1. Introduction

Nickel free high nitrogen austenitic stainless steels are technologically important materials that exhibit a versatile range of mechanical properties.\(^1\)–\(^4\) In addition to savings associated with Ni, they have unique combination of strength, toughness and corrosion resistance properties. However, these steels have a complex processing schedule that involves high nitrogen gas pressure exposure to molten or solid alloy at high temperature.\(^5\)–\(^8\) It is necessary to understand the scientific aspects that govern choice of composition and its influence on processing and properties. There are two critical aspects. Firstly, the amount of nitrogen content that can be imparted into the alloy by various processing and secondly, the necessary minimum nitrogen required to form a stable austenitic microstructure at room temperature.\(^5\)–\(^8\) It is necessary to understand the scientific aspects that govern choice of composition and its influence on processing and properties. There are two critical aspects. Firstly, the amount of nitrogen content that can be imparted into the alloy by various processing and secondly, the necessary minimum nitrogen required to form a stable austenitic microstructure at room temperature. Though, there is published information on nitrogen solubility and alloy design principles and properties, there are considerable deviations observed in the experimental and the theoretical models. This paper analyses these data and brings out various inconsistencies in the predictive equations. In addition, an attempt has been made to evolve certain empirical guidelines for designing such alloys.

2. General Method of Assessing Nitrogen Solubility

The solubility of nitrogen in steel is given by the reaction,

\[
\frac{1}{2} \{N_2\} \rightarrow [N] \quad \text{(1)}
\]

The equilibrium constant,

\[
K = f_N [\%N](p_{N_2})^{0.5} \quad \text{(2)}
\]

Where, \(f_N\) is the Henrian activity coefficient, \(p_{N_2}\) is the partial pressure of nitrogen and \(\%N\) is in wt%.

The equilibrium constants for reaction (1) and nitrogen solubility in pure iron, Fe–Cr and Fe–Cr–Mn alloys in molten and solid states, as determined by various studies are compiled in Table 1. The equilibrium constants ob-

| Expression | Temperature range(\(^{\circ}\)C) | Reference |
|------------|-------------------------------|-----------|
| Pure liquid iron | log \(K = -1.888 T -1.246\) | 1600 | Sipsworth et al., 1974 |
| | log \(K = -293 T -1.16\) | 1600-1800 | Feichtinger, 1994 |
| | log \(K = -322 T -1.182\) | 1600-1800 | Anson, 1996 |
| | log \([\%N] = -850 T -0.91\) | 1536-2100 | Raghavan, 1988 |
| Liquid Fe-20\%Cr alloy | log \(K = 1467.6 T -1.28\) | 1600-1800 | Anson, 1996 |
| Fe-Cr-Mn-N alloys | Log(K) = -850 T -0.905 | 1600-1800 | Svzyshin et al., 1999 |
| Pure ferrite iron | log \([\%N] = 0.97 T -1640\) | 450-911 | Raghavan, 1988 |
| | log \([\%N] = 4.477 T +525\) | | Raghavan, 1988 |
| Pure austenite iron | log \([\%N] = -2.14 T +723\) | 911 to 1392 | Raghavan, 1988 |
| Fe-Cr austenite | log \([\%N] = -1.655 T +0.097 T -0.00147\) | 1250 | Raghavan, 1988 |
| | log \([\%N] = -1.637 T +0.124 T -0.00236\) | 1150 | Raghavan, 1988 |
| | log \([\%N] = -1.613 T +0.136 T -0.00255\) | 1050 | Raghavan, 1988 |
| Fe-Cr-Mn austenite | log \(K = 656 T -2.09\) | -- | Georgiev, 1994 |
| | log \(K = 2833.6 T -17.219 +3.689log(T)\) | -- | Arsov, 1994 |
tained by different expressions for pure molten iron at 1600°C show reasonably good agreement. The value works out to be around 0.044. The equilibrium constant at 1000°C in solid austenite phase works out to be around 0.026. The Henrian activity coefficient, $f_N$ is given by Wagner’s formulation involving interaction parameters. In high Cr high N steels, higher order parameters are reported to have significant influence.9,10) The interaction parameters of various elements on nitrogen in steel available in various literature10–13) is compiled in Table 2(a) for molten iron and in Table 2(b) for solid austenite. It can be seen that the data reported in literature vary significantly and this in itself may lead to inaccuracies in the calculation of nitrogen solubility.

Based on experimentation, Grigerenko et al14,15) gave the following equation for solubility of nitrogen in molten steel as per Eq. (1):

$$\log \left( \frac{\%}{\text{wt}} \right) \left( \frac{\%}{\text{wt}} \right)^2 \left( \frac{\%}{\text{wt}} \right)^3$$

where, $f_N$ is the Henrian activity coefficient, $e_N^i$, $r_N^i$, $q_N^i$ are the first, second and third order interaction parameters of element $j$ on N respectively. The interaction parameter values in Table 2(a), were used with the above equation to calculate the nitrogen solubility.

