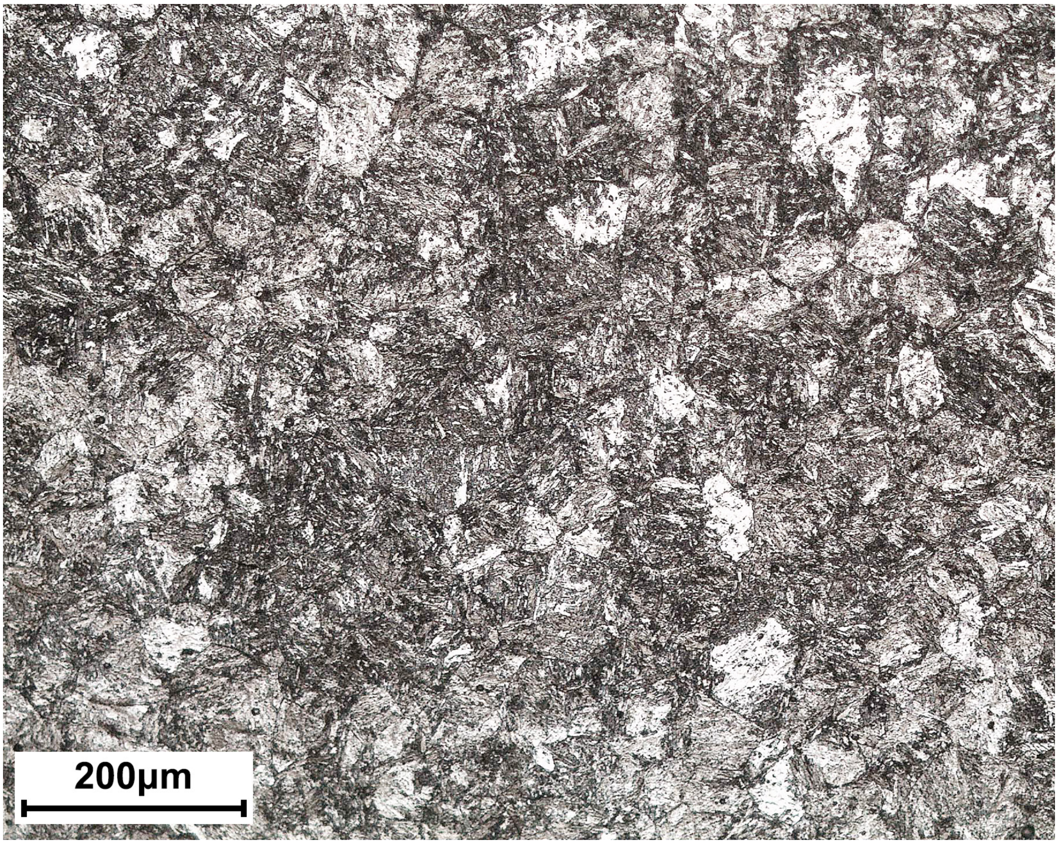
MICROSTRUCTURES AND FORMS OF STAINLESS STEEL CORROSION

For the micrographs that follow, hearfelt thanks to the following laboratories:

- Laboratories of the Department of Mechanical Engineering, Politecnico di Milano,
  I-20156 Milano, Via La Masa, 1
  (Piero Pellin, Maurizio Pardi, Silvia Barella, Silvia Cincera, Mattia Bellogini,
  Fabrizio D'Errico, Andrea Casaroli, Marco Boniardi)

- Hammer S.r.l. Laboratories,
  I-20017 Rho - Milano, Via Risorgimento, 69/22
  (Patrizia Maio, Marco Feraboli, Luca Bonvini)

- Omeco S.r.l. Laboratories,
  I-20900 Monza - Monza Brianza, Via Monviso, 56
  (Alessandra Marelli, Marco Casaril, Clemente Marelli)



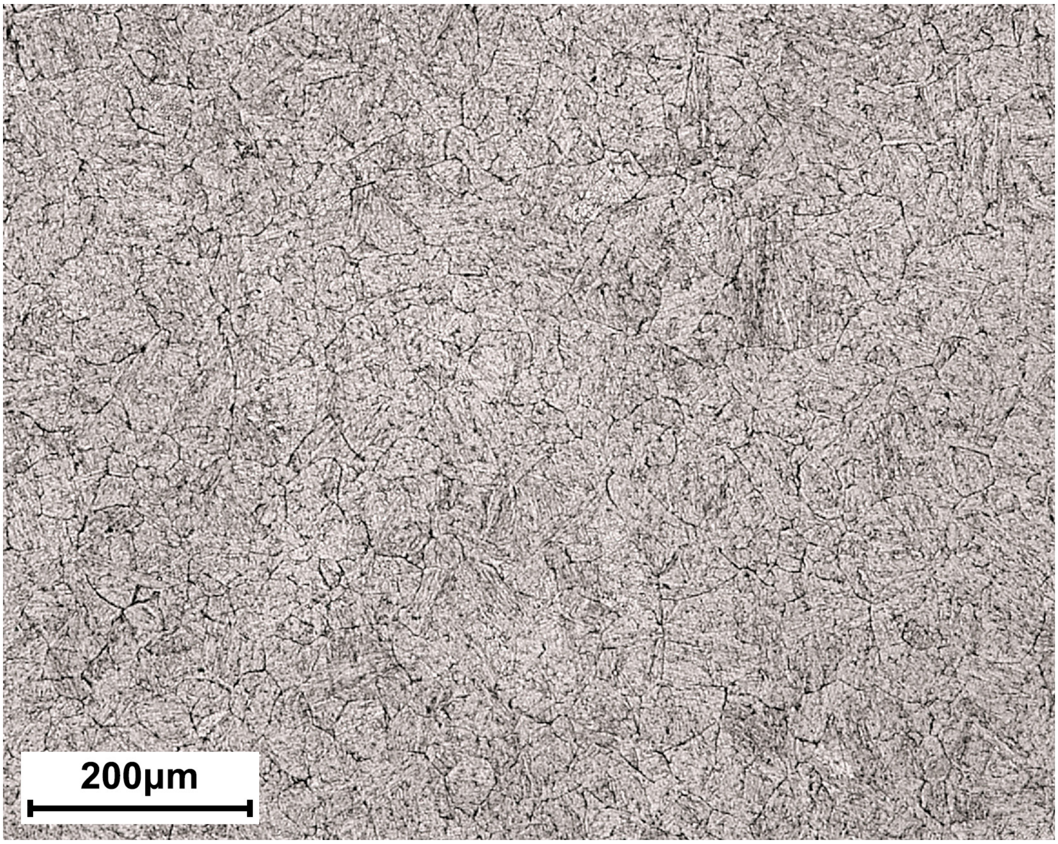
Round bar after quenching and tempering at 650°C

Martensitic stainless steel grade EN X20C13 (similar to AISI 420)

Metallographic etching: Vilella

Homogeneous martensitic structure

Source: Hammer S.r.l. Laboratories, Rho – Milano



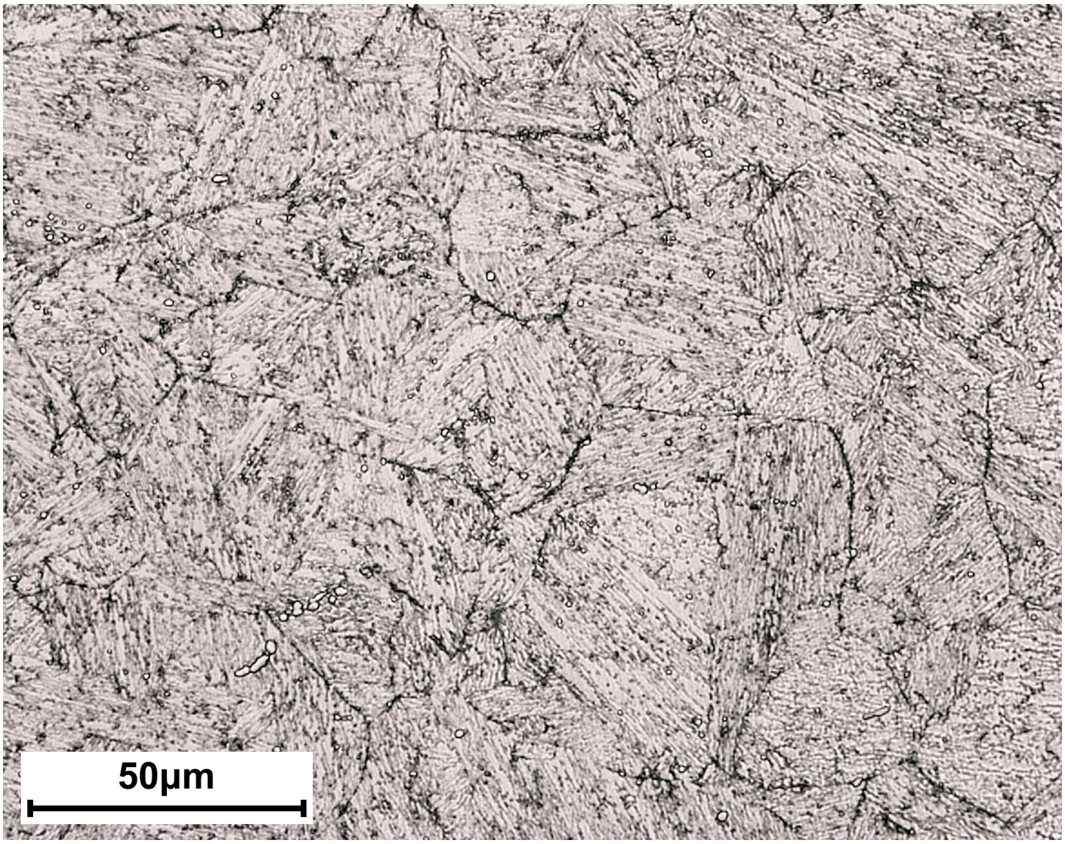
Semi-finished product after forging, solution annealing and aging at 620°C

Martensitic *PH* Stainless Steel grade EN X5CrNiCuNb16-4 (similar to 17-4 PH)

Metallographic etching: Vilella

Homogeneous martensitic structure with carbide precipitation
at prior-austenite grain boundaries

