LOW-NICKEL AUSTENITIC STAINLESS STEELS: METALLURGICAL CONSTRAINTS

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ABSTRACT

Fluctuations in the nickel price continue to drive the search for alternatives to nickel in austenitic stainless steels, even after nearly a century of general use of austenitic stainless steel, and more than fifty years since development of the 200-series alternatives. In this paper, the metallurgical constraints are defined, and quantified where possible, as a basis for understanding why the prospects for nickel replacement are quite limited. The constraints relate to three distinct roles of nickel, namely austenite formation, austenite stabilization, and corrosion resistance. Nickel decreases the general corrosion rate in reducing acids, but this is a relatively unimportant effect, since Type 304 stainless steel has limited applicability in reducing acids. The more important effect of nickel substitution is on pitting corrosion resistance, where manganese has a strongly negative effect, nitrogen improves pitting corrosion resistance, and copper has variable effect. With regards to austenite formation, nitrogen has a strong effect, copper a weak effect, and manganese has a weak to negative effect (its main role is to increase nitrogen solubility). Austenite stabilization relates to avoiding martensite formation during cold deformation. All alloying elements decrease the M_d temperature, and in many cases more strongly than does nickel; nitrogen-alloyed low-nickel stainless steels are expected to have a smaller tendency toward martensite formation during cold work. Nickel replacement also affects the mechanical and processing properties, for example by the strong strengthening effect of nitrogen and the potential negative effect of copper alloying on hot workability. The conclusion is that there is no simple direct replacement for nickel; while low-nickel and nickel-free austenitic grades can be used successfully, this requires careful consideration of the conditions.

1   INTRODUCTION

Stainless steel producers are significant consumers of ferroalloys, including ferrochromium, ferromanganese, ferrotitanium, ferrosilicon, ferronickel, and nickel. This paper focuses on nickel; stainless steel production uses two-thirds of primary nickel [1], and nickel is a major contributor to the price and price volatility of austenitic stainless steels. The volatility of the nickel market has recently been emphasized by the indefinite idling of the just-completed $2.2 billion Ravensthorpe nickel mine in western Australia [2]. Nickel (and copper) have been described as "precious-like metals", in that these metals have been the "object of speculative investment as are gold, silver and platinum-group metals" [3].

Given the high and volatile price of nickel, there is a long history of searching for alternatives to nickel in stainless steel. The most successful development has been the 200-series steels, dating from the 1950s [4]. These Cr-Mn-Ni-N stainless steels can have similar corrosion resistance to Type 304 in many environments, typically contain only 4% Ni, and accounted for nearly a tenth of stainless steel production in 2006 [5]. Yet, while the 200-series steels are well established, the ambivalence to their use is well illustrated by the sub-heading "An opportunity or threat to the image of stainless steel?" of a recent information brochure on these steels [6].

This paper summarizes the main roles of nickel in austenitic stainless steels, to provide a metallurgical basis for understanding the effects of nickel substitution.

2   POSSIBLE NICKEL SUBSTITUTES AND THEIR EFFECTS

Nickel plays several roles in stainless steels; two of the important metallurgical roles are formation of austenite during annealing (typically at 1000-1100°C), and stabilization of austenite. "Stabilization" refers to avoidance of transformation of austenite to martensite, which can occur during cold deformation. Martensite formation can lead to excessive work hardening and delayed cracking.

2.1   Corrosion

Austenitic stainless steels which have higher nickel contents have lower corrosion rates in dilute sulphuric acid [7]. While this is undoubtedly the case, the active corrosion rate of Type 304 in this environment is high and renders this steel inappropriate as a material choice, so while the corrosion rates of lower-nickel steels are even higher in this environment, none of these steels should be used in dilute sulphuric acid under conditions of active corrosion. This is illustrated by Figure 1, which compares the corrosion rate in dilute sulphuric acid of Type 201, Type 304 and Hercules™, which has a lower nickel and higher manganese content than 201. Indicative chemical compositions of these and other austenitic steels are given in Table 1.