Pure iron has low solubility (0.044% N) in the molten as well as in the solid state. Increasing the Cr content, increases the nitrogen solubility.16)
Nitrogen solubility in the presence of both Cr and Mn in steel shows deviation from Sievert's law. The solubility of nitrogen in a 18%Cr–18%Cr alloy is shown in Fig. 2. The figure shows that nitrogen solubility is enhanced at high nitrogen gas pressure and the delta ferrite region shrinks at high nitrogen gas pressures. Thus, it is understood that to achieve high nitrogen content in steels, the presence of large amounts of Cr and Mn is required.

2.1. Alternative Methods to Assess Nitrogen Solubility

Langenberg used an empirical method to calculate nitrogen solubility at 1600°C. The influence of an alloying element on nitrogen solubility was used as a measure of the activity coefficient. Their experimental and predicted nitrogen solubility showed good agreement.

A carbon equivalent method was proposed by Schurmann et al., where an equivalent C concentration at 1600°C was defined by,

\[
\%\text{C}_{eq} = 0.123\%\text{C}_{eq} + 0.003\%\text{C}_{eq}^2
\]

Similarly, a chromium equivalent method, attributed to the work by Satir et al., calculated \(f_N\) for \(\%\text{Cr}_{eq}\) values between 22 and 24 and at \(N_2\) gas pressure of 0 to 100 atm as,

\[
\log f_N = -0.048\%\text{Cr}_{eq} + 3.5 \times 10^{-4} \%\text{Cr}_{eq}^2 + 0.13\%\text{N}
\]

The \(C_{eq}\) and \(C_{req}\) values at 1600°C for various elements are given in Table 3. For temperatures other than 1600°C, a temperature correction term is introduced for the Henrian activity coefficient that is used for both the methods was given by,

\[
\log \left( f_N \right) = (-0.75 + 3.280/T) \cdot \log f_{N,1873}
\]

These methods are empirical by their very nature and does not seem to take care of the first and second order interaction parameters over large composition ranges.

The solubility of nitrogen in solid Fe–Cr–Mn–Ni–N system was established using solid phase nitriding of thin steel strips. Solid state nitriding gave the following expressions for nitrogen solubility in the ferrite and austenite phases in this system,

\[
\log \%\text{N}_f = -3.511 - 1.606/T + \log (p_{N_2})^{0.5}
\]

\[
\log \%\text{N}_g = 2.833.6/T - 17.219 + 3.689 \log (T)
\]

2.2. Inconsistencies in Nitrogen Solubility Calculations

There is direct experimental data on nitrogen solubility available in literature for a few nickel free high nitrogen austenitic stainless steels namely, 15%Cr–15%Mn, 20%Cr–9%Mn and 18%Cr–18%Mn. Grigerenko reported that in 18%Cr–18%Mn steel, nitrogen obeyed Sievert's law up to about 0.8 to 1.0% N, beyond which there was deviation attributed to contribution from \(\epsilon_N\). The experimentally measured nitrogen solubilities in molten Fe–Cr–Mn alloys obtained by Langenberg, Anson et al., and Grigerenko et al. are compared with values predicted by different calculation methods as shown in Table 4. The experimental data of nitrogen solubility in
The austenite phase of Fe–Cr–Mn alloys obtained by Georgiev et al.,18 Arsov et al.,19 and Feichtinger et al.,10 have been compared in Table 5. It can be seen that the nitrogen solubility predicted by different methods widely differ from experimentally determined values. Hence, care has to be exercised in using nitrogen solubility calculations. As there are several sources of data available, for the interaction parameter values as shown in Table 2(a), errors are likely on this count as well.

| Temperature (°C) | Phases | Cr (%) | Mn (%) | N (%) | % Nitrogen Exp. | % Nitrogen Cacl. | Reference |
|-----------------|--------|--------|--------|-------|----------------|-----------------|-----------|
| Pure Fe         | δ-ferrite | 0       | 0      | 1      | --             | 0.011           | Feichtinger, 1994 |
| Pure Fe         | γ-Fe   | 0       | 0      | 1      | --             | 0.026           | Feichtinger, 1994 |
| Pure Fe         | 13.6   | 1       | 1      | --     | --             | 0.55            | Arsov, 1993   |
| Pure Fe         | γ-Fe   | 0       | 0      | 1      | --             | 2.80            | Lula, 1986    |
| Pure Fe         | γ-Fe   | 0       | 0      | 1      | --             | 2.35            | Lula, 1986    |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.96           | 3.41            | Exp. data of Georgiev |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.96           | 3.41            | Exp. data of Georgiev |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.24           | 0.91            | Feichtinger, 1994 |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.24           | 0.91            | Feichtinger, 1994 |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.24           | 0.91            | Feichtinger, 1994 |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.24           | 0.91            | Feichtinger, 1994 |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.24           | 0.91            | Feichtinger, 1994 |
| Cr-Mn-Fe Austenite | γ-Fe   | 18.62  | 18.74 | 1      | 0.24           | 0.91            | Feichtinger, 1994 |

The nitrogen mass transfer in steels report, that the presence of surface-active elements, O and S in the austenite phase of Fe–Cr–Mn alloys obtained by Georgiev et al.,20 Arsov et al.,19 and Feichtinger et al.,10 have been compared in Table 5. It can be seen that the nitrogen solubility predicted by different methods widely differ from experimentally determined values. Hence, care has to be exercised in using nitrogen solubility calculations. As there are several sources of data available, for the interaction parameter values as shown in Table 2(a), errors are likely on this count as well.