Source: Hammer S.r.l. Laboratories, Rho – Milano



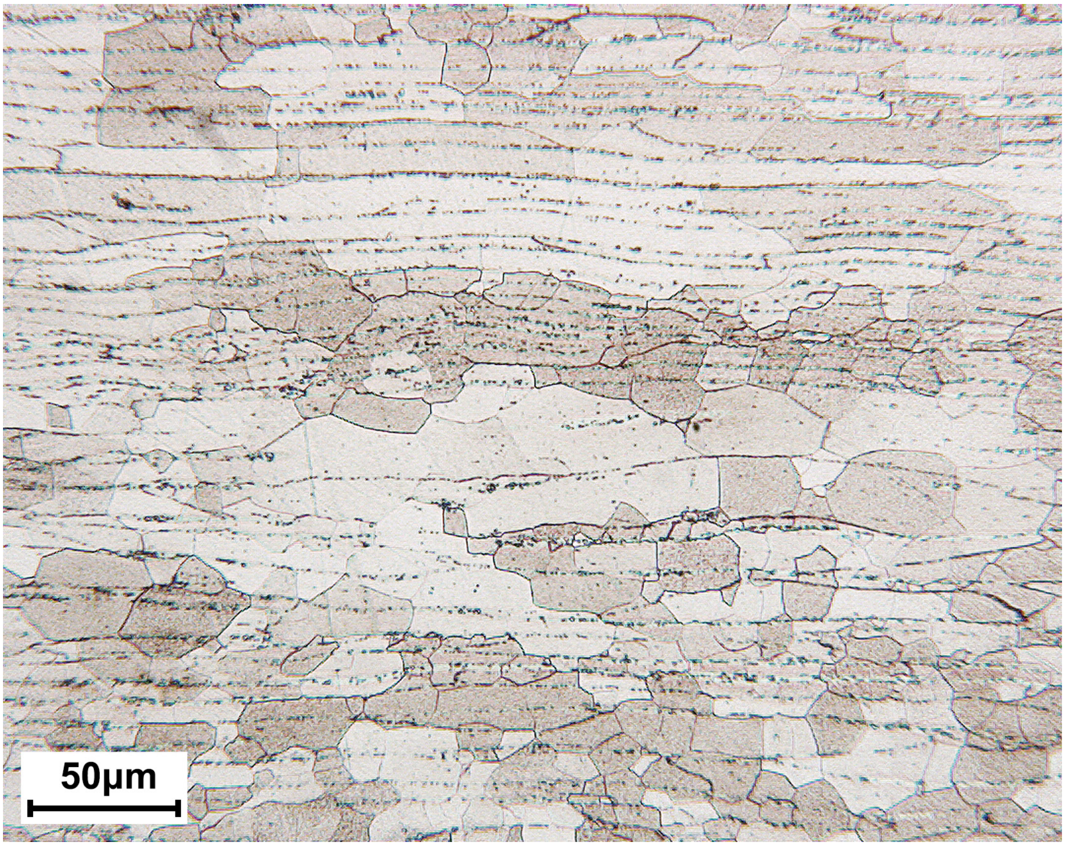
Details of the previous image at higher magnification

Martensitic *PH* Stainless Steel grade EN X5CrNiCuNb16-4 (similar to 17-4 PH)

Metallographic etching: Vilella

Homogeneous martensitic structure with carbide precipitation
at prior-austenite grain boundaries

Source: Hammer S.r.l. Laboratories, Rho – Milano



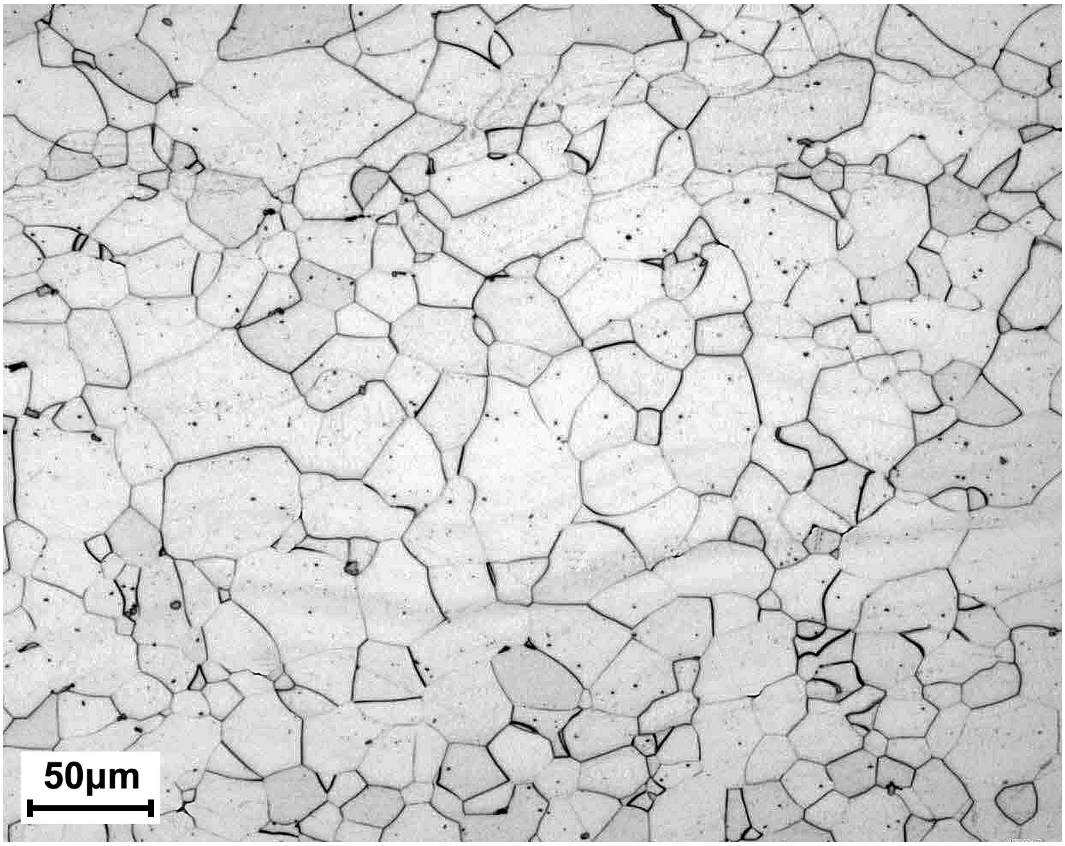
Cold rolled strip after full annealing

Ferritic stainless steel grade EN X6Cr17 (similar to AISI 430)

Metallographic etching: Vilella

Homogeneous ferritic grains with carbides arranged along the rolling direction

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



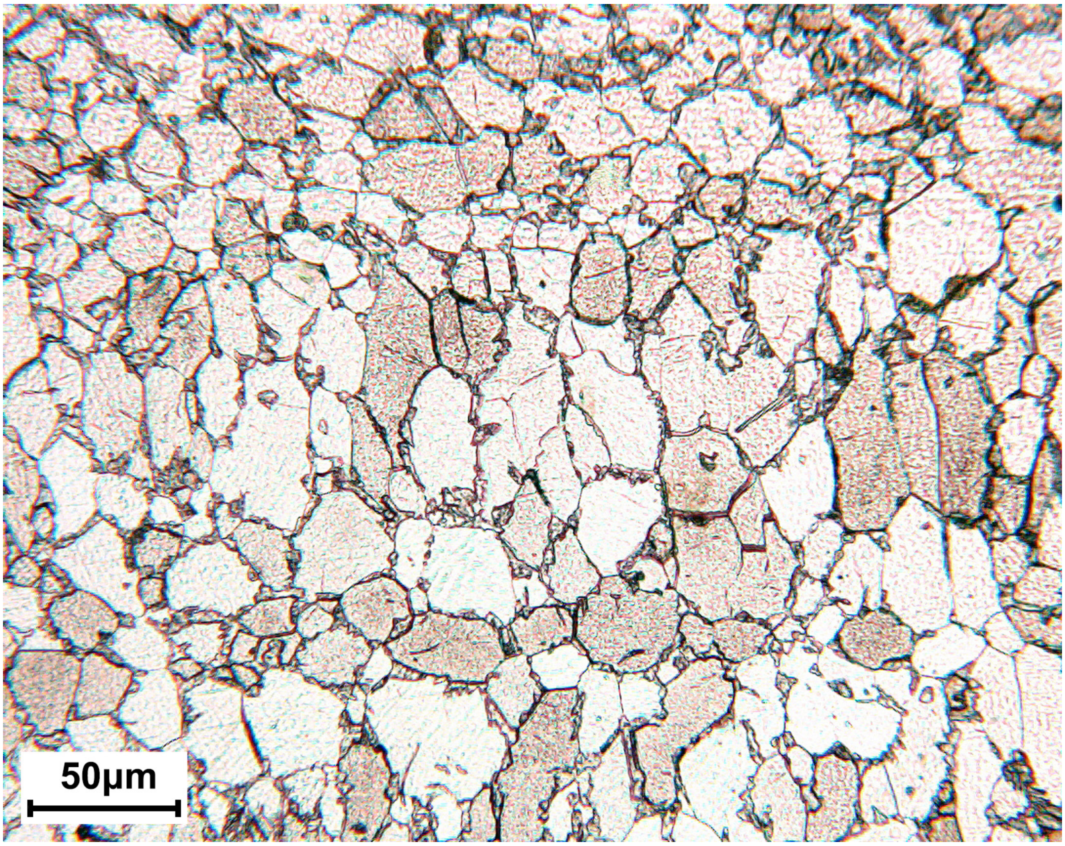
Cold rolled strip after full annealing

Ferritic stainless steel grade EN X2CrTiNb18 (similar to AISI 441)

Metallographic etching: Vilella

Homogeneous ferritic grains

Source: Omeco S.r.l. Laboratories, Monza – Monza Brianza



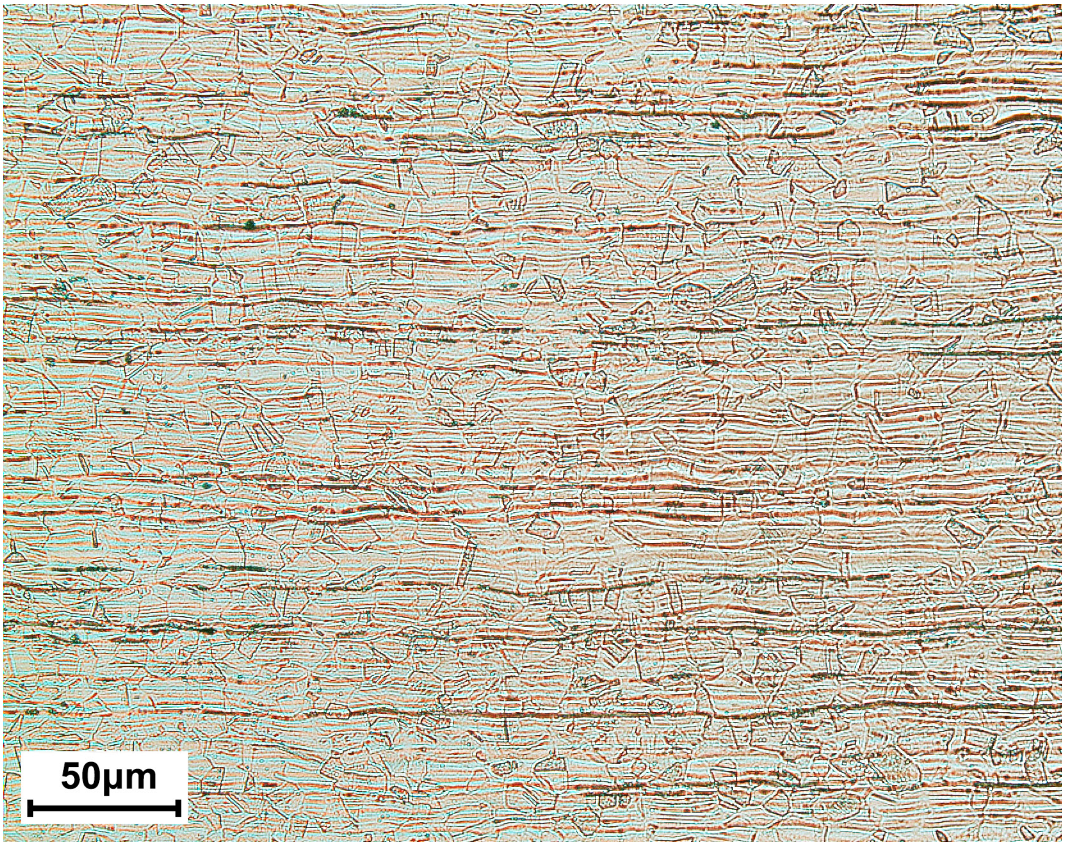
Cold rolled and fully annealed strip; heat affected zone after spot welding

