

Cr-Ni grades

The Cr-Ni grades are "general purpose grades" mainly alloyed with chromium and nickel, but with no molybdenum. These grades are sometimes referred to as 18-8 type of stainless steels, indicating the approximate chromium and nickel content respectively.

Some grades are alloyed with nitrogen to improve the strength, or with sulphur to improve machinability. There are also stabilized grades where titanium or niobium is added to increase the mechanical properties at high temperatures by the formation of hardening carbides. Earlier, titanium and niobium stabilisation was also used to avoid detrimental carbide precipitates on welding, but for modern low-carbon Cr-Ni steels this is not necessary.

Cr-Mn grades

In the Cr-Mn grades, also referred to as "200-series" grades following the AISI/ASTM nomenclature, the nickel content is decreased and the austenitic microstructure is maintained by replacing some of the nickel with manganese and nitrogen. The chemical composition of grade 4372 is around 17 % Cr, 4 % Ni and 7 % Mn. This grade has almost the same formability, corrosion resistance and weldability as grade 4301, but with higher strength.

Cr-Ni-Mo

These are also "general purpose grades", but with increased corrosion resistance owing to alloying with molybdenum (2–3 %), and are sometimes referred to as "acid-proof" type of stainless steels. The chromium content is around 17 % and the nickel content 10–13 %.

Some grades are alloyed with nitrogen to improve the strength, or with sulphur to improve machinability. There are also stabilized grades where titanium or niobium is added to increase the mechanical properties at high temperatures by the formation of hardening carbides. Earlier, titanium and niobium stabilisation was also used to avoid detrimental carbide precipitates on welding, but in modern, low carbon Cr-Ni-Mo steels this is not necessary.

High performance austenitics

The high performance austenitic stainless steels were developed for use in very demanding environments and have even higher alloying content. The chromium content varies between 17 and 25 %, nickel between 14 and 25 % and molybdenum between 3 and 7 %. Many of the grades are also alloyed with nitrogen to further increase the corrosion resistance and strength. Some grades are alloyed with copper to increase the resistance to certain acids.

The austenitic grades 254 SMO® and 4529 are sometime referred to as 6Mo superaustenitic grades, and 654 SMO® as a 7Mo superaustenitic grade.

High temperature austenitic grades

The high temperature austenitic stainless steels are designed primarily for use at temperatures exceeding 550 °C, i.e. in the temperature range where creep strength is the dimensioning factor. The compositions of these steels are designed to provide a long service life in dry gases at high temperatures (800–1150 °C), i.e. good oxidation resistance rather than resistance to aqueous corrosion.

The high temperature austenitic grades are characterised by high chromium (17–25 %) and high nickel (8–20 %) content but containing no molybdenum. Silicon is added in some grades to increase the oxidation resistance. The Outokumpu MA grades are alloyed with silicon and also with cerium to further increase the resistance to oxidation, and with nitrogen to improve the creep strength.