3. Kinetic Factors Governing Nitrogen Alloying

Most studies on nitrogen mass transfer in steels report, that the presence of surface-active elements, O and S in steel influence the nitrogen mass transfer. It is also reported that O has greater influence than S.21 In pure molten iron, nitrogen absorption at atmospheric pressure is not observed till these elements are below 0.02 to 0.04 wt%.15,19 Increase in Cr and Mn content is reported to have no significant increase in absorption rate.19 The nitrogen absorption in molten steels purged with N2 gas in a pressurized atmosphere showed increased N pick-up.23 The nitrogen absorption increased with higher purge rate and higher retention time of the nitrogen gas bubble in the molten steel. The pressure is reported to retain the nitrogen absorbed by the melt. Since all literature report that the surface-active elements have a role in nitrogen mass transfer, then they can be effectively added to the melt to a critical minimum level to prevent the alloyed nitrogen from evolving out of the melt. No work is in progress in this direction. While moderate presence of S and O would not affect the steel property, the big steel bath processes employing high pressures can be simplified if nitrogen alloyed can be locked by minute additions of S and O to the bath. If S and O are to be removed subsequently simple ESR processing as done by Balachandran et al. would be adequate.22 Nitrogen solubility is reported to be more in arc melting compared to induction melting due to N getting absorbed in the arc plasma.22

Nitrogen alloying in commercial processes is carried out predominantly with the use of additions of nitrided ferro-alloys to the molten metal bath such as in Pressure ESR,23 air induction melting,24 and Electric arc furnace.22,24 In the pressure ESR process, though there is a high pressure nitrogen gas atmosphere, there is no mass transfer from the gas phase to the molten metal phase.23 The slag used in ESR does not have high nitride capacities.15,26 It is for this reason that the process warrants use of nitrided ferro-alloys. The pressure is reported to retain the nitrogen content in the molten metal bath. Recent studies by Balachandran et al. shows that nitrogen can be retained in conventional ESR as well.22 The slags used in ESR show nitrogen absorption to increase with decreasing slag viscosity and increasing carbon content in slag.15,26 It was found that the basic slag has more nitrogen solubility than acidic slag. Lime-alumina slags free of iron content could dissolve N as cyanides or also as cyanamides. However, N mass transfer through slag phase is limited. Hence, for large scale nitrogen alloying in these processes, balanced nitrided ferro-alloy addition is required.23 There are however large scale production processes that have nitrogen alloying from gas phase such as the arc-slag melting process,25 Big steel bath process,27 AOD process28 etc. In these processes, effective removal of S and O followed by nitrogen gas purging at high pressures ensures high degree of nitrogen alloying in molten steel. Since nitrogen steel can be made by solid state nitriding, the nitrogen mass transfer in solid state is of interest. The nitrogen absorption rate is reported to increase with reduced thickness of oxide layers on the metal surface10,29 and increased temperature.26

4. Alloy Design Principles of Nickel Free High Nitrogen Austenitic Stainless Steels

Steels are generally reported to acquire corrosion resis-
tance, when Cr content is greater than 12%. Conventional austenitic stainless steels have metastable austenite phase.30) Nickel in these steels expands the austenite phase field and promote sluggishness of phase transformation. Other economically viable austenite stabilisers are carbon, copper, manganese and nitrogen. Among these, carbon has a tendency to sensitise the steel, copper leads to hot shortness and manganese alone cannot totally replace Ni16,24) to form austenite phase. This leads to nitrogen as the best alloying additive.

Thermodynamics of Fe–Cr–N system31) show that for 12% Cr content, the austenite phase exists in a narrow range of nitrogen composition, which increases with increasing Cr content. Beyond the range, Cr2N and CrN phases are formed. At high Cr levels, there is the formation of ferrite, austenite and Cr2N type nitrides. The problem with this system is that the nitride can precipitate out readily at lower temperature aging32) and they are not stable against martensitic transformation.33) Hence, one of the alternative was to have Mn in the Fe–Cr–N system. Then, it is necessary to know the minimum limits of N and Mn contents required to make a stable austenitic stainless steel.