Ferritic stainless steel grade EN X6Cr17 (similar to AISI 430)

Metallographic etching: Vilella

Homogeneous ferritic grains surrounded by martensite

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



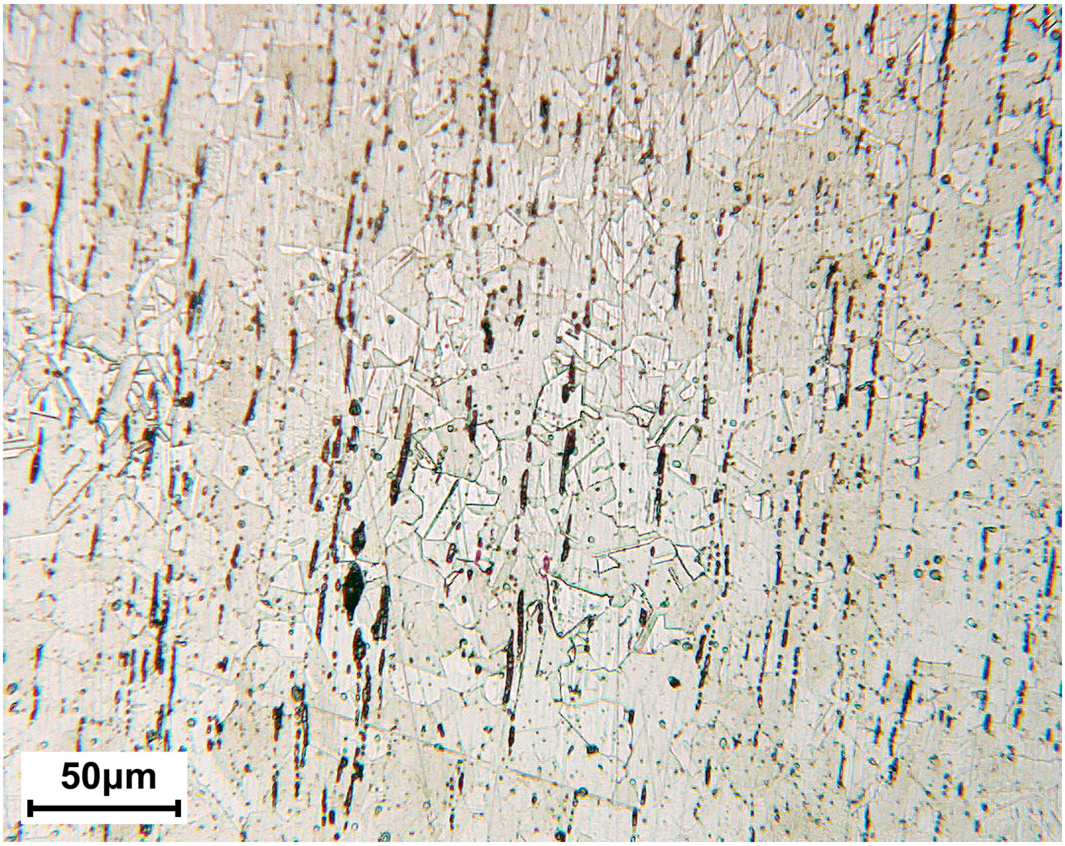
Round bar after cold drawing and solution annealing

Austenitic stainless steel grade EN X5CrNi18-10 (similar to AISI 304)

Metallographic etching: Oxalic acid (electrolytic etching)

Homogeneous austenitic grains with shear bands arranged along the drawing direction

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



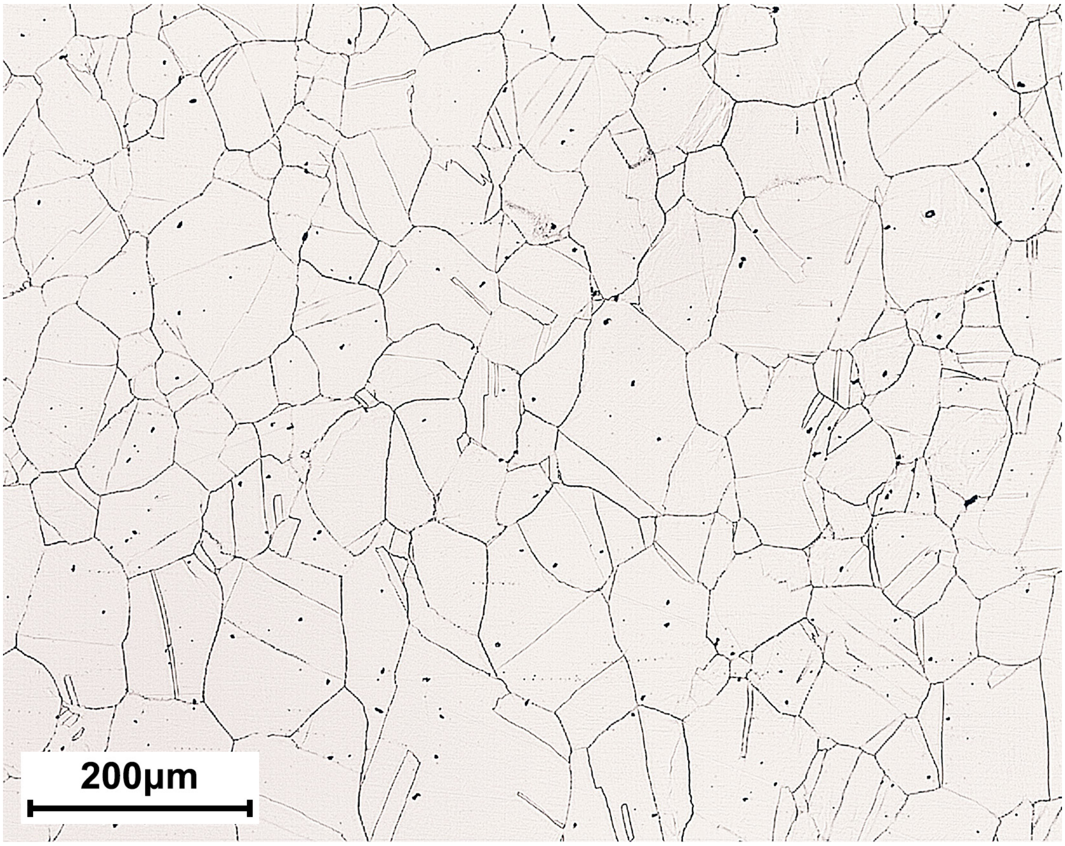
Round bar after cold drawing and solution annealing

Austenitic stainless steel grade EN X8CrNiS18-9 (similar to AISI 303)

Metallographic etching: Oxalic acid (electrolytic etching)

Homogeneous austenitic grains with manganese arranged along the drawing direction

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



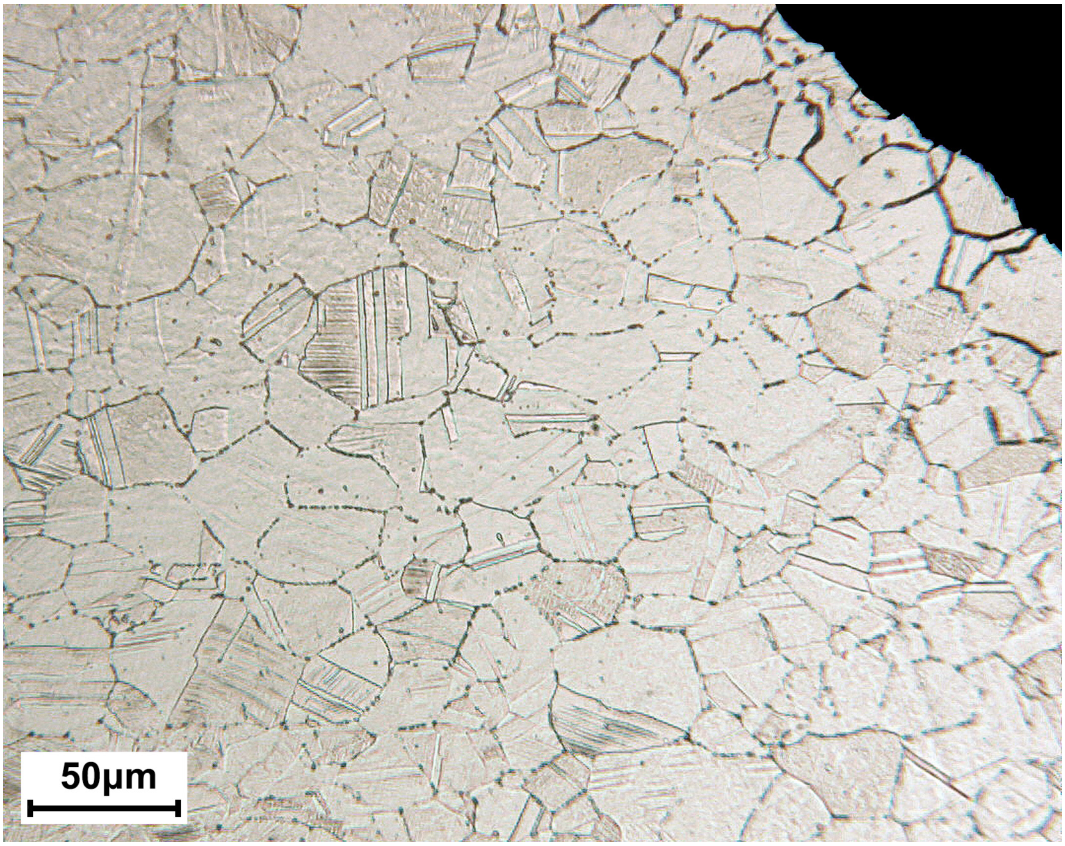
Semi-finished product after forging and solution annealing

Austenitic stainless steel grade EN X2CrNiMoN17-13-3 (similar to AISI 316LN)

Metallographic etching: Oxalic acid (electrolytic etching)

