The Influence of Nitrogen on Microstructure and Properties of Highly Alloyed Stainless Steel Welds

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The influence of nitrogen on the microstructure and properties of austenitic and duplex stainless steel welds is reviewed. Three aspects are covered: intermetallic phase formation, nucleation and growth of austenite in ferrite and nitrogen balance in TIG welding.

The effect of nitrogen on the precipitation of deleterious intermetallic phases is analysed for duplex and austenitic steels by thermodynamic means and the differences in response of nitrogen alloying illuminated. Also the replacement of molybdenum by tungsten is discussed.

Nitrogen alloying made the duplex grades weldable. The duplex steels, designed to comprise approximately equal amounts of ferrite and austenite, solidify in a ferritic mode and a rapid transformation of ferrite to austenite is a prerequisite. Nitrogen has a beneficial effect on the austenite reformation in the HAZ (Heat Affected Zones) on cooling. This has been confirmed by both experiments and calculations. Attempts have been made to improve the nucleation of austenite and thus to increase the possibilities for welding by more demanding techniques which involve rapid cooling through the critical temperature range 1350°C to 1000°C.

Nitrogen is added to many of the modern stainless steels because of its favourable effects on both strength and corrosion resistance. This implies that the welding procedure must consider the risk of nitrogen escape from the weld pool. Avoiding nitrogen losses may be accomplished by applying e.g. nitrogen-containing shielding gas. Applying balanced shielding gases is generally successful but on occasion reproducibility problems may arise. Correcting measures require insights in the process and the mechanisms controlling the nitrogen fluxes in TIG welding. These can be illuminated using a simple process model that accounts for alloy composition, shielding gas nitrogen content, weld pool shape and size. It is suggested that the main reasons for lack of reproducibility may be found in the batch to batch variation in surfactant content that controls the weld pool shape via the Marangoni effect and surface mass transfer reactions.

KEY WORDS: stainless steels; austenitic stainless steels; duplex stainless steels; austenite reformation; microstructure; intermetallic phases; alloying elements; nitrogen; welding; shielding gas; mechanisms; phase transformations.

1. Introduction

Duplex grades are readily welded with good results if the recommended practices are followed. The heat input is however of critical concern for two reasons: the cooling rate should be slow enough to allow reasonable austenite reformation in HAZ and fast enough to avoid the formation of intermetallic phases. The practical implication is a risk for nitride precipitation if austenite reformation is insufficient, with consequences for corrosion resistance and impact toughness. Similar arguments are valid for intermetallic phase formation but in this case more concern is placed on the effect on impact energy.

The effect of alloying elements and other factors on the tendency to intermetallic precipitation in stainless steels has been the subject of numerous investigations. An excellent review was presented recently by Karlsson11 where the effect of intermetallic phase precipitation was discussed in terms of welding of duplex stainless steels. It is generally agreed that nitrogen favourably influences the tendency to intermetallic phases in austenitic steels but the effect in duplex grades is less clear and is rarely discussed. For the metallic elements, it seems that the general conclusions in earlier studies on the detrimental effect of W and Mo on the precipitation of intermetallic phases in duplex stainless steels23 are now questioned e.g. Ref. 3) where positive effects of tungsten in contrast to molybdenum is presented. An attempt to clarify the individual roles of the alloying elements in austenitic and duplex grades is presented below.

Duplex grades solidify in a ferritic mode. Consequently, the heat affected zone close to the fusion line will have a fully ferritic structure at temperatures above approximately 1350±50°C depending on alloy composition. In order to obtain the desired weld properties of a duplex stainless steel it is imperative to maintain a reasonable phase ratio of ferrite to austenite after welding. The transformation kinetics must be rapid and the addition of nitrogen was the solution to make the duplex grades weldable. It has been shown that
the transformation is then controlled by the redistribution of nitrogen (para-equilibrium) instead of requiring diffusion of slowly diffusing metallic elements. In the weld metal the desired phase ratio is obtained by a combination of nitrogen and an increased nickel content. For the heat affected zones (HAZ) a number of factors have been identified being crucial in terms of austenite reformation after ferritization.\textsuperscript{5–7)} A higher nitrogen content increases the kinetics by raising the lower temperature limit for single phase ferrite and thus both increases the driving force for austenite formation and decreases the temperature range where ferrite grain growth prevails. Furthermore, the nitrogen diffusion coefficient is temperature dependent and if the austenite is formed at higher temperature the austenite growth rate will be enhanced. A secondary effect is that the decreased grain growth will increase the number of nucleation sites for austenite since austenite nucleates primarily on the ferrite grain boundaries. It has been demonstrated that the nitrogen diffusion rate in the ferrite governs the kinetics and, consequently, the transformation can be categorised as para-equilibrium controlled.\textsuperscript{7)} In the case that the phase transformation is nucleated at grain boundaries, the rate limiting parameter is the grain size since the distance of nitrogen diffusion restricts the austenite growth rate, in particular in the final stage of transformation. However, in the case of coarse grains, intragranular nucleation of Widmanstätten austenite will occur instead. Another important consequence of a limited grain size is that, following simple stereological principles, a growing film of austenite will more rapidly yield a sufficient austenite fraction. From a technical point of view this implies that a wider process window in the welding procedure is available, in this case permitting more rapid cooling rate from the ferritic range. A further increase of the reformation kinetics by e.g. enhancing the nucleation, would thus widen the process window and allow the use of more demanding welding procedures.