As emphasized by Speidel[14], resistance to localized corrosion (pitting and crevicing) is of much greater importance, and for fully austenitic stainless steel nickel has a minor effect on localized corrosion. The "Measure of Alloying for Resistance to Corrosion" (MARC) was proposed as one correlation for summarizing the effects of the alloying elements for austenitic steels[14]:

$$MARC = Cr + 3.3Mo + 20N + 20C - 0.5Mn - 0.25Ni \qquad (1)$$

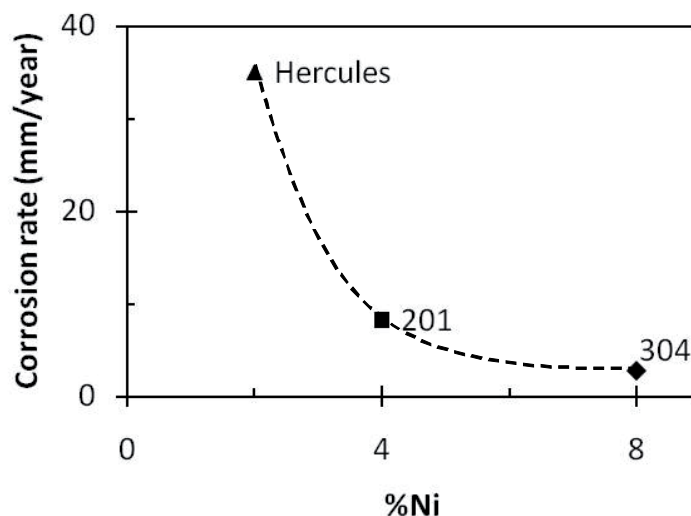where the alloy contents are in mass percentages.

Figure 1:   Comparison of the active corrosion rates of different austenitic stainless steels in 5% H_2SO_4 at 25°C[9].

Table 1: Approximate compositions (mass percentages) of Type 304 stainless steel and some lower-nickel austenitic stainless steels[9][10][11][12][13]. "MARC" is a calculated index of predicted localized corrosion resistance[14], and "PRE-Mn" is a modified pitting resistance equivalent[16].

Name	Cr	Ni	Mn	Mo	Cu	N	C	MARC	PRE-Mn
AISI304	18	8	1	-	-	0.05	0.03	17	19
AISI201	17	4	6	-	-	0.2	0.05	17	17
Indian 1% Ni	15	1	10	-	2	0.12	0.1	14	9
Indian 4% Ni	16	4	7	-	1.5	0.1	0.1	16	12
Cromanite	19	0.9	10	-	-	0.4	0.08	23	21
Hercules	16.5	2	9	-	-	0.25	-	17	15
US Pat 5,286,310	17	3	7	-	2.5	0.2	-	17	16
US Pat 6,267,921	17	0	20	3	-	0.7	-	31	28

Calculated MARC values are given in Table 1. According to this, Hercules and 201 should have similar localized corrosion resistance to 304, and that of Cromanite should be better. These predictions do not tally with our own results and those from the literature, which indicate that Cromanite has a similar pitting potential to 304, whereas the localized corrosion resistance of Hercules and 201 is generally poorer[6][9]. The implication is that general correlations like MARC can give a broad indication of the effects of alloying elements (especially for more highly alloyed steels), but should not be used as a substitute for actual corrosion testing data. The MARC correlation is certainly more useful than the pitting resistance equivalent (PRE)[15], though, since the latter does not account for the deleterious effect of manganese. It appears that a better correlation with the pitting potential of Cr-Mn-Ni-N stainless is obtained with the following modified PRE expression[16]:

$$PRE\text{-}Mn = Cr + 3.3Mo + 30N - Mn \qquad (2)$$

The negative effect of manganese on pitting corrosion resistance is probably due to at least two factors: Corrosion pits form at manganese sulphide inclusions[17], and the repassivation rate of austenitic stainless steels has been shown to be lower for steels with higher manganese contents[18].