Homogeneous austenitic grains

Source: Hammer S.r.l. Laboratories, Rho – Milano



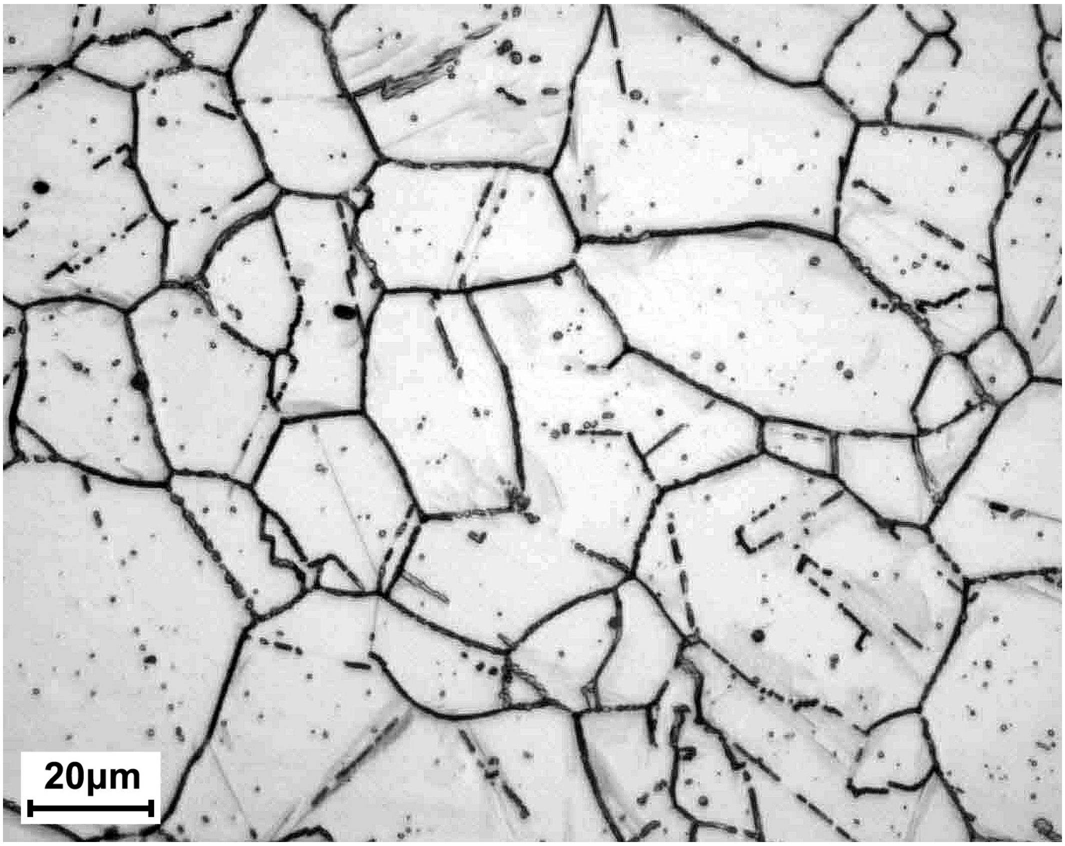
Cold drawn strip after solution annealing and sensitization

Austenitic stainless steel grade EN X5CrNiMo17-12-2 (similar to AISI 316)

Metallographic etching: Oxalic acid (electrolytic etching)

Homogeneous austenitic grains with carbide precipitation at grain boundaries

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



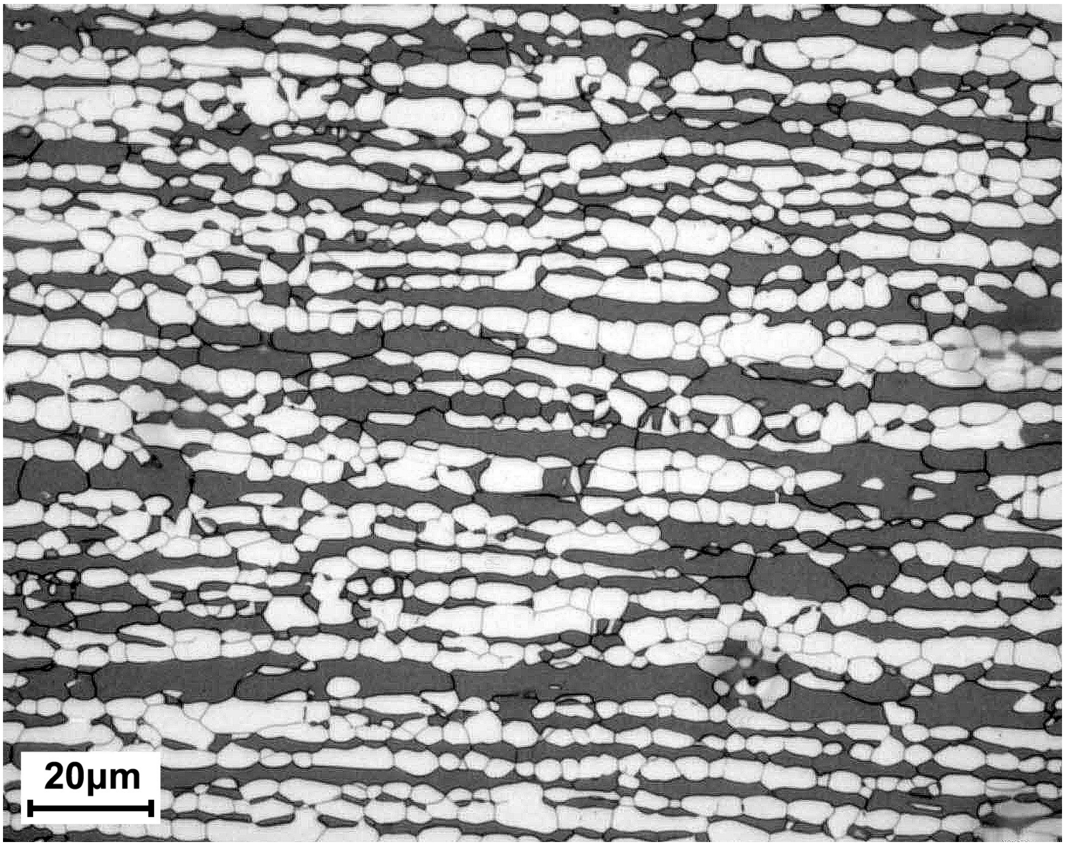
Hot rolled sheet after solution annealing and sensitization

Austenitic stainless steel grade EN X2CrNiMo17-12-2 (similar to AISI 316L)

Metallographic etching: Oxalic acid (electrolytic etching)

Homogeneous austenitic grains with carbide precipitation at grain boundaries

Source: Omeco S.r.l. Laboratories, Monza – Monza Brianza



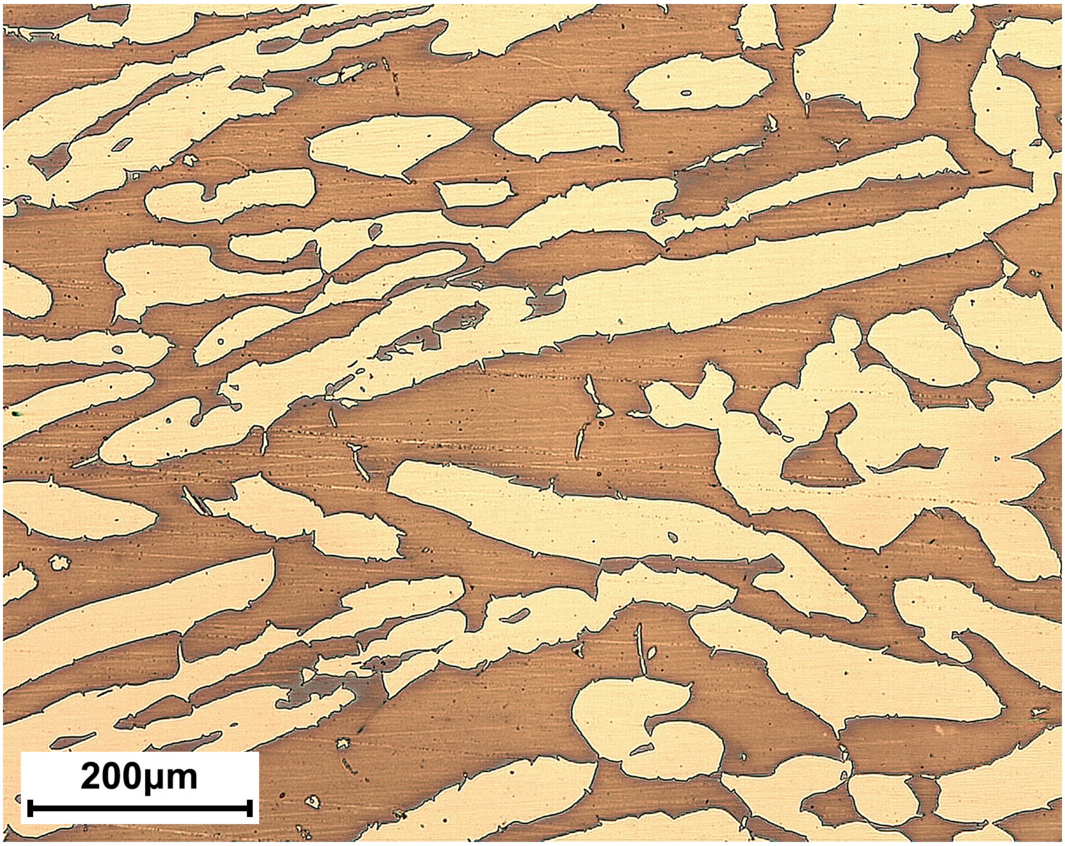
Hot rolled sheet after solution annealing

Duplex stainless steel grade EN X2CrNiMoN22-5-3 (similar to 2205)

Metallographic etching: Oxalic acid followed by caustic soda (electrolytic etching)

Homogeneous austenitic grains and homogeneous ferritic grains extended along the rolling direction

Source: Omeco S.r.l. Laboratories, Monza – Monza Brianza



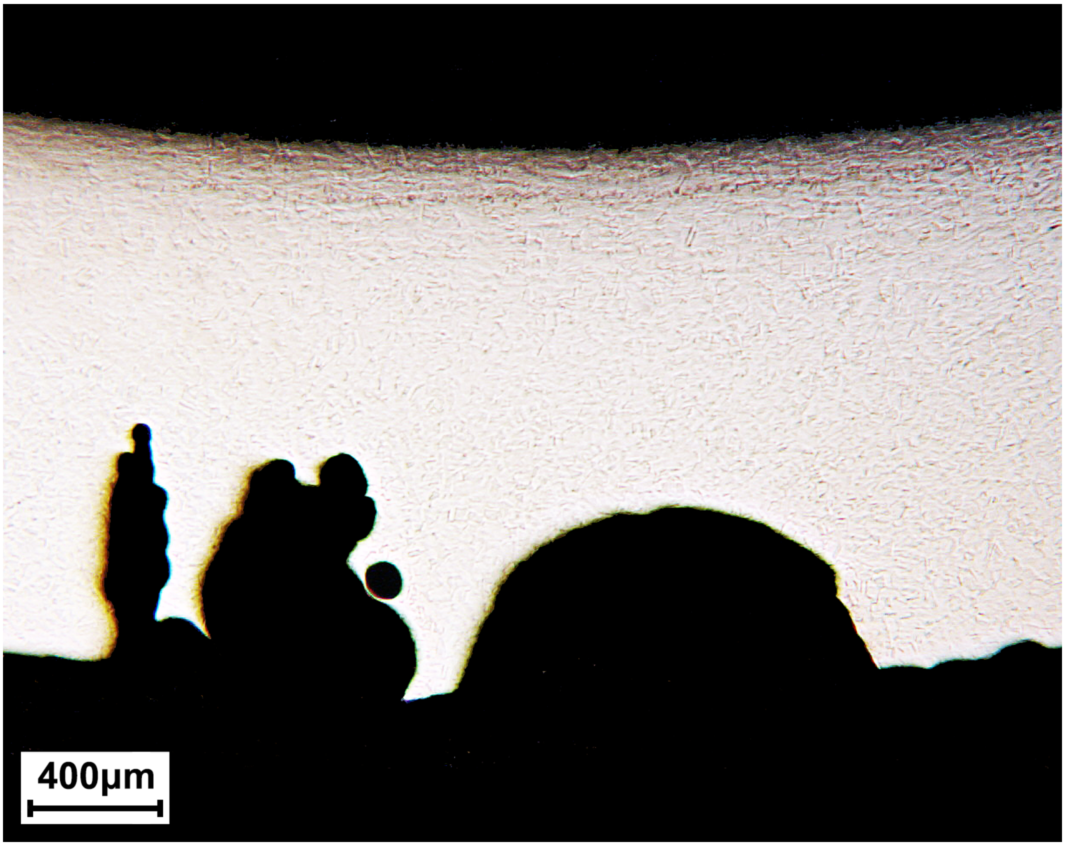
Semi-finished product after forging and solution annealing