Analysis of the Fe–Cr–Mn phase diagram at temperatures of 800 to 1 200°C shows that, when Cr is greater than 13%, Mn alone cannot produce a fully austenitic structure.16) At high Cr contents greater than 15%, there is the formation of sigma phase. This necessitates addition of other austenite stabilisers such as Ni or C or both. Thus, a 18% Cr steel with 0.1% C and 8% Mn requires 4 to 5% Ni and 0.15% N for getting stable austenitic microstructure at room temperature.24) Each 0.05% N is found to be equivalent to 1% Ni in its austenite stabilizing effect. In steels with 10 to 35% Cr and 2 to 23% Mn, increasing nitrogen content expanded the austenite field and shifted the sigma phase to higher Cr contents.24)

Three prominent methods used for designing Ni-free austenitic stainless steels are attributed to Carney,25) Hsiao et al.34) and Hull.35) The analysis by Carney et al. are shown in Fig. 3(a) and 3(b). The austenite phase field in a 0.4% N steel decreases with increasing Mn content. At 0.3% N content variation in Mn contents does not have any effect in decreasing the austenite field. With increasing temperature, the austenite field decreases.

Hsiao et al.34) observed that in steels with Mn content between 5 and 14%, the minimum %(%(C+N)) required for complete austenitic structure is given by,

\[
\%(C+N) = 0.078 \cdot (%Cr - 12.5) \quad \ldots \ldots \ldots (11)
\]

The stability of carbides present in the Fe–Cr–Mn–C system at 1150°C as evolved by Hsiao et al. is shown in Fig. 4(a). For a chosen carbon content the Cr content required to get a carbide free structure (along the line B) in Fig. 4(a) could be found. This, along with Eq. (11) can be used for finding the minimum nitrogen content necessary achieving fully austenitic microstructure. The steel designed as per this procedure could, however, have higher C content, which may impart deleterious effects at low temperature aging conditions. The stability of the steel against martensitic transformation is found using,
When Cr content is greater than 15%, about 12% Mn is required to avoid martensite transformation. If Mn is less than 12% and Cr greater than 15%, then a mere increase in ...(12)

Hull35) obtained a modified Schaffler’s diagram for nitrogen containing steels that has been extensively used for designing nickel free austenitic steels. It is useful for steels with 0 to 22% Ni, 0 to 20% Mn and 0 to 0.15% N. In this diagram, the Cr and Ni equivalent terms are given by:

\[\text{Nieq} = \%\text{Ni} + \%\text{Co} + 0.1\%\text{Mn} - 0.01(\%\text{Mn})^2 + 18(\%\text{N}) + 30(\%\text{C})\] ..................................(13)

\[\text{Cr_{eq}} = \%\text{Cr} + 1.5\%\text{Mo} + 1.5\%\text{W} + 0.5\%\text{Si} + 2.3\%\text{V} + 1.75\%\text{Nb} \] ..................................(14)

At Mn content greater than 10%, the Ni_{eq} is found to decrease with increase in Mn content, thus implying that Mn behaves as a ferrite stabiliser. In steels that possess a high Cr_{eq}, a high Ni_{eq} is needed to get a fully austenitic microstructure. Very high Mn contents further lead to the formation of undesirable intermetallic phases. The Schaffler’s diagram as modified by Hull is given in Fig. 5. Fully austenitic microstructure is obtained in alloys where,

\[\text{Ni_{eq}} > (\text{Cr_{eq}} - 8) \] ..................................(15)

It may be observed that Schaffler’s diagram predicts that there is a minimum Ni_{eq} at a Cr_{eq} of about 18%. This is true in a Fe-Ni-Cr equilibria. The lowest Ni content (~8%) to make a fully austenitic stainless steel was found to be for 18% Cr content,27) which is validated in the Schaffler’s diagram as well. This trend observed in the Fe-Cr-Ni system need not be true for Fe-Cr-Mn-N equilibria as well. Hence, the range 12 to 18% Cr content, avoided for use in conventional stainless steels, may prove beneficial in Fe-Cr-Mn-N system. The Cr content slightly above 12% may require lower N content to stabilize the austenite, which may require lower N2 pressure requirement during production of the steels or may have lower deformation load requirement during processing or may result in lower strength and better ductility etc. Hence, it is questionable to assume that a Ni_{eq} minimum exists in Fe-Cr-Mn-N system. Hence, the use of Schaffler’s diagram based alloy design principle is inaccurate especially in the 12 to 18% Cr content range in Cr-Mn-N steels.

Feichtinger10) has reported certain calculations based on Schaffler’s diagram evolved by Hull35) to find out N solubility at its saturation in molten and solid Fe-Cr-Mn steels in a bid to predict the composition required to form stable austenite and the corresponding nitrogen alloying technique. The plots were developed for 12 to 18% Cr containing steels, the range in which calculations showed that the prediction from the diagram has inconsistencies when applied to alloy systems in published data. Hence, the theoretical calculation adopted by Feichtinger based on Schaffler’s diagram requires careful scrutiny.