Copper (which can contribute to forming the austenite structure, as discussed in the next section) has a limited (and variable) effect on localized corrosion[19].

The strong effect of nitrogen to improve localized corrosion resistance is evident from equation (1). Nitrogen is also a strong austenite former (as discussed in the next section), and hence nitrogen is commonly used in lower-nickel stainless steels.

2.2 Austenite formation

A sufficiently high content of austenite-forming elements such as nickel, nitrogen, carbon and copper are required in the steel to allow the desired austenite structure to form at annealing temperatures, and to persist to room temperature. Expressions giving the chromium and nickel equivalents for annealing at 1075°C are as follows[14]:

$$Cr_{eq} = Cr + 1.5Mo + 0.48Si$$
$$Ni_{eq} = Ni + 18N + 30C + 0.33Cu + 0.1Mn - 0.01(Mn)^2 \qquad (3)$$

where the alloy contents are in mass percentages.

The minimum required nickel equivalent to ensure a fully austenitic structure at 1075°C is then given by [14]:

$$Ni_{eq} \text{ (required)} = 1.2Cr_{eq} - 13 \qquad (4)$$

As equations (2) and (3) illustrate, for a given chromium content in the steel (as required for corrosion resistance), there are a few possibilities to achieve the required nickel equivalent: a lower nickel content would have to be balanced by higher nitrogen, copper or manganese (the extent to which the

carbon content can be increased is limited by the danger of sensitization). Limits to the use of manganese, copper and nitrogen are discussed below.

Equation (3) shows that the largest austenite-stabilizing effect of manganese is expected at 5% Mn, and that would be equivalent to only 0.25% Ni, yet as Table 1 indicates manganese additions greater than 5% are commonly used in lower-nickel austenitic stainless steels. The predicted effect of manganese was tested for a temperature of 1075°C by using equilibrium phase calculations with FactSage and the FSstel steel database[20]. The results are summarized in Figure 2, which gives the nickel content which is required to give a fully austenitic structure, for different manganese contents. The figure confirms the weak austenite forming ability of manganese (the nickel content required for austenite formation changes little if manganese is added), and that the nickel replacement effect of manganese is zero around 10% Mn, and is negative at higher manganese contents. The strong nickel replacement effect of nitrogen is evident from the figure, as is the moderate effect of copper.

Copper can be seen (from equation [3] and Figure 2) to have roughly one-third the austenite-forming (or "gammagenic"[12]) ability of nickel. Since the price of nickel is historically about three times that of copper, there is no cost advantage to using copper instead of nickel to form austenite. Also, the extent of copper addition has to be limited to avoid surface quality problems such as hot shortness during rolling[21]. Copper in stainless steel does have antimicrobial properties, for frequently cleaned surfaces (such as cookware)[22]. Copper alloying lowers the work-hardening rate (counteracting the prominent strengthening effect of nitrogen), which can be advantageous in manufacturing[11][23].
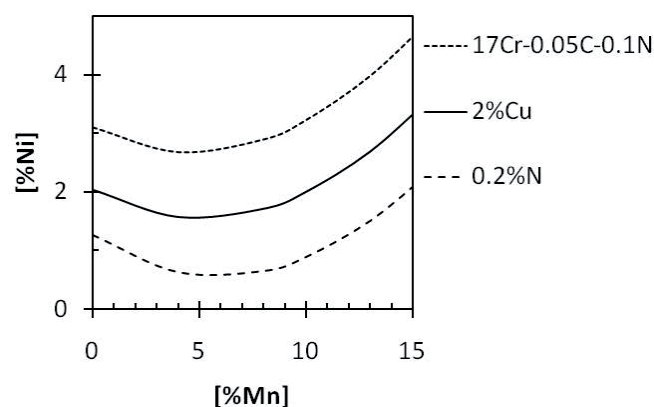

Figure 2:   Calculated nickel contents in 17%Cr-0.05%C-0.1%N stainless steel, and with added Cu and higher N, required to obtain a fully austenitic structure at 1075°C.