Duplex stainless steel grade EN X2CrNiMoN22-5-3 (similar to 2205)

Metallographic etching: Caustic soda (electrolytic etching)

Austenite grains (light color) in ferritic matrix (dark color)

Source: Hammer S.r.l. Laboratories, Rho – Milano



Piping

Austenitic stainless steel grade EN X5CrNi18-10 (similar to AISI 304)

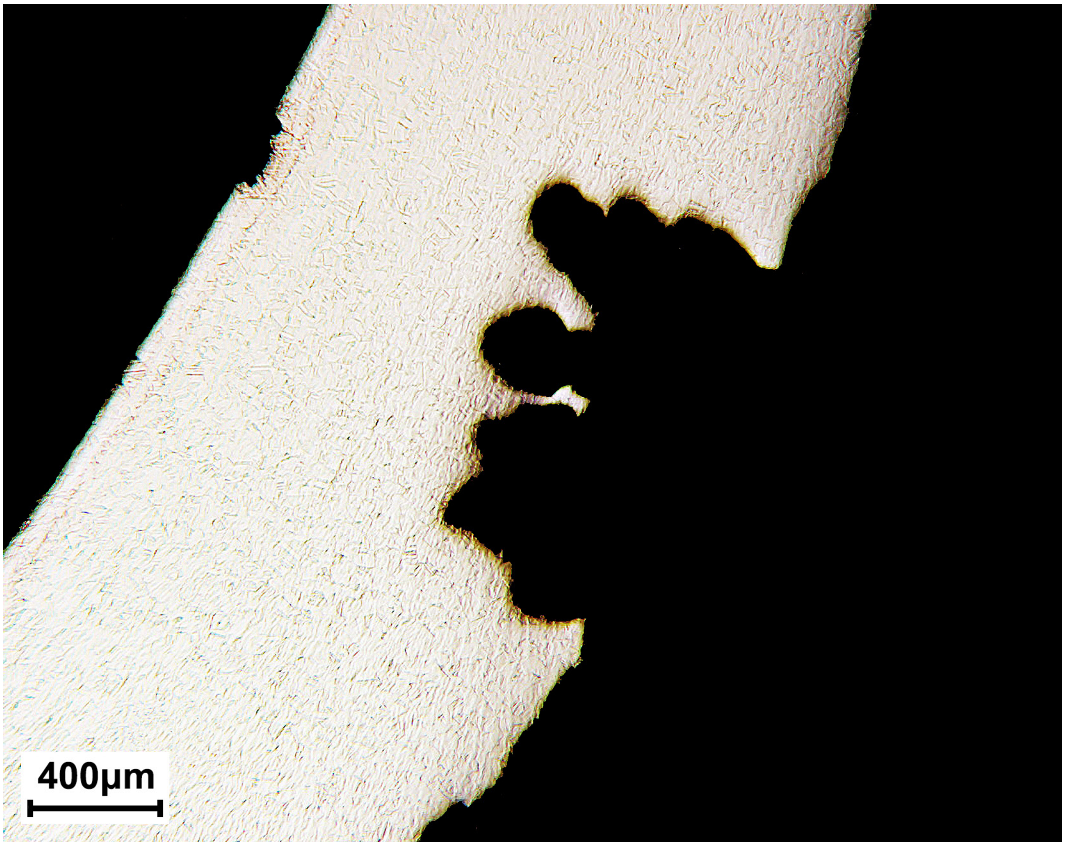
Metallographic etching: Oxalic acid (electrolytic etching)

Pitting corrosion in stagnant freshwater; temperature ~60°C

Pitting with multiple cavities

Homogeneous austenitic grains

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



Piping

Austenitic stainless steel grade EN X5CrNi18-10 (similar to AISI 304)

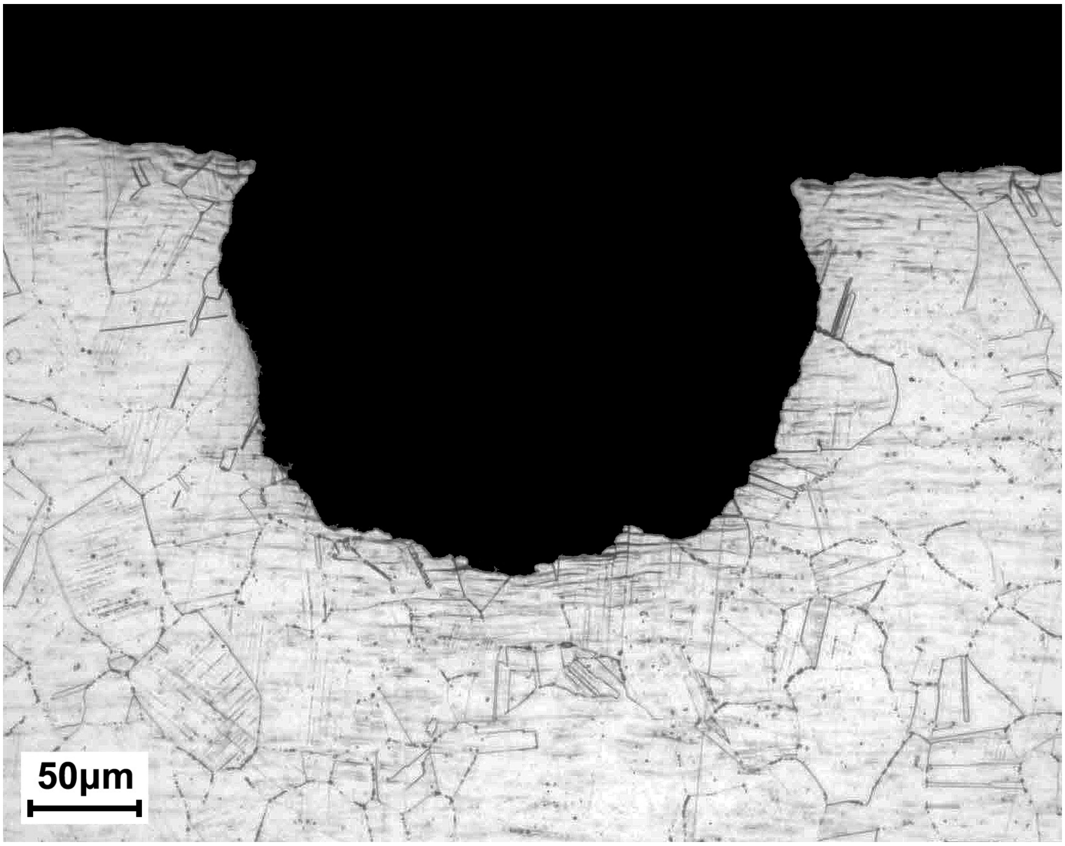
Metallographic etching: Oxalic acid (electrolytic etching)

Pitting corrosion in stagnant freshwater; temperature ~60°C

Pitting with multiple cavities

Homogeneous austenitic grains

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



Piping for heat exchanger

Austenitic stainless steel grade EN X5CrNiMo17-12-2 (similar to AISI 316)

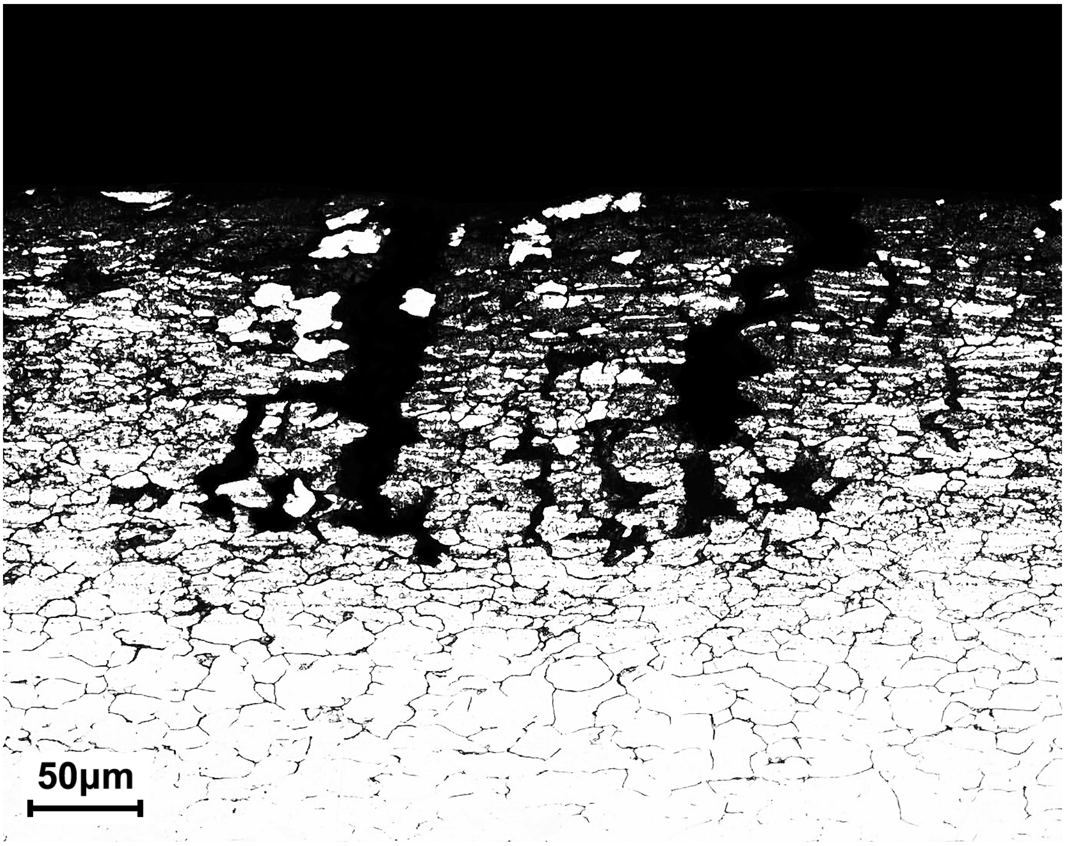
Metallographic etching: Oxalic acid (electrolytic etching)