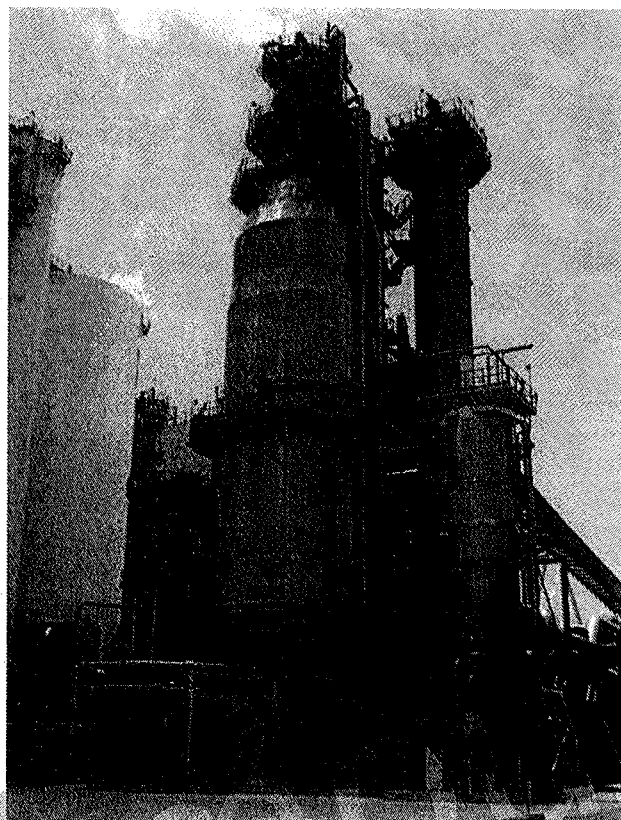


Figure 2:6. Continuous digester at Veracel in Brazil made in duplex 2205.

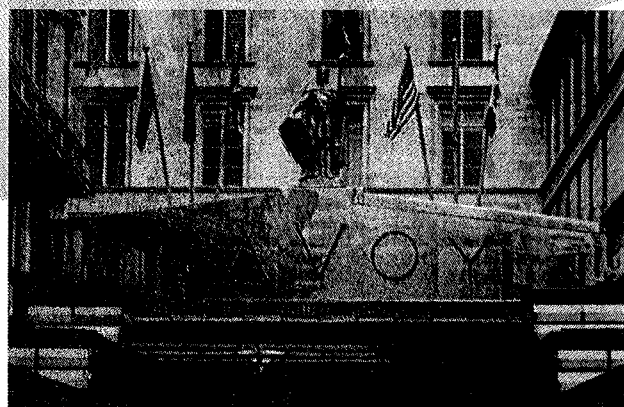


Figure 2:7. Savoy Hotel, London. The sign, made of standard austenitic Cr-Ni type of stainless steel with a polished surface, was completed in 1929.

The effects of alloying elements

The different alloying elements have specific effects on the properties of the stainless steel. It is the combined effect of all the alloying elements, heat treatment and to some extent, the impurities that determine the property profile of a certain steel grade. In order to understand why different grades have different compositions a brief overview is given of the main alloying elements and their effects on the microstructure and properties. The effects on important material properties are discussed in more detail in the later chapters. It should be noted that the effect of the alloying elements differs in some aspects between the different categories of stainless steels.



Figure 2:8. Lloyd's Building, London, completed 1986. Cladding in the austenitic Cr-Ni-Mo stainless steel 316 with HyClad® Linen surface finish.

Chromium (Cr)

This is the most important alloying element and it gives stainless steels their basic corrosion resistance. All stainless steels have a Cr-content of at least 10.5% and the corrosion resistance increases with increasing chromium content. Chromium also increases the resistance to oxidation at high temperatures and promotes a ferritic microstructure.

Nickel (Ni)

The main reason for the nickel addition is to promote an austenitic microstructure. Nickel generally increases ductility and toughness. It also reduces the corrosion rate in the active state and is thus advantageous in acid environments. In precipitation hardening steels nickel is also used to form the intermetallic compounds that are used to increase the strength. In martensitic grades nickel addition combined with lowered carbon content improves the weldability.

Molybdenum (Mo)

Molybdenum significantly increases the resistance to both uniform and localised corrosion. It somewhat increases the mechanical strength and strongly promotes a ferritic microstructure. However,