Evidently manganese alloying additions of 6-10% are not primarily used to form austenite. Rather, manganese serves to increase the solubility of nitrogen in liquid and solid steel[21]. Figure 3 shows the predicted effect of manganese alloying on the solubility of nitrogen in liquid stainless steel, for two of the literature correlations and from FactSage predictions.

Solid-state solubility of nitrogen is also an important consideration, especially the substantial decrease in solubility that occurs when the steel transforms to ferrite, generally upon solidification [21]. This effect is illustrated in Figure 4, which gives the calculated partial pressure of nitrogen in equilibrium with dissolved nitrogen in Type 201 and Cromanite steels, with compositions taken to be those in Table 1. The partial pressure is predicted to increase to a maximum of approximately 2 atm close to full solidification, at which temperature the steels are predicted to be fully ferritic; final solidification is predicted to occur by formation of some austenite. (This ferrite-austenite solidification mode agrees with the predicted weld solidification mode [13],[23],[25].) Despite this large partial pressure, these steels are (or were, in the case of Cromanite) produced by conventional continuous casting, and can be welded successfully without porosity [13],[23]. (It appears that entrapment of nitrogen bubbles in the weld metal – leading to weld porosity – is affected by both steel composition and welding parameters[26]; for example, we have observed porosity in autogenous welds in Cromanite, for welding with nitrogen-containing shielding gas without added oxygen[27].) If these steels did not contain manganese, the equilibrium partial pressure of nitrogen would have been substantially higher, increasing the danger of development of porosity during atmospheric-pressure solidification

processing. It is likely that some porosity is produced in nitrogen-alloyed low-nickel steels during continuous casting, but that this is removed during subsequent hot working[28].
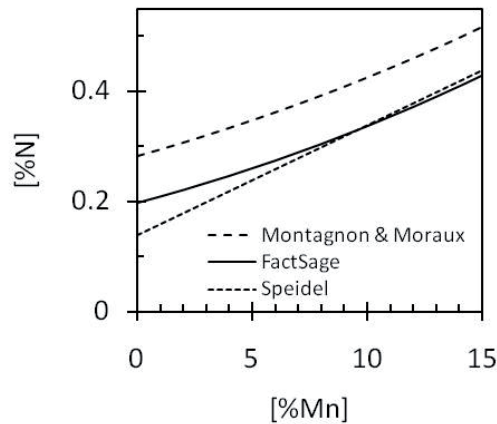

Figure 3: Calculated effect of manganese alloying on the solubility of nitrogen in molten stainless steel containing 17% Cr (and no additional alloying elements other than Mn and N); results are for the correlations of Montagnon and Moraux [12], Speidel [14], and FactSage calculations for 1600°C.
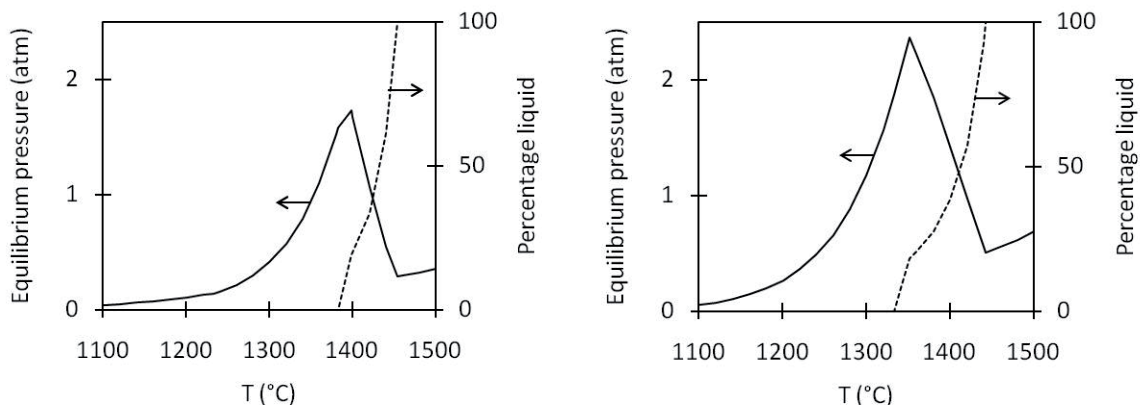