Pitting corrosion in sea water; temperature ~50°C

Detail of a rounded pit

Homogeneous austenitic grains

Source: Omeco S.r.l. Laboratories, Monza – Monza Brianza



Welding joint on piping

Austenitic stainless steel grade EN X5CrNi18-10 (similar to AISI 304)

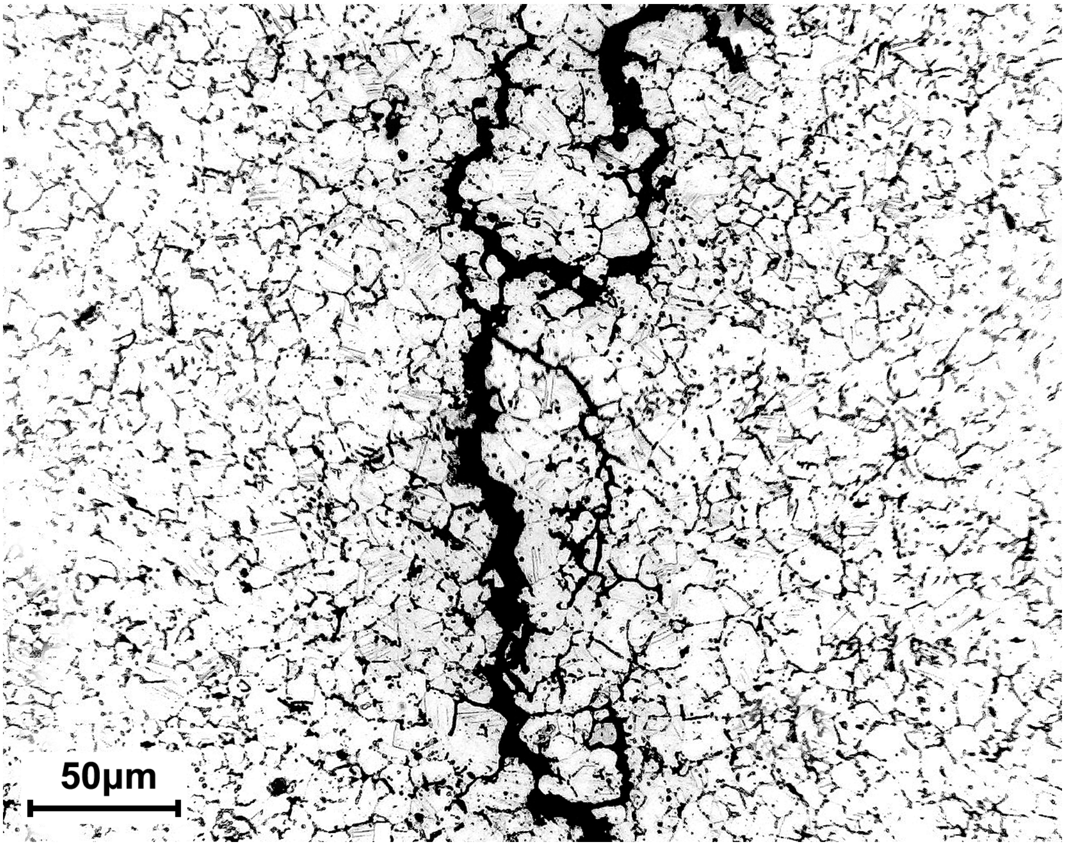
Metallographic etching: Oxalic Acid (electrolytic etching)

Intergranular corrosion in water solution (*pH* 5.5); temperature ~20°C

Multi-branched intergranular cracks

Homogeneous austenitic grains with carbide precipitation at grain boundaries

Source: Omeco S.r.l. Laboratories, Monza – Monza Brianza



Gas check valve

Austenitic stainless steel grade EN X5CrNi18-10 (similar to AISI 304)

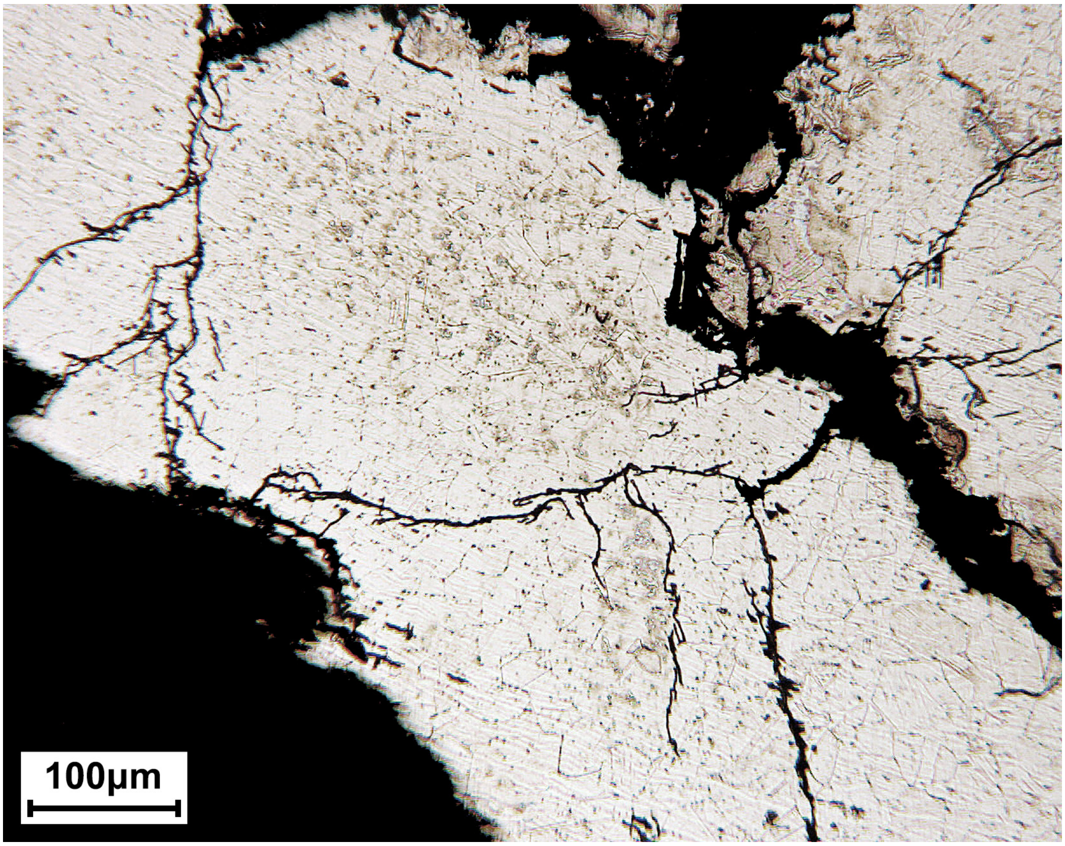
Metallographic etching: Oxalic Acid (electrolytic etching)

Intergranular corrosion in high humidity atmosphere; temperature ~20°C

Multi-branched intergranular cracks

Homogeneous austenitic grains with carbide precipitation at grain boundaries

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



Piping

Austenitic stainless steel grade EN X5CrNi18-10 (similar to AISI 304)

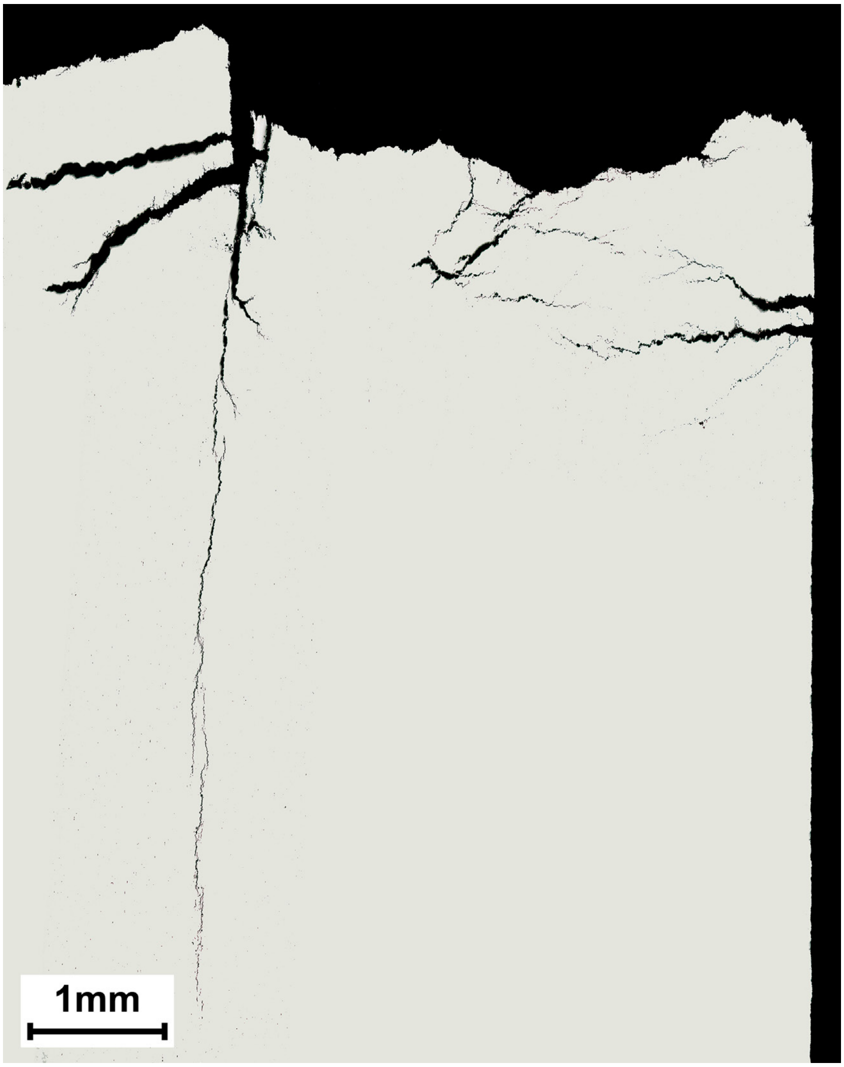
Metallographic etching: Oxalic Acid (electrolytic etching)

Stress corrosion cracking in water-based solutions containing chlorides; temperature ~80°C