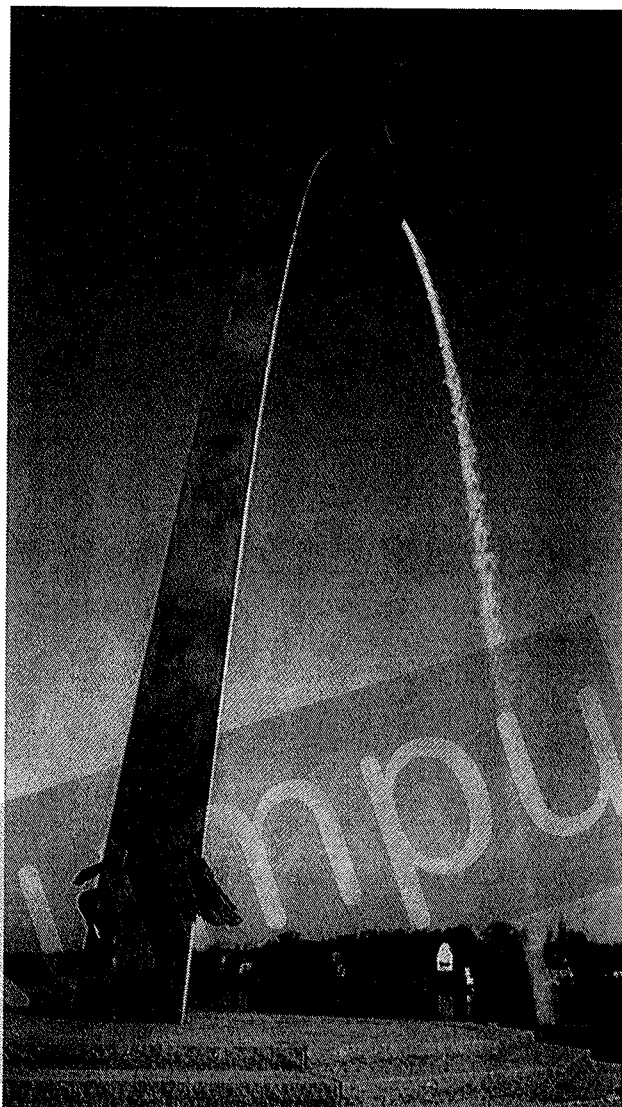


Figure 2:9. The sculpture "God our father, on the Rainbow", Nacka Strand, Stockholm, Sweden. Sculpture designed by Carl Milles, made in the superaustenitic grade 254 SMO®.

molybdenum also enhances the risk for the formation of secondary phases in ferritic, duplex and austenitic steels. In martensitic steels it will increase the hardness at higher tempering temperatures due to its effect on the carbide precipitation.

Copper (Cu)

Copper enhances the corrosion resistance in certain acids and promotes an austenitic microstructure. It can also be added to decrease work hardening in grades for improved machinability. It may also be added to improve formability.

Manganese (Mn)

Manganese is generally used in stainless steels in order to improve hot ductility. Its effect on the ferrite/austenite balance varies with temperature: at low temperature manganese is an austenite stabiliser but at high temperatures it will stabilise ferrite. Manganese increases the solubility of nitrogen and is used to obtain high nitrogen contents in duplex and austenitic stainless steels. Manganese, as an austenite former, can also replace some of the nickel in the stainless steel.

Silicon (Si)

Silicon increases the resistance to oxidation, both at high temperatures and in strongly oxidising solutions at lower temperatures. It promotes a ferritic microstructure and increases the strength.

Carbon (C)

Carbon is a strong austenite former that also significantly increases the mechanical strength. However, it also reduces the resistance to intergranular corrosion caused by carbide formation, which was a problem in the early stainless steels. The modern grades do not suffer from intergranular corrosion due to the low carbon content. In ferritic stainless steels carbon will strongly reduce both toughness and corrosion resistance. In the martensitic steels carbon increases hardness and strength, but decrease the toughness.

Nitrogen (N)

Nitrogen is a very strong austenite former that also significantly increases the mechanical strength. Nitrogen increases the resistance to localised corrosion, especially in combination with molybdenum.

In ferritic stainless steels nitrogen will strongly reduce toughness and corrosion resistance. In the martensitic steels nitrogen increases both hardness and strength but reduces the toughness.

Titanium (Ti)

Titanium is a strong ferrite former and a strong carbide former, thus lowering the effective carbon content and promoting a ferritic structure in two ways. In austenitic steels with increased carbon content it is added to increase the resistance to intergranular corrosion (stabilised grades) but it also increases the mechanical properties at high temperatures. In ferritic stainless steels titanium is added to improve toughness, formability and corrosion resistance. In martensitic steels titanium lowers the martensite hardness by combining with carbon and increases the tempering resistance. In precipitation hardening steels titanium is used to form the intermetallic compounds that are used to increase the strength.