In several published literature, the minimum nitrogen content to form complete austenitic microstructure in Fe-Cr-Mn-N steels have been reported.36–43) These were compared with the predictions by the alloy design principles discussed above. The results are shown in Table 6. The method propounded by Carney cannot be applied to many alloys due to the fact that their Cr and N contents were lower than the limits considered by others. According to the method proposed by Hsiao et al.,34) the value of % (C+N) [Eq. (12)] becomes negative or zero for steels with Cr content of 12%. The method based on Hull’s modified Schaffler diagram, predicts presence of martensite in most of these steels having Cr between 12 to 18%, while the experimental data indicate otherwise. Hence, caution should be

Table 6. Minimum nitrogen content required to get stable and fully austenitic microstructure in various steels.

| Base Composition (wt %) | %N | Observed microstructure | Reference | Predicted microstructure |
|------------------------|----|------------------------|-----------|-------------------------|
| 0.1C-18Cr-15Mn         | 0.45 | γ                       | Whitenberger | γ, γ, γ                 |
| 0.05C-14Cr-14.5Mn      | 0.13 | γ                      | Shyne et al. | γ, γ, γ                |
| 0.05C-14Cr-14.2Mn      | 0.20 | γ                      | Shyne et al. | γ, γ, γ                |
| 0.00-14Cr-14.5Mn       | 0.36 | γ                      | Shyne et al. | γ, γ, γ                |
| 0.003-16Cr-14.5Mn      | 0.49 | γ                      | Shyne et al. | γ, γ, γ                |
| 1Cr-12Mn-2Mo           | 0.2  | γ                      | Haddick     | γ, γ, γ                 |
| 12Cr-16Mn-1.5Si        | 0.2  | γ                      | Haddick     | γ, γ, γ                 |
| 0.005-15Cr-25Mn-1C-1Ni | 0.2  | γ                      | Suemone et al. | NA, γ, γ               |
| 12Cr-5Mn              | 0.6  | γ                      | Loo et al.  | NA, γ, γ                |
| 12Cr-10Mn             | 1.15 | γ                      | Loo et al.  | NA, γ, γ                |
| 0.2C-11Cr-15Mn        | 0.17 | γ                      | Hoshi       | NA, γ, γ                |
| 0.1C-12Cr-15Mn        | 0.2  | γ                      | Hoshi       | NA, γ, γ                |
| 0.12C-12Cr-15Mn       | 0.1  | γ                      | Hoshi       | NA, γ, γ                |
| 0.1C-12Cr-20.9Mn-0.9Ni | 0.216 | γ                    | Hoshi       | NA, γ, γ                |
| 0.1C-12Cr-15.6Mn-0.9Ni | 0.232 | γ                    | Hoshi       | NA, γ, γ                |
| 0.1C-12Cr-15.1Mn      | 0.2  | (γ + f)                | Miyahara al | γ, γ, γ                |
| 0.2C-12Cr-15.1Mn      | 0.1  | (γ + f)                | Miyahara al | γ, γ, γ                |
| 0.2C-11Cr-15Mn        | 0.17 | γ                      | Miyahara al | γ, γ, γ                |
| 0.2C-12Cr-15.2Mn      | 0.1  | (γ + f)                | Miyahara al | γ, γ, γ                |
| -0.008W-0.9Ni         |       | γ                      | Hoshi       | NA, γ, γ                |
| 0.19C-118Cr-14.7Mn    | 0.2  | γ                      | Miyahara et al | γ, γ, γ               |
| -1.68W-0.8Ni          |       | γ                      | Miyahara et al | γ, γ, γ               |
| 0.005C-12Cr-15Mn      | >0.4% (C+N) | γ                | Hoshi       | NA, γ, γ                |

NA: Principles cannot be applied; γ: austenite phase; f: martensite phase; γ*: Probably austenite (extrapolation of Carney’s data)
be exercised in using these alloy design principles to actual experimental results obtained in these alloys.

To evaluate the relative merits of the three methods described above, one particular steel composition of commercial interest was assessed, by calculating the minimum concentration of nitrogen required to form a stable austenitic microstructure, using the various alloy design principles discussed above. The steel chosen has a base composition 0.12%C–1.0%Si–18%Mn with varying Cr contents. Here, a Si concentration of 1% was chosen because Si is used as a deoxidiser and sometimes nitrogen is added to the melt in the form of nitried ferro-silicon or silicon nitride. The results of the calculation are presented in Fig. 6. The lines demarcates the fully austenite region from the two-phase region. The method proposed by Hsiao et al.,34) predicts the lowest requirement of nitrogen content to give a fully austenitic microstructure, whereas Hull’s Schaffler’s diagram predicts the highest nitrogen content. In an alloy with 18% Cr content, the minimum nitrogen required to stabilise austenite is about 0.32% N according to Hsiao,34) 0.42% as per Carney25) and about 0.46% N as per Hull.35) While Carney’s data is reported for a solution treatment temperature of 1246°C, the other two data are for lower solution temperatures. Hsiao’s data has a wide Mn concentration range (12 to 18%) taken for the dependence between (C+N) and %Cr to get austenite phase. Use of Hull’s technique would ensure that the nitrogen level predicted is well above those predicted by others and is safer for use.