When the level of nitrogen alloying increases, which is the general trend in the materials development worldwide, the driving force for the escape of nitrogen increases, leading to a larger risk for losing the desired properties. This may be more severe in high nitrogen alloys since these advanced niche materials are often used in demanding applications, where even small losses may lead to a weld with substantially inferior properties in relation to the base material, with consequences for the service performance. It is often possible to find a set of welding parameters that yield correct microstructure and alloy composition. Welding using systematic variations of welding parameters and shielding gases has supplied important knowledge on the practical attainment of a desired nitrogen content.\textsuperscript{5–13)} However the technique does not provide mechanistic information that could be used for guidance in instances in which the results diverge in spite of operating within the recommended process window. In order to make rational decisions, the mechanisms controlling the net nitrogen content of the weld metal must be identified, understood and mastered.

2. Formation of Intermetallic Phases

According to the PRE (Pitting Resistance Equivalent)\textsuperscript{14)} concept the corrosion resistance is increased by the addition of Cr, Mo, W and N. However, the same metallic elements that increase the corrosion resistance, to a varying degree, also favour the precipitation of intermetallic phases. In order to shed light on this complex subject an experimental and theoretical investigation was undertaken.\textsuperscript{4)} Three duplex stainless steels were annealed to produce limited amounts of intermetallic phase \textit{i.e.} at the nose of the TTT curve, which is of major technical importance, and to investigate the effect on impact energy. Impact energy testing is a sensitive mechanical test to reveal early stages of intermetallic phase formation.\textsuperscript{15)} The ambition was to clarify the individual effects of nitrogen, tungsten and molybdenum on the growth rate of sigma phase using the Thermocalc\textsuperscript{16)} and Dicta\textsuperscript{17)} databases and to correlate the results to the experiments. Materials from commercial production, with chemical composition given in Table 1, were solution annealed and subsequently isothermally heat-treated at 850°C in a resistance-heated weld simulator and quenched into brine. Charpy V-notch impact energy testing was performed at $-40$°C. The microstructures after ageing 300 s at 850°C are presented in Fig. 1.

A clear difference in intermetallic phase fraction is

\begin{table}[h]
\centering
\caption{Chemical composition of investigated materials [wt%].}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
 & C & Si & Mn & Cr & Ni & N & Mo & W \\
\hline
0W & 0.015 & 0.027 & 0.43 & 24.88 & 6.95 & 0.25 & 3.81 & 0.01 & 0.12 \\
1WCu & 0.022 & 0.33 & 0.63 & 25.08 & 6.97 & 0.23 & 3.55 & 0.58 & 0.60 \\
2WCu & 0.012 & 0.39 & 0.41 & 25.25 & 6.94 & 0.27 & 3.22 & 2.13 & 0.60 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{Duplex microstructures after ageing 300 s at 850°C. LOM. Intermetallic phases dark, ferrite light grey and austenite white. The intermetallic phase nucleate primarily in phase boundaries and grow preferably into the ferrite. Electrolytic etching in NaOH.}
\end{figure}
shown in Fig. 1 for the alloys. In 0W only sigma phase was present, while in the other two materials both sigma and chi were precipitated, however chi phase dominated in 2WCu and sigma phase in 1WCu.

The result from Charpy Impact Energy testing is presented in Fig. 2. The relative drop in the impact toughness of the three steels gives the same ranking as the absolute values. After 10 s ageing only limited effects are observed but after 30 s ageing at 850°C the two tungsten-alloyed materials display a significant decrease in impact energy. After 300 s all materials display reduced impact energy but the material without tungsten additions still exhibits considerable toughness.