Multi-branched intergranular cracks

Homogeneous austenitic grains with carbide precipitation at grain boundaries

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



Connecting bolt of a forked collar socket

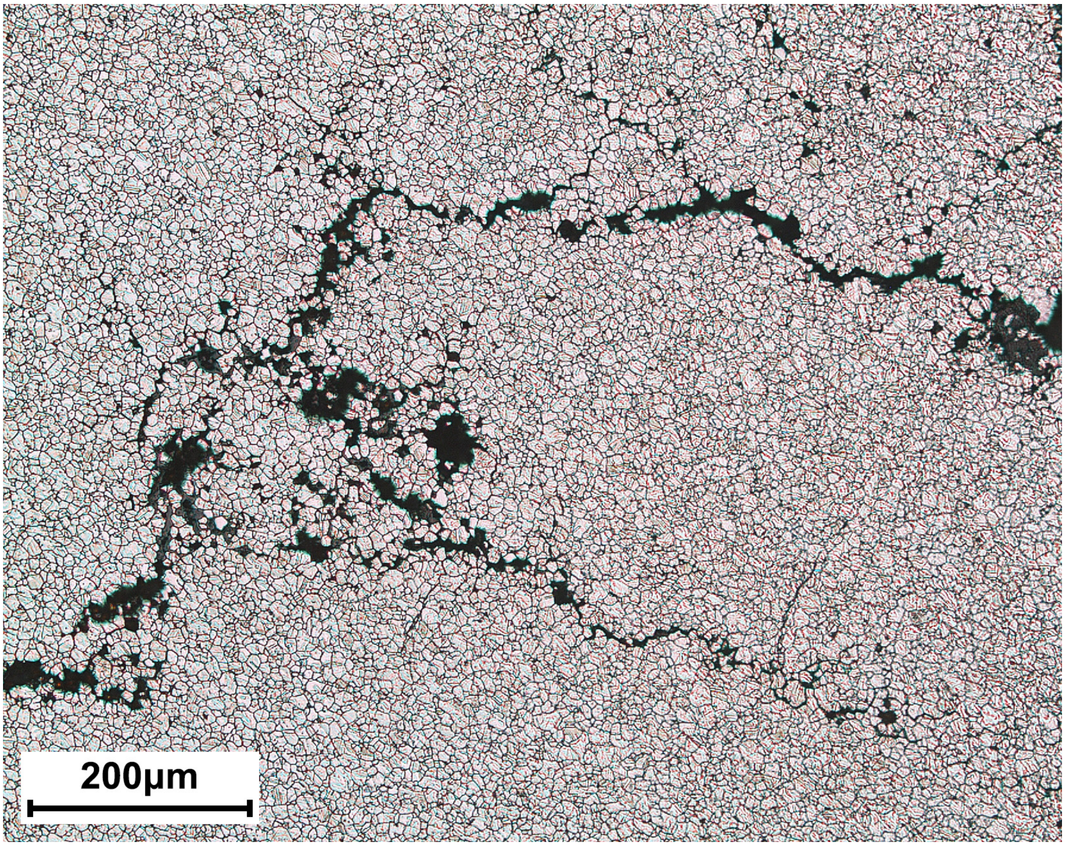
Austenitic stainless steel grade EN X10CrNi18-8 (similar to AISI 301)

Sample after polishing (without etching)

Stress corrosion cracking in high humidity atmosphere containing chlorides; temperature ~40°C

Multi-branched intergranular cracks

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



Details of the previous sample at higher magnification (after etching)

Austenitic stainless steel grade EN X10CrNi18-8 (similar to AISI 301)

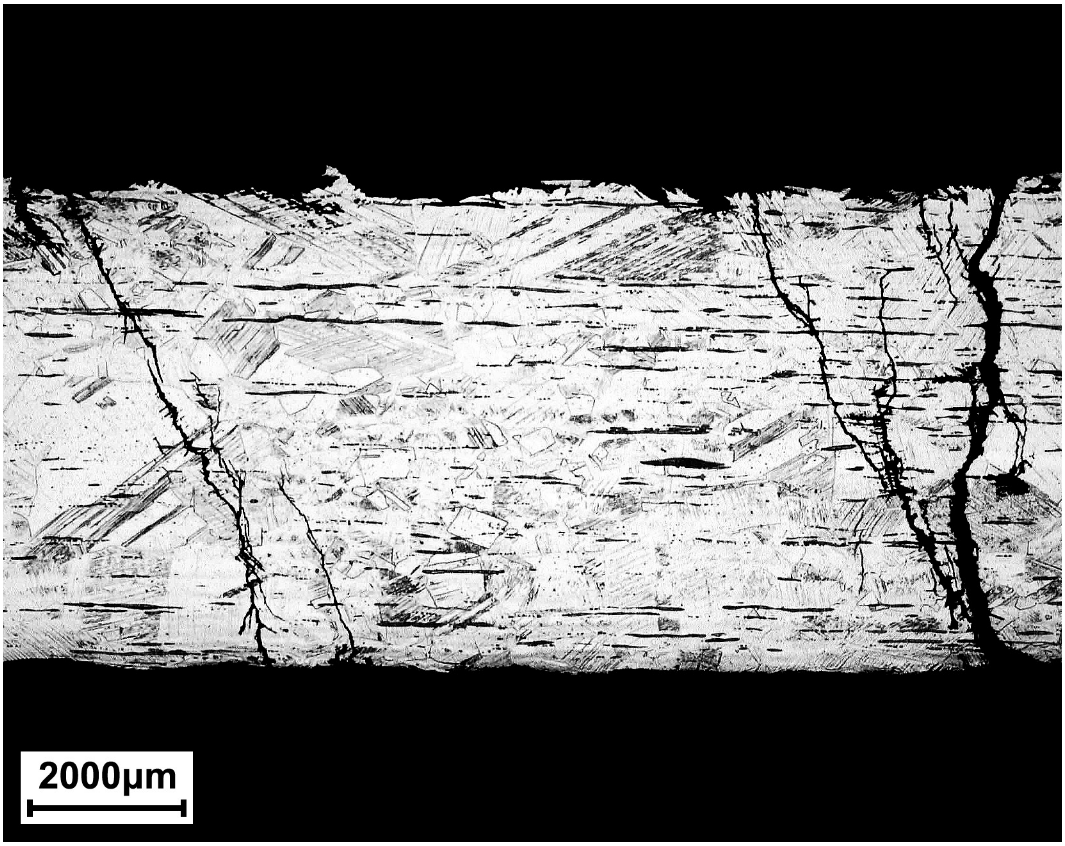
Metallographic etching: Oxalic Acid (electrolytic etching)

Stress corrosion cracking in high humidity atmosphere containing chlorides; temperature ~40°C

Multi-branched intergranular cracks

Homogeneous austenitic grains with carbide precipitation at grain boundaries

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



Piping

Austenitic stainless steel grade EN X8CrNiS18-9 (similar to AISI 303)

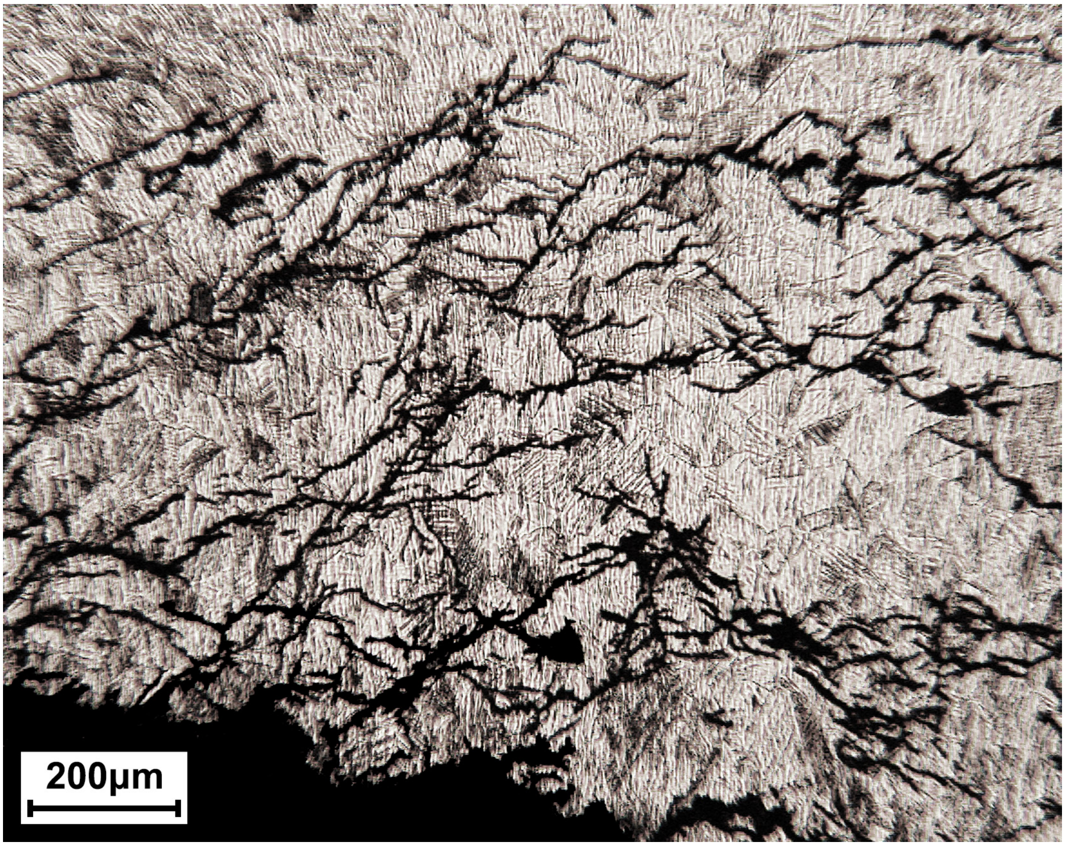
Metallographic etching: Oxalic Acid (electrolytic etching)

Stress corrosion cracking in water-based solutions containing chlorides; temperature 80°-100°C

Multi-branched intergranular cracks

Homogeneous austenitic grains

Source: Omeco S.r.l. Laboratories, Monza – Monza Brianza



Fixing screw

Austenitic stainless steel grade EN X5CrNi18-10 (similar to AISI 304)

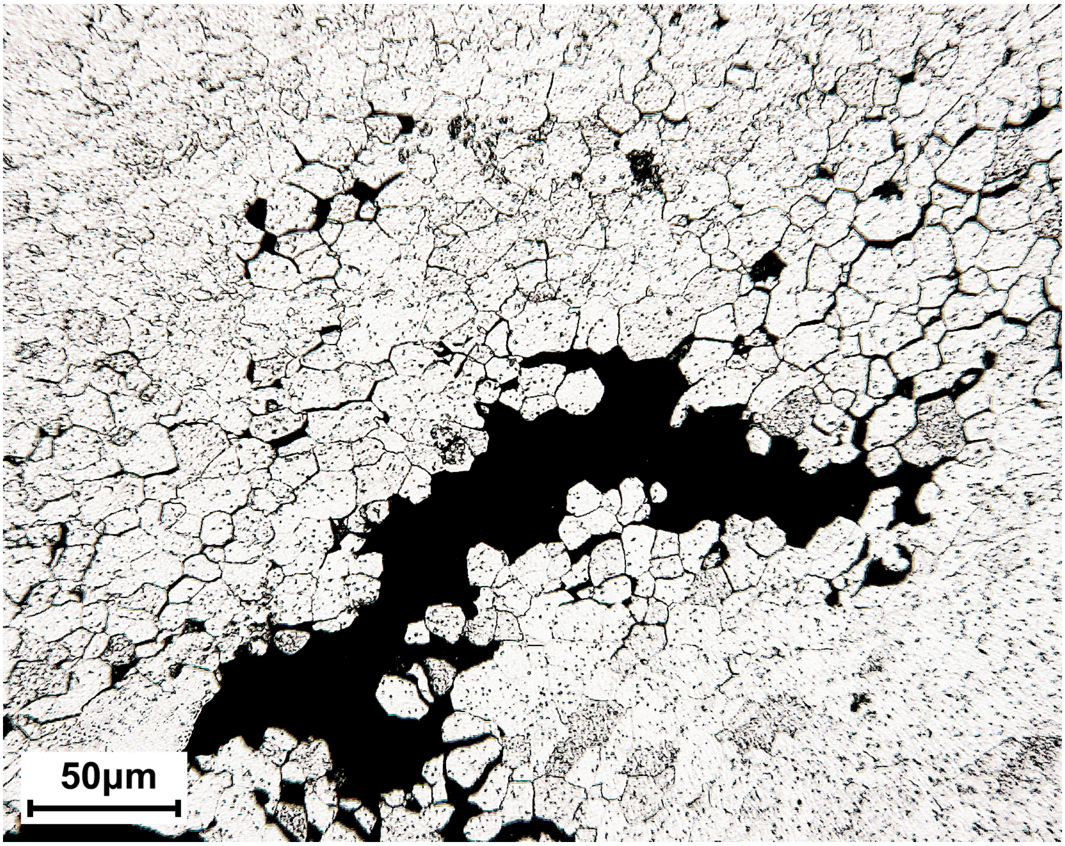
Metallographic etching: Oxalic Acid (electrolytic etching)