An attempt was made to analyse all data in literature together.25,31–43) The border line compositions data that gives complete austenite was subjected to a multiple regression analysis. The minimum nitrogen content required for getting fully austenitic matrix for a chosen alloying elemental concentration was found to be,

\[
[N_{\text{min}}] = -0.88(\text{wt}\%C) + 0.046(\text{wt}\%Cr) \\
-0.0009(\text{wt}\%Mn) + 0.038(\text{wt}\%Mo) \\
-0.053(\text{wt}\%Si) + 0.082(\text{wt}\%Ni) \\
-0.208(\text{wt}\%Cu) - 0.032(\text{wt}\%W) - 0.278 ...
\]

The above equation is valid for 12 to 24% Cr, 10 to 20% N, 0.05 to 0.6% C, 1 to 3% Mo, 0.1 to 1.5% Si and 0.05 to 1.1% N. The predictions from this regression equation is also plotted in the Fig. 6. This equation when combined with N solubility Eq. (3) can predict the minimum equilibrium nitrogen pressure required to make the final N alloy in the molten steel.

5. Detrimental Precipitation in Nickel Free High Austenitic Stainless Steels

It is well known that these steels are prone for precipitation in a temperature range between 550 to 950°C.4,24,34,44–51) Usually, all types of precipitation lead to fall in ductility and toughness of these steels. Three type of precipitations were established, namely, grain boundary Cr23C6 type carbide, transgranular Cr7C3 type carbides and lamellar CrN type nitrides. The lamellar precipitation is predominant in steels with a high nitrogen content and low carbon content, while the transgranular carbides are predominant in long time aging of high carbon low nitrogen steels. The Cr2N type lamellar nitride precipitation may be associated with the formation of sigma phases as well due to depletion of N from the matrix and associated destabilization of the nitrogen austenite.21) The regions along these precipitates are found to be very weak often resulting in intergranular failures.

A computed pseudo binary phase diagram for a low carbon 18%Cr–18%Mn–Fe alloy as a function of the nitrogen content, evaluated by Frisk et al.,52) based on solution thermodynamic model is shown in Fig. 7. At 1100°C, a minimum of 0.6% N is required to get fully austenitic matrix. Between 1100 and 850°C, the N content required for forming fully austenitic matrix decreases from 0.6 to 0.3% N. Between 0.5 and 2.5% N and at temperature below 920°C, (\(\gamma + \varepsilon\)) phases form. The \(\varepsilon\)-phase is CrN type nitride. The nitrogen solubility at a pressure of 1 bar (0.1 MPa) is superimposed on the phase diagram. The phase diagram shows the presence of a miscibility gap involving (\(\gamma + \varepsilon\)) phase. The nitride forming tendency is a strong function of Cr and N contents. As the Cr activity lowers with decreasing Cr contents, a lowering of Cr from say 18% in the phase diagram to about 12% is expected to shift the (\(\gamma + \varepsilon\)) region to
lower temperatures. It has also been reported that increasing nitrogen content from 1 to 1.6% N resulted in enlargement of \((\gamma + \varepsilon)\) region\(^{23}\) leading to lamellar precipitation at lower aging temperatures. Thus, it may be useful to have steels with just adequate Cr for desired corrosion resistance application. This will ensure that Cr\(_2\)N formation is suppressed.

There were reports by Hsiao et al.\(^{45}\) and Hetzmanczyk\(^{46}\) that the Cr\(_2\)C\(_6\) type transgranular precipitation is preferred as it gives some strengthening to the steel in spite of moderate reduction in ductility. Studies by Hsiao et al. showed that in steels with 12 to 21% Cr, 11 to 13% Mn and Carbon 0.3% and N <0.3% gave transgranular precipitates.\(^{45}\) Many others who have investigated the precipitation reactions have used steels with higher Cr and Mn contents and the lamellar nitride precipitation in these steels ultimately deteriorated the ductility of the material. Investigations by the Balachandran\(^{54}\) showed long time aging at temperatures of 600°C showed transgranular carbide precipitation but in addition, there was film type Cr\(_2\)C\(_6\) carbide formation along the grain boundary that resulted in extremely poor ductility and intergranular fracture.

The property deterioration in the aging temperature range (550 to 920°C) is a serious aspect that limits the use of these steels for high temperature applications. Hence, alloy designing should aim at development of alloying components that either suppresses the detrimental precipitation or alter the precipitation morphology so that the associated properties damages are contained.