The Thermocalc database was used for calculating the driving force for precipitation of sigma and chi phase, Fig. 3. The positive effect of nitrogen alloying in austenitic grades has been recognised earlier e.g. Refs. 18, 19). The subject was also discussed in Refs. 20, 21) where the effect of nitrogen on the Cr and Mo activities was suggested to be the determining factor. This is illustrated in Fig. 4 where the driving force for precipitation of sigma phase in a superaustenitic grade is presented as a function of temperature and nitrogen content. Nitrogen displaces the start of precipitation to lower temperatures.

However, if a similar calculation is performed for the superduplex 0W steel, the result is dramatically different. Only a very small effect is observed for sigma phase precipitation, Fig. 5. The main reason for the limited effect of nitrogen in the duplex grades is that there is only a small effect on the chromium activity because of the simultaneous change in phase fraction, Fig. 6. (In the duplex grade an increased nitrogen content will give an increased austenite fraction as well as a slightly increased nitrogen content in the austenite which will affect the chromium activity.) The chromium activity for the superaustenitic steel has been included in Fig. 6 for comparison.

These results imply that the influence of the metallic elements will be more crucial in the case of duplex stainless steels, and confirm the observations in Fig. 1 above.

The DICTRA database was utilised to illuminate the effects of molybdenum and tungsten. Figure 7 shows the chromium profile across the sigma-ferrite phase boundary.
calculated after 60 s and 600 s ageing at 800°C. A limited depletion of the ferrite adjacent to sigma phase can be observed. If all the molybdenum is substituted by tungsten, the growth rate increases substantially, see Fig. 8. The sigma phase thickness has increased by a factor of two. The same calculation was performed for the alloys 1WCu and 2WCu, see Figs. 9 and 10.

The thickness of the sigma phase is significantly larger for 1WCu and 2WCu than for the 0W alloy. There are several possible explanations for this behaviour, the diffusion rate of tungsten as compared to molybdenum being one, the driving force for precipitation another. However, the diffusion rate is only responsible for a limited contribution to the increase in growth rate, see Fig. 11, probably less than 10%. The driving force for precipitation is substantially
higher for the tungsten alloyed material, Fig. 12, and may thus be the controlling factor.

The results show that the positive influence of nitrogen on the kinetics of intermetallic precipitation observed in austenitic grades is less evident in duplex steels. This is related to the change in austenite–ferrite phase ratio occurring in the duplex case. This makes the balance of metallic alloying elements more important for duplex steels. In the austenitic steels the nitrogen will instead decrease the activities of primarily chromium.

The ageing response of the investigated materials was different, with higher amounts of intermetallic phases precipitated in the tungsten-alloyed materials. This was confirmed using metallography and reflected by the more rapid embrittlement than for the tungsten-free material. The results confirm the trends suggested in Ref. 2) regarding the effect of tungsten on the TTT curve. Tungsten alloyed steels displayed more rapid growth of intermetallic phases. The diffusion coefficient of molybdenum is quite similar to that of tungsten so the difference could instead be related to the different compositions of the sigma phase in the alloys and the differences in driving force. Also calculations of the growth rate of intermetallic phases using the Dictra database confirmed the experimental results.

3. Nucleation and Growth of Austenite in HAZ of Duplex Stainless Steels

Duplex grades solidify in a ferritic mode and the heat affected zone close to the fusion line will thus have a fully ferritic structure at temperatures in the temperature range 1350±50°C depending on alloy composition. In order to obtain the desired weld properties of a duplex stainless steel it is important to maintain the desired phase ratio of ferrite to austenite after welding. The transformation kinetics on cooling must be rapid, which is achieved by the addition of nitrogen. It has been shown that the transformation is then controlled by the redistribution of nitrogen (para-equilibrium) instead of requiring diffusion of slowly-diffusing metallic elements if nitrogen is absent. In order to investigate the possibility of further enhancing the austenite formation of a duplex stainless steel EN 1.4462 by improving the nucleation conditions, the effect of TiB₂ particles was explored Ref. 22). The idea originated from an investigation by Westin²³ where a number of additives stimulating nucleation of ferrite in the liquid state were studied. The TiB₂ particles were found to be most efficient of a number of different additives investigated and resulted in a fine grained microstructure. No effect was however seen regarding the nucleation of austenite from the liquid state.

