NICKEL IN STAINLESS STEELS

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Abstract

Nickel is widely used as an alloying element in many stainless steels but the recent increased raw material cost has encouraged users to look at lower nickel or nickel-free alloys. However, initial cost is not the only issue – service performance over the life of a component is much more significant to the user. This paper looks at the rôle of nickel and how it contributes to fabricability, toughness, corrosion resistance and high temperature strength.

The process of material selection to achieve the desired combination of economic and other performance characteristics over the full life cycle of a product is examined. To have maximum confidence in the outcome of the selection, it is necessary to have both good data on the alloys and also a history of service performance. However, the final material choice is a balance of many factors including availability, fabricability and environmental benefits.

Case studies illustrate potential material choices and demonstrate how nickel continues to be an important alloying element, giving cost-effective service.

Metallurgy

Chromium is the key alloying element which makes stainless steels "stainless". More than 10.5% needs to be added to steel to allow the protective oxide film to form which provides the corrosion resistance and bright, silvery appearance. In general, the more chromium which is added, the greater the corrosion resistance. That discovery was made about a century ago yet even some of those early stainless steels also contained nickel. Today about two thirds of the tonnage of stainless steel produced each year contains nickel, even though nickel is an expensive alloying addition. What is the rôle of nickel and why is it used so extensively?

Metals with an austenitic (face centred cubic) crystal structure are particularly tough and ductile. Aluminium, copper and nickel itself are good examples. Nickel is an austenite forming alloying addition which can produce stainless steels having an austenitic structure, stable at room temperature, see Figure 1.

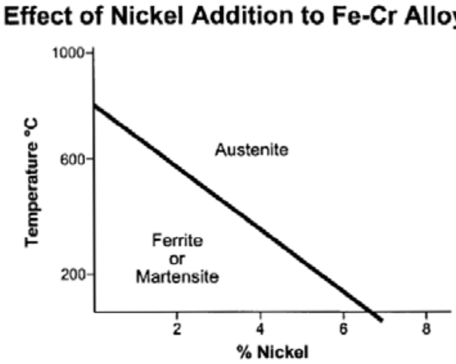

Figure 1. The effect of nickel.[1]

Austenitic stainless steels have a particularly attractive combination of properties. That is the primary reason for adding nickel and gives rise to the most common grade of stainless steel in use today, Type 304, often referred to as “18/8” since it has the approximate composition 18 % chromium and 8 % nickel.

There are other alloying elements which are austenite formers, most notably carbon, nitrogen, manganese and copper. The relative effectiveness of them as austenite formers can be seen in the expression:

$$\text{Nickel equivalent} = \text{Ni\%} + 30\text{C\%} + 30\text{N\%} + 0.5\text{Mn\%} + 0.3\text{Cu\%} \quad \text{(by weight)}$$

Manganese was first used as an addition to stainless steel in the 1930’s. The 200-series of low nickel, austenitic grades was developed further in the 1950’s when the cost of using nickel was particularly high.[2] More recent improvements in melting practices have allowed the controlled addition of increased amounts of nitrogen – a potent austenite former. However, all the low nickel austenitic grades commercially available today still contain some deliberate additions of nickel.[3] An important feature of these grades is that the reduction in nickel content cannot be completely replaced by manganese and nitrogen, with the result that the chromium content must also be reduced in order to maintain the austenitic structure. As we will see below, this side effect reduces the corrosion resistance of these alloys compared with the standard 300-series nickel grades.

One feature of all the austenitic grades is that they are not ferromagnetic at room temperature – except sometimes when cold-worked. This is of advantage in some applications where magnetism is undesirable. But a further significant benefit is that austenitic end-of-life scrap can readily be segregated by simple magnetic separation. Nickel is the most valuable element which is being recycled and, when the majority of austenitic stainless steels were 300-series, their recycling was simple. However, when 200-series scrap is mixed in with 300-series, recycling of the valuable nickel component is more complex.[3]

As the total content of austenite formers is reduced, the structure changes from austenite to a mixture of austenite and ferrite (body centred cubic). These are the duplex stainless steels. All the commercially important duplex grades, even the “lean duplexes”, contain about 1% or more nickel as a deliberate addition. Most duplex stainless steels have higher chromium contents than the standard austenitic grades. Compared with the overall composition, the ferrite phase is enriched in ferrite-stabilising elements, and the austenite phase is enriched in the austenite-stabilising elements. The austenite phase may have 6-10% less chromium than the overall value, and be enriched in nickel by 20%-40%. There is some minimum nickel content necessary to ensure solubility of these levels of chromium: the higher the mean chromium level, the higher the minimum nickel content must be. This is similar to the case for the 200-series noted above.