Stress corrosion cracking in water-based solutions containing chlorides; temperature 50°-90°C

Multi-branched intergranular cracks

Strain-hardened austenitic grains

Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano



Washing machine drum

Ferritic stainless steel grade EN X6Cr17 (similar to AISI 430)

Metallographic etching: Vilella

Stress corrosion cracking in water-based solution containing chlorides; temperature 90°C

Multi-branched intergranular cracks

Homogeneous ferritic grains

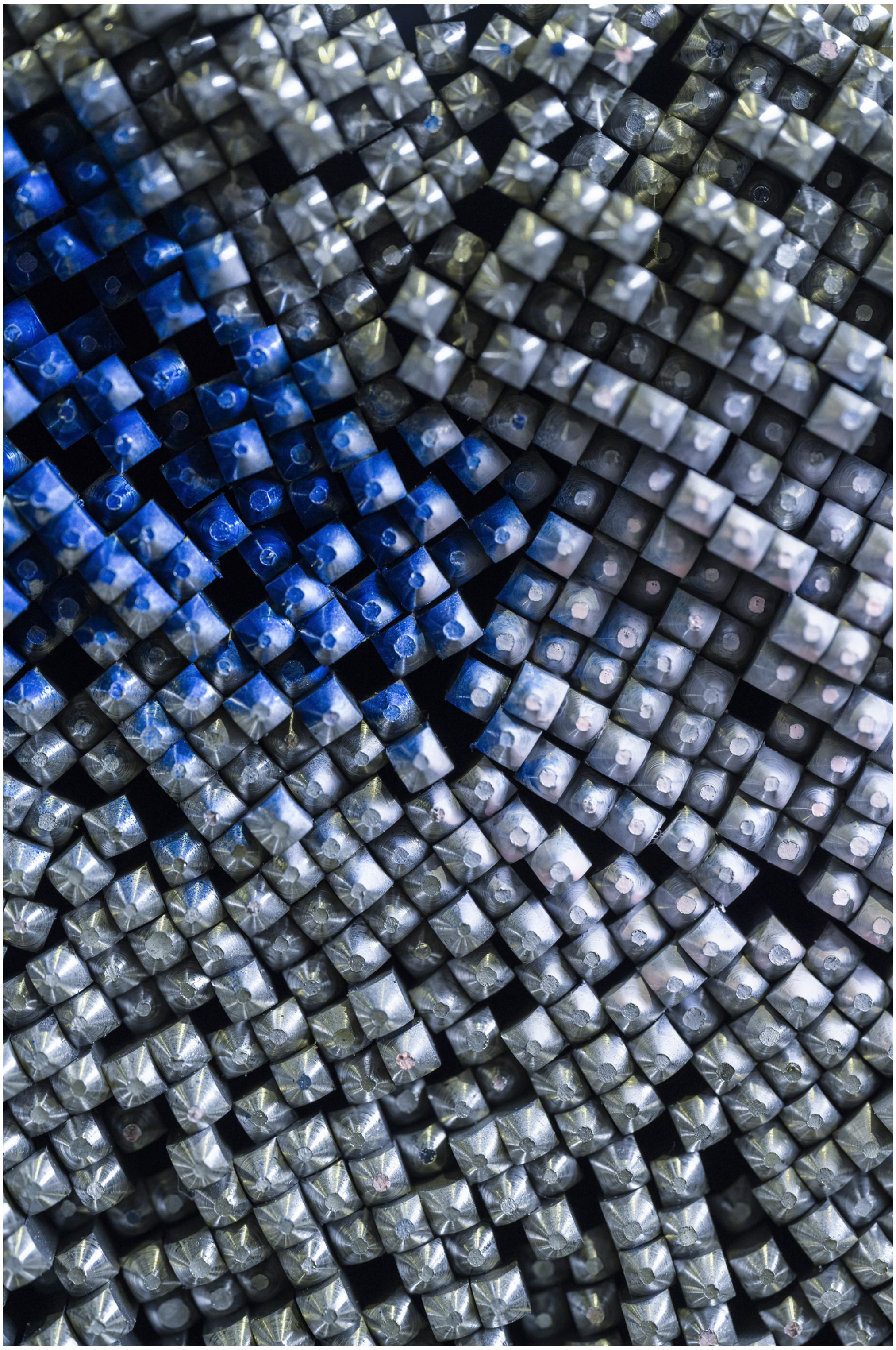
Source: Laboratories of the Department of Mechanical Engineering, Politecnico di Milano – Milano

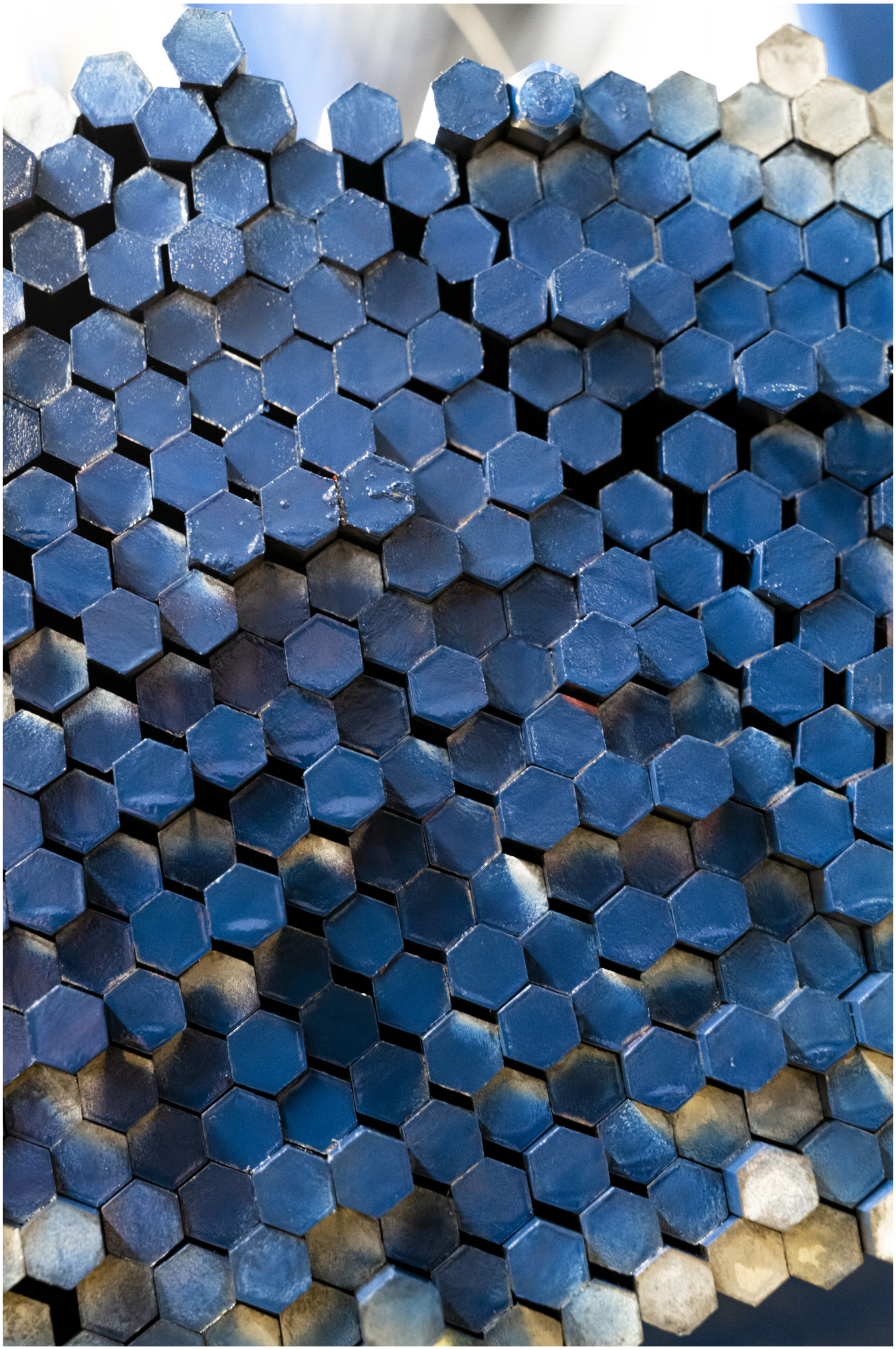
Santa Caterina del Sasso Hermitage , Leggiuno - Varese - repair work

Tie rod in austenitic stainless steel and frame in galvanized carbon steel

Galvanic corrosion; temperature range 0°-30°C

Source: Marco Boniardi





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Marco V. Boniardi (Milano, 1964)

Full Professor of Metallurgy with the Department of Mechanical Engineering at Politecnico di Milano. For more than thirty years he has been involved in research and technological transfer activities in the sectors of Metallurgy and Materials Science. His main fields of interest are stainless steels, carbon and alloy steels, heat treatments and thermochemical treatments, fatigue, fracture mechanics, corrosion, steel production and transformation processes. In addition to standard issues in the sector of Metallurgy, his competence also includes fires, explosions and forensic ballistics. Author of more than 130 scientific publications, he cooperates with a number of Italian and international companies as regards forensic engineering, failure analysis and malfunctions during operation. He has also provided expert testimony in incidents widely covered by the media (such as the Viareggio train derailment and the Costa Concordia wreckage). He is the coordinator of the Failure Analysis & Forensic Engineering course that is held every two years.
Together with Andrea Casaroli he is the founder of the website **www.fa-fe.com**.

Andrea Casaroli (Piacenza, 1984)

Adjunct Professor of Metallurgy and Machine Design with the Department of Mechanical Engineering at Politecnico di Milano, and of Metallurgy at the University of Pavia. For more than ten years he has been involved in research activities in the metallurgical field as regards stainless steels, carbon and alloy steels, functional coatings and mechanical behaviour of materials. He also deals with failure analysis and industrial accidents and has acquired extensive expertise in fire investigations and fire resistance of materials. Author of more than 30 scientific publications, he cooperates with Italian and international companies in solving problems connected with mechanical failure, corrosion, fatigue and malfunctioning of industrial components and plants.
Together with Marco V. Boniardi he is the founder of the website **www.fa-fe.com**.

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