The choice of alloying elements for altering the Cr\(_2\)N type of precipitation is very limited because most elements form stable carbides or nitrides. Thermodynamic analysis of solubility product of various carbides and nitrides in the Fe–Cr–Mn–N austenite could give an idea about the choice of alloying elements. However, the non-availability of solution thermodynamic data restricts precise calculations. In spite of this, a crude approximation may be arrived from analysis of standard free energy of formation of the various carbides and nitrides as a function of temperature.\(^{55}\) There are many stable carbide and nitride formers with very high negative free energy of formation. They include TiC, ZrC, VC, TaN, Ta\(_2\)N, Nb\(_2\)C ZrN, TiN, Cr\(_2\)C\(_6\) etc. It is because of the high stability of Cr\(_2\)C\(_6\), it is readily precipitated along grain boundaries in austenite over that of Cr\(_2\)N during aging. Very stable carbide and nitride formers have to be avoided to achieve a precipitate free fully austenitic microstructure during solution treatment. Elements that form carbides and nitrides, whose standard free energy of formation values are closer to that of Cr\(_2\)N is more desirable. Some typical compounds are shown in Fig. 8. It was found that carbide formers, in general, have very large values of negative free energy of formation. Since Cr\(_2\)C\(_6\) has higher stability than carbides of Nb, V, Mo etc., it may not be a good approach to precipitate carbides during aging. Formation of such carbides have been reported.\(^{51}\) This implies that nitrogen steels should have low carbon content in it, unless there is a technique to modify the carbide precipitation morphology. Dulis\(^{50}\) has reported that controlled deformation at aging temperatures could give transgranular type Cr\(_2\)C\(_6\) carbides that improves strength at moderate loss in ductility.

The stability of nitride forming elements Mo\(_2\)N and VN show very close free energy of formation values to that of Cr\(_2\)N. Though solution thermodynamic interaction parameters can alter the solubility product of these two precipitates, it can be said that they are good choice of alloying elements. Depending on their solution thermodynamics they can either precipitate potentially in a transgranular fashion against lamellar morphology of Cr\(_2\)N. Since Mo\(_2\)N has lower stability than Cr\(_2\)N, it may precipitate in the matrix only if Mo activity significantly changes in the austenite. The comparable stability of Mo\(_2\)N should ensure that it redissolves at higher temperature. VN on the other hand has more stability and may fix the N rather than Cr\(_2\)N as reported by Miyahara.\(^{41}\) Microadditions of V and Nb have been reported to form carbonitride precipitates transgranularly and though they reduced N available for forming lamellar Cr\(_2\)N precipitation and retarded it.\(^{42}\) But they could not totally prevent lamellar precipitation.

Another alternative is to assess if the lamellar Cr\(_2\)N precipitate itself can be precipitated in a transgranular morphology. It may be possible to achieve this by controlled deformation of the steel in the high temperature regime (just lower than 920°C, Fig. 7) where the Cr\(_2\)N (\(\varepsilon\)-phase) just starts to precipitates. Since the matrix is ductile, as the precipitates forms, the high temperature deformation would ensure redistribution of Cr\(_2\)N precipitates in transgranular fashion in addition to eliminating the composition inhomogeneity that may result during precipitation. These are approaches that are needed for future development.

6. Ductile to Brittle Transition

Nickel-free high nitrogen austenitic stainless steels exhibit DBTT, a phenomenon not common in conventional austenitic stainless steels. The DBTT is reported to be a function of nitrogen content as follows:\(^{33}\)

\[
\text{DBTT (K)} = 300 \times (\% \text{N}) - 30 \quad (17)
\]

Hence, considerations on DBTT could be a limiting factor.
in choosing nitrogen content of the alloys. With increase in nitrogen content there is decrease in the young’s modulus of the material and surface energy while there is increase in interplanar spacings. This along with the fact that nitrogen chemically interacts in the strain field is reported to lead to cleavage stress predominating over the plastic flow stress.\(^{51}\)

To ward off the DBTT, the steel designer has to look for elements that can alter these factors. Addition of 2 to 4% Ni alleviates the problem associated with DBTT\(^{66}\) but then the steel is not Ni free. Addition of austenite stabilizing element Cu should be carefully assessed in this context.

7. Designing Alloys with Targeted Mechanical Properties

Studies by Pickering showed how individual alloying elements in a Cr austenitic stainless steel contributes to strength enhancement.\(^{58}\) There are some empirical equations and theoretical models that were evolved to predict the room temperature strength of austenitic stainless steels in general as shown in Table. 7. These models when applied to published data showed discrepancies in the predicted values of strength in the case of nickel free Cr–Mn–N steels. Hence, an effort was made to analyse all published strength data as a function of composition, grain size and degree of cold working.\(^{1–68}\) During the analysis it was found that the data regarding grain sizes, and finer details about impurity concentrations etc were missing in several literature. This resulted in grouping the data into three categories. All available strength data was regression fit as a function of

(i) composition alone in the solution annealed steels
(ii) composition and grain size in the solution annealed steels
(iii) composition and degree of cold work.