With the ferritic stainless steels, nickel is known to lower the ductile-to-brittle transition temperature (DBTT), i.e. the temperature at which the alloy becomes brittle. Chromium has the opposite effect, and some of the superferritic alloys can easily have a DBTT well above 20 °C. The DBTT is also a function of other factors such as grain size and other alloying additions. Some of the superferritic grades contain an intentional addition of nickel to improve the DBTT, especially of welds.

The martensitic grades are hardenable by heat treatment. Some contain nickel which not only improves toughness but also allows a higher chromium content giving increased corrosion resistance.

Finally, the precipitation hardening grades can develop very high strength by heat treatment. There are various families of PH grades but all are nickel-containing.

Formability

The face centred cubic metal structure of the nickel austenitic stainless steels gives them good tensile ductility and very good formability, as reflected in comparative forming limit diagrams. The common 18%Cr, 8%Ni grade shows particularly good stretch forming characteristics but has a somewhat lower limiting drawing ratio than some ferritic grades. Slightly higher nickel contents increase the stability of the austenite further and reduce the work hardening tendency, so increasing suitability to deep drawing. Unlike the low nickel, high manganese grades, they are not prone to delayed cold cracking.[3] This good formability has led to the widespread use of 300-series austenitic grades for items with demanding formability such as kitchen sinks, pots and pans.

Figure 2. Deep drawn double sink, courtesy, Stala.

Weldability

Many pieces of equipment have to be fabricated by welding. There are significant differences in weldability between stainless grades of any particular structural family, especially between low alloyed and high alloyed grades. However in general, the nickel austenitic grades have better weldability than other types.[4] Unlike the ferritic grades, they are not prone to embrittlement as a result of high temperature grain growth and the welds have good bend and impact properties. They are also more weldable in thick sections – say above 2 mm.

Whilst the austenitic grades have lower thermal conductivity and higher thermal expansion than other grades, these differences can be accommodated by suitable fabrication practices. As a

result, nickel-containing grades such as Types 304 and 316 are the most widely fabricated stainless steels around the world.
The duplex grades are far more weldable than the ferritic grades for equivalent alloy content, but even the standard and superduplexes require more attention to the details of the welding procedure than the equivalent austenitic grades. The 200-series alloys have welding characteristics most similar to the 300-series alloys.

Toughness

Toughness – the ability of a material to absorb energy without breaking - is essential in many engineering applications. Most stainless steels have good toughness at room temperature but with decreasing temperature, the ferritic structure becomes progressively more brittle so that ferritic stainless steels are not suitable for use at cryogenic temperatures. In contrast, the common austenitic stainless steels retain good toughness even to liquid helium temperatures, so grades such as Type 304 are widely used for cryogenic applications.

High Temperature Properties

The addition of nickel provides the austenitic grades with significantly better high temperature strength – particularly the ability to resist creep – than other grades. These grades are also much less prone to embrittlement at room temperature as a result of exposure at intermediate and high temperatures which may cause the formation of deleterious phases. Nickel also promotes the stability of the protective oxide film and reduces spalling during thermal cycling. Consequently, the austenitic grades are used for high temperature applications and where fire resistance is needed. It is worth noting that there is a continuum in composition between the austenitic stainless steels and the nickel-based superalloys, which are used for the most demanding high temperature applications such as gas turbines.

Corrosion Resistance

As already discussed, it is the formation of the chromium-rich oxide layer which is at the heart of the corrosion resistance of stainless steels. However, particularly in the presence of chlorides, this layer is susceptible to damage which can lead to the onset of localised corrosion such as pitting and crevice corrosion. Stainless steels are often ranked for their resistance to the initiation of such localised corrosion by the Pitting Resistance Equivalent (PRE):

$$PRE = Cr\% + 3.3Mo\% + 16N\%$$

Both molybdenum and nitrogen increase resistance to pit initiation in the presence of chlorides. Nickel does not appear in the equation but nickel is important in reducing the rate at which both pitting and crevice corrosion propagate after initiation, see Figure 3.