Figure 4: Calculated effect of temperature (and solidification) on the partial pressure of N_2 in equilibrium with dissolved nitrogen in Type 201 (left) and Cromanite (right) steels (compositions as in Table 1).

The possibility to alloy substantial amounts of nitrogen into stainless steels at ambient pressure, improved localized corrosion resistance in nitrogen-alloyed stainless steels, and the strong austenite-forming effect of nitrogen all contribute to the extensive use of nitrogen in low-nickel stainless steels. Indeed, it appears not to be possible to produce low-nickel austenitic stainless steels without nitrogen alloying. Nitrogen, as an interstitially dissolved element, does have a significant strengthening effect in these steels[14][21], which can be an advantage is some applications, and which requires adjustment if a nitrogen-alloyed low-nickel stainless steel is substituted for Type 304 in fabrication which involves cold work (such as deep-drawing)[6]. The strengthening effect of nitrogen can be counteracted by copper, though; this is illustrated by a recently developed European 200 series steel, which achieves essentially the same yield and tensile strength as Type 304, while containing around 0.15% N and 1.5% Cu[24].

2.3   Austenite stability

In most austenitic stainless steels, the austenite structure is not stable at room temperature, and tends to transform to martensite when the steel is cold worked; the amount of transformation to martensite upon heavy cold working should be limited to 10% or less, to avoid excessive wear or cracking of cold-working tools such as dies[11]. The tendency to form martensite can be related to the M_d temperature, which is the temperature at which deformation will result in a defined martensite content in the steels (so steels which are more stable have lower M_d temperatures). A correlation for the M_{d30} temperature (where 50% martensite forms upon deformation in tension to a true strain of 0.30) is as follows[29]:

$$M_{d30} \ (°C) = 497 - 462(\%C+\%N) - 9.2\%Si - 8.1\%Mn - 13.7\%Cr - 20\%Ni - 18.5\%Mo \qquad (5)$$

Angel [29] fitted this equation to measured M_{d30} temperatures for a range of austenitic stainless steel compositions, containing up to 9.1% Mn. Although equation (5) was developed for steels with lower nitrogen contents than typically encountered in low-nickel stainless steels, it does give a general indication of the relative effects of the elements. For example, the ratio of the coefficients of nitrogen to nickel for austenite stabilization in equation (5) (a ratio of 23) is greater than for austenite formation in equation (3) (a ratio of 18). This implies that low-nickel steels which substitute nitrogen for nickel, and are sufficiently highly alloyed with nitrogen to obtain 100% austenite during annealing, should have a smaller tendency to form martensite during deformation than regular austenitic Cr-Ni stainless steels. This prediction is supported by application data[16].

3   CONCLUSIONS

There is no single direct substitute for nickel in austenitic stainless steels. However, the required alloying changes to maintain an austenitic structure when nickel is reduced are readily calculated. Nitrogen is the main alloying element which can replace some or all nickel, supported by manganese additions (to increase solubility), and sometimes copper (to reduce strength). An inevitable result of nitrogen alloying is increased strength, and a likely combined effect of the nitrogen and manganese additions is a slight reduction in resistance to localized corrosion. In general, the tendency of low-nickel austenitic stainless steels to form martensite during deformation is expected to be somewhat smaller than that of Type 304.

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