The predictions resulted in reasonably good fit with published data, when such an approach was adopted. The values were within ± 40 MPa. The analysis carried out is valid for steels in a composition range 12 to 21% Cr; 12 to 22% Mn; 0.01 to 0.6% C; 0.01 to 1.5% N; 0 to 3% Mo; 0.1% V; 0.2 to 1.15% Si and Ni < 0.8%. Thus, a rough estimates of the strength (in MPa) of these steels in the solution annealed conditions as a function of a chosen steel composition (in wt%) and grain size (in micron) could be found using the following equations.

Strength data in the annealed condition as function of chosen composition is given by,

\[
\text{UTS} = 121.20(\text{wt}\%\text{C}) + 337.04(\text{wt}\%\text{N}) - 0.20(\text{wt}\%\text{Mn}) + 7.74(\text{wt}\%\text{Cr}) + 4.14(\text{wt}\%\text{Si}) - 303.47(\text{wt}\%\text{P}) - 2962.42(\text{wt}\%\text{S}) - 3.63(\text{wt}\%\text{Mo}) - 73.42(\text{wt}\%\text{Ni}) - 46.22(\text{wt}\%\text{Cu}) - 267.20(\text{wt}\%\text{V}) + 647.29.....(18a)
\]

\[
\text{YS} = 3.03(\text{wt}\%\text{C}) + 335.60(\text{wt}\%\text{N}) + 5.08(\text{wt}\%\text{Mn}) + 8.41(\text{wt}\%\text{Cr}) - 9.39(\text{wt}\%\text{Si}) - 172.71(\text{wt}\%\text{P}) - 94.95(\text{wt}\%\text{S}) - 21.94(\text{wt}\%\text{Mo}) + 15.19(\text{wt}\%\text{Ni}) - 94.25(\text{wt}\%\text{Cu}) + 3 188.33(\text{wt}\%\text{V}) + 176.62.....(18b)
\]

Strength data in the annealed condition as function of chosen composition and grain size (expressed in microns) is given by,

\[
\begin{align*}
\text{YS} = 257.69(\text{wt}\%\text{C}) + 479.49(\text{wt}\%\text{N}) + 5.74(\text{wt}\%\text{Mn}) + 1.46(\text{wt}\%\text{Cr}) + 92.58(\text{wt}\%\text{Si}) - 449.09(\text{wt}\%\text{P}) + 7354.36(\text{wt}\%\text{S}) - 1.07(\text{grain size}) + 235.17 \quad \text{(19a)}
\end{align*}
\]

\[
\begin{align*}
\text{UTS} = 266.08(\text{wt}\%\text{C}) + 441.1(\text{wt}\%\text{N}) + 32.41(\text{wt}\%\text{Mn}) + 21.92(\text{wt}\%\text{Cr}) - 54.73(\text{wt}\%\text{Si}) - 602.23(\text{wt}\%\text{P}) + 1156.23(\text{wt}\%\text{S}) - 0.82(\text{grain size}) - 234.57 \quad \text{(19b)}
\end{align*}
\]

Strength data as a function of chosen composition and degree of cold work is given by,

\[
\begin{align*}
\text{UTS} = 680.35(\text{wt}\%\text{C}) + 603.27(\text{wt}\%\text{N}) - 19.33(\text{wt}\%\text{Mn}) - 5.05(\text{wt}\%\text{Cr}) - 19.14(\text{wt}\%\text{Si}) + 102.73(\text{wt}\%\text{P}) - 3 066.21(\text{wt}\%\text{S}) - 75.08(\text{wt}\%\text{Mo}) - 16.33(\text{coldwork}) + 904.87 \quad \text{(20a)}
\end{align*}
\]

\[
\begin{align*}
\text{YS} = 952.39(\text{wt}\%\text{C}) + 655.23(\text{wt}\%\text{N}) + 34.28(\text{wt}\%\text{Mn}) + 1.56(\text{wt}\%\text{Cr}) - 7.41(\text{wt}\%\text{Si}) - 736.13(\text{wt}\%\text{P}) + 7 829.12(\text{wt}\%\text{S}) + 9.95(\text{wt}\%\text{Mo}) + 22.36(\text{coldwork}) - 535.48 \quad \text{(20b)}
\end{align*}
\]

Using the above equations it is possible to predict the strength level for a chosen alloy composition, grain size and degree of cold working. The above equations along with Eq. (16) would enable choice of nickel free high nitrogen austenitic stainless steels with a targeted strength levels.

8. Conclusion

The theoretical principles required for development of nickel free high nitrogen austenitic stainless steels have been analysed. There were discrepancies in the N-solubility data owing to the variations in the solution thermodynamic data. The alloy design principle required to design nickel free austenitic stainless steels was analysed. Empirical equation to predict the minimum nitrogen content to get a complete austenite and estimation of strength, as functions of composition has been obtained.

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