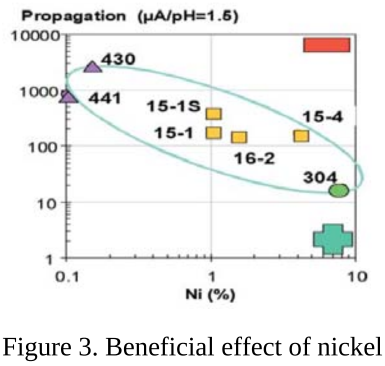

Figure 3. Beneficial effect of nickel in reducing the propagation rate of pitting and crevice corrosion.[3]

Nickel also influences the resistance of stainless steels to another form of localised corriosion, chloride stress corrosion cracking. In this case however, there is a minimum in resistance at nickel contents of around 8%: stress corrosion cracking resistance increases markedly at nickel levels which are both lower and higher than this.

In general, increasing the nickel content of stainless steels, including ferritic grades, also increases their resistance to reducing acids like sulphuric acid. Other elements such as molybdenum and particularly copper also have a strong influence in this regard.[5] However, there are potential drawbacks to using nickel in this way in the ferritic grades, related to stress corrosion cracking resistance and formation of intermetallic phases.

Lustre

At first sight, all stainless steel grades look similar. However, side-by-side comparisons of identical surface finishes do show differences in colour and lustre. Appearance and aesthetic qualities will always be a matter of taste but the 200-series grades can seem darker and the ferritic grades cooler in appearance than the nickel austenitic grades. In some architectural applications, a grayer colour might be preferred, but generally consumers prefer a brighter, whiter metal, as witnessed by the popularity of the 300-series.

Choosing the right grade

How is a design engineer to select the most appropriate grade of stainless steel from the range available? Choosing an alloy with suitable corrosion resistance for the expected service is a good starting point. That alloy should have a sufficient margin of safety to allow for excursions which might occur outside the normally expected operating conditions since an operator may want to push a plant to deliver higher throughputs by use of higher temperatures and pressures than were allowed for in the original design.

As the trend towards risk-based inspection increases, a higher corrosion resistance can be used to justify a reduced inspection frequency. The combination may lower overall cost. Process equipment downtime is often overlooked but can be a very expensive side effect of choosing an inadequate material. Furthermore, equipment failure may cause release of harmful chemicals which can have a severe human or environmental impact - with consequent legal repercussions. For all these reasons, it is rarely good practice to select a grade which is only just capable of resisting the design environment.

A conservative approach to selection for corrosion resistance can also be justified where maintenance of product purity is paramount, such as in the food and pharmaceutical industries.

For many applications, mechanical properties are not critical, for example, purely decorative architectural uses. However, when mechanical properties are an important design consideration, it may be possible to take advantage of the higher strength of cold worked austenitic grades or the duplex grades in order to reduce the total weight and hence overall cost of the material used. Lighter weight may also lead to lower installation and support structure costs.

Fabricability is an important consideration for many applications whether in buildings, chemical plant or consumer items. This may apply not just to the material characteristics but also to the level of welding skill needed. This alone may rule out less fabricable grades in some applications and it is the excellent fabrication characteristics of the austenitic stainless steels which often leads to their selection.

There are many situations where specific physical properties are required which then restricts the grades under consideration. For example, low magnetic permeability austenitic stainless steel must be used in a MRI (magnetic resonance imaging) facility.

Ready availability of material in all the necessary forms for a project can be a major consideration. That is where the established “commodity grades”, such as Types 304 and 316, can have a distinct advantage because they are stocked very widely. This is unlikely to be the case with more specialised, proprietary grades until they have become well-established. A related point is the familiarity which suppliers, fabricators and users have with the long-established, widely used grades. It is another reason why the majority of applications are still satisfied by a handful of grades.

There is increasing emphasis on selecting materials which contribute to a low environmental impact. This should be seen in a broad context, which covers not only the raw materials and end-of-life recycling credits but also the contribution to reduced environmental impact throughout the operating life of the project. For example, reduced energy consumption as a result of improvements in process efficiency may be far more important than the energy content of the raw material.

Only when the above requirements have been evaluated and satisfied should cost considerations be used to make the final material selection. And the appropriate tool to use then is full life cycle costing. Even among materials that are otherwise suitable property-wise, the least expensive initial cost material may well be a much more expensive choice in the long term. For these reasons, nickel is almost certain to remain a major alloying element in stainless steels for the foreseeable future.

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