Niobium (Nb)

Niobium is both a strong ferrite and carbide former. Like titanium it promotes a ferritic structure. In austenitic steels it is added to improve the resistance to intergranular corrosion (stabilised grades) but it also enhances mechanical properties at high temperatures. In ferritic stainless steels niobium and/or titanium is sometimes added to improve toughness and to improve resistance to sensitization to minimize the risk for intergranular corrosion. In martensitic steels niobium lowers the hardness and increases the tempering resistance. In the US it is designated Columbium (Cb).

Aluminium (Al)

Aluminium improves oxidation resistance, if added in substantial amounts. It is used in certain heat resisting grades for this purpose. In precipitation hardening steels aluminium is used to form the intermetallic compounds that increase the strength in the aged condition.

Cobalt (Co)

Cobalt is used as an alloying element in martensitic steels where it increases the hardness and tempering resistance, especially at higher temperatures.

Vanadium (V)

Vanadium forms carbides and nitrides at lower temperatures, promotes ferrite in the microstructure, and increases the toughness. It increases the hardness of martensitic steels due to its effect on the type of carbide present. It also increases tempering resistance. It is only used in hardenable stainless steels.

Tungsten (W)

Tungsten is present as an impurity in most stainless steels although some special grades have additions for improving pitting corrosion resistance, e.g. the superduplex grade 4501.

Sulphur (S)

Sulphur is added to certain stainless steels, the free-machining grades, in order to increase the machinability. At the levels present in these grades sulphur will slightly reduce corrosion resistance, ductility, weldability and formability. At Outokumpu the trademark PRODEC® (PRODUCTION Economy) is used for some grades with balanced sulphur levels to improve machinability. Lower levels of sulphur can be added to decrease work hardening in grades for improved formability. Slightly increased sulphur content also improves the weldability of the steel.

Cerium (Ce)

Cerium is one of the rare earth metals (REM) and is added in small amounts to certain heat resisting grades in order to increase the resistance to oxidation at high temperature.

Effect on microstructure

The effect of the alloying elements on the microstructure of stainless steels is summarised in the empirical Schaeffler DeLong diagram (Figure 2:10). The diagram is based on the fact that the alloying elements can be divided into ferrite-stabilisers and austenite-stabilisers. This means that they favour the formation of either ferrite or austenite in the microstructure. If the austenite-stabilisers ability to promote the formation of austenite is related to that for nickel, and the ferrite-stabilisers likewise compared to chromium, it becomes possible to calculate the total ferrite and austenite stabilising effect of the alloying elements in the steel. This gives the so-called chromium and nickel equivalents in the Schaeffler DeLong diagram:

$$\text{Nickel equivalent} = \%Ni + 0.5 \times \%Mn + 30 \times (\%C + \%N)$$

$$\text{Chromium equivalent} = \%Cr + \%Mo + 1.5 \times \%Si + 0.5 \times \%Nb$$

In this way it is possible to take the combined effect of alloying elements into consideration. The Schaeffler DeLong diagram was originally developed for weld metal, i.e. it describes the structure after melting and rapid cooling but it has also been found to give a useful preview of the effect of the alloying elements for wrought and annealed material. However, annealed steels with predicted ferrite contents in the range 0–5% according to the diagram contain in practice smaller amounts of ferrite.

It should also be mentioned that the Schaeffler DeLong diagram is not the only diagram for assessment of ferrite contents and structure of stainless steels. Several different diagrams have been published, all with slightly different equivalents, phase limits or general layout. The WRC-92 diagram developed through collaboration in the international welding community is widely used.

Physical metallurgy

Phase transformations in stainless steels

Stainless steels are designed by carefully balancing the alloying elements so that an appropriate microstructure is maintained during processing and the required final structure and properties are achieved by heat treatment. Inappropriate heat treatment, service at high temperatures or welding can, however, lead to the formation of other phases. These may be thermodynamically stable or kinetically favoured in lower temperature regimes and can have a major influence on mechanical properties and corrosion resistance.

Solidification and solid state transformations

As a stainless steel solidifies from the melt, dendrites are formed when the temperature drops below the liquidus, Figure 3:1. These may be austenite (which has an fcc structure) or ferrite (which has a bcc structure) depending on the composition of the steel, see Figure 3:6). For some steel compositions the other phase may also solidify directly from the melt, giving rise to a solidification structure denoted AF or FA depending on whether the first solidifying phase is austenite or ferrite respectively. This situation, with two phases forming from the melt, is denoted peritectic solidification and is often desirable in austenitic grades, because the small amount of ferrite has a higher solubility for impurities such as sulphur and phosphorus and can therefore counteract a tendency to hot cracking. Figure 3:2 shows the calculated phase fractions as a function of temperature for the superaustenitic grade 254 SMO®, which shows primary austenite solidification with a small amount of ferrite. In order to obtain an austenitic structure but avoid the precipitation of intermetallic phases, a final annealing process is done at 1000–1200 °C, with the higher temperatures being used for higher alloyed grades.

Below the solidus, further transformations occur in the solid state. An important example is the formation of austenite in duplex grades which have a primary ferritic solidification mode. This is illustrated in Figure 3:2 for the duplex grade 2205, which solidifies ferritically and then undergoes solid state transformation. The austenite forms both along grain boundaries and in a so-called Widmanstätten pattern within the ferrite grains as seen in the microstruc-

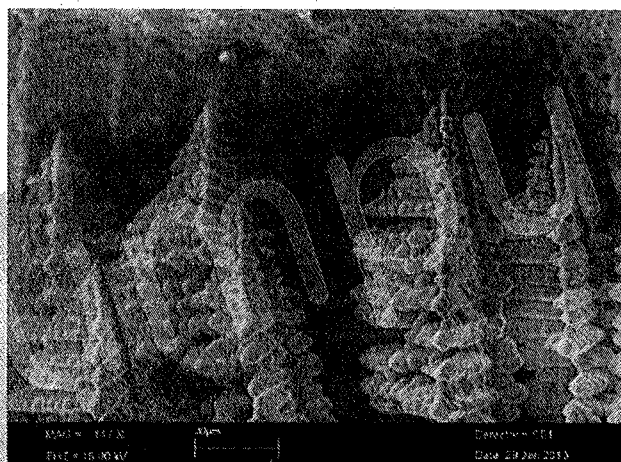


Figure 3:1. Solidification structure showing dendrites which have grown into the melt.

ture in Figure 3:3. The final microstructure after annealing contains approximately equal fractions of austenite and ferrite. In order to achieve the correct phase balance it is important that duplex stainless steels are annealed within a fairly narrow temperature window, typically 950–1120 °C.

Ferritic grades show ferritic solidification and are annealed at lower temperature, typically 750–1000 °C, to avoid ferrite grain growth. For some grades, particularly those which are not stabilized, there is a risk of partial austenitisation, and subsequent martensite formation on quenching, if the annealing temperature is too high.

In martensitic steels, the austenite begins to transform to martensite on quenching below the temperature denoted M_s (martensite start). Some martensite can also form in so-called metastable-austenitic, and recently also in duplex grades, where it is promoted by deformation. This process is typically characterized by the M_{d30} temperature, at which 30% deformation (strictly speaking a true strain of 0.3) gives 50% martensite. Various empirical formulae exist to describe the effect of composition on M_{d30} (in °C), one of the most common is that developed by Nohara which also takes the effect of grain size into account:

$$M_{d30} = 552 - 462(C+N) - 9.2Si - 8.1Mn - 13.7Cr - 29(Ni+Cu) - 18.5Mo - 68Nb + 1.42(ASM-8)$$