A laboratory ingot of dimensions 90×90 mm was forged down to 60×60 mm. (During forging considerable cracking took place.) The chemical composition is presented in Table 2, where the composition of a conventional reference material is also given.

Subsize Charpy V blanks with dimensions 5×10×55 mm were machined and subsequently subjected to weld simulation using a resistance heated weld simulator. The thermal cycles included heating to 1 390°C using a heating rate of 150°C/s, time at temperature 0, 5, 10, and 30 s. The cooling rate from the holding temperature to RT was 430°C/s, achieved by water jet impingement. The resulting microstructure was evaluated in terms of ferrite grain size and austenite fraction using automatic image analysis. The orientation relationship between ferrite and austenite was assessed by EBSP techniques (Electron Back-Scattering Pattern).

The microstructure, after weld simulation is presented in Fig. 13 for the conventional grade. Note however that the cooling rate is very high and chosen solely in order to differentiate between the materials. The TiB₂ particles were found to be most efficient of a number of different additives investigated and resulted in a fine grained microstructure. No effect was however seen regarding the nucleation of austenite from the liquid state.

The austenite fraction in the TiB₂ modified material was 40 %, compared to an area fraction of about 12 % in the reference 2205 material after cooling at 430°C/s. This is a significant improvement.

Considerable grain growth occurred in the non-modified material (about 150 μm grain size) compared to the modified material with a grain size of less than 40 μm. The limited grain growth is in this case due to the occurrence of particles which contribute to the decreased grain boundary
mobility, Fig. 14. Also the presence of B, in particular in connection with Mo, contributes a substantial solute drag effect. The sub-size Charpy impact energy was similar for the modified and non modified and approx. 50 J.

EBSP techniques were used to assess the crystallographic relationship of austenite precipitated both intra- and intergranularly in the ferrite. In Fig. 15 a typical GB austenite precipitate is shown. The precipitate has a plane, faceted surface towards one of the adjacent grains and a dendritic shape towards the other grain. In contrast, all the intragranular austenite precipitates display plane ferrite/austenite phase boundaries. The austenite in Fig. 15 displays a dendritic morphology versus one grain and a plane phase boundary versus the other grain. This in contrast to the TiB$_2$ modified high nitrogen material in Fig. 14, which has a dendritic morphology on both sides.

The shape of the austenite grains with one plane and one dendritic surface indicates that the nucleation is oriented. When the austenite displays an orientation relationship, the lattice coherency will place restrictions on the growth rate and the continued growth will take place preferentially into the opposite ferrite grain where no orientation relationship exists.

It was found that all grains with a plane interface between austenite and ferrite followed an orientation relationship according to Kurdjumov Sachs or Nishiyama. This means that the close packed planes of the austenite are in parallel to the close packed plane of the ferrite, i.e. \{111\}_austenite/\{110\}_ferrite.

The same situation was observed for the austenite nucleated intragranularly which also had plane interfaces. In the case of dendritic growth mode, no such orientation relation was seen but instead an arbitrary relationship was observed. In the TiB$_2$ modified material the GB precipitates invariably displayed a dendritic shape and no orientation relationship with the ferrite could be observed. In Fig. 16 a result from the EBSP measurements for non-modified material is presented, where the conjunct 111 and 110 poles demonstrate a special orientation relationship. The corresponding situation for the TiB$_2$ modified material is presented in Fig. 17.

4. Calculated Austenite Reformation Kinetics for the Investigated Steels

In order to achieve an estimate as to how the nucleation and nitrogen content respectively contribute to the resulting austenite fraction, a calculation using the same technique as presented in Ref. 5) was performed. The result of the calculation on the effect of nucleation alone is presented in Fig. 18. Since the ferrite grain size is of significance, the calculations were performed in steps. The calculated grain size effect is denoted with an arrow in the figure. In the figure results from Ref. 5), concerning the same non-modified material with a nitrogen content of 0.18N, are also shown for comparison. Then the nucleation parameter was in-
creased by factors of 3 and 10. It is however clear from the calculations that the effect of the increased nucleation rates saturates and levels off and the effect of nucleation is thus fairly limited in this case. However if also the nitrogen content is adjusted to correspond to the TiB₂ modified material, the situation is quite different and the correspondence with the experimental results becomes quite satisfactory, Fig. 19.

Weld simulation thus indicated that the combined effect of increased nitrogen content from 0.18 to 0.32 mass% and additions of TiB₂ gave an increase of the austenite reformed from the fully ferritic range from 10% to about 40%, using a very high cooling rate of 430°C/s. In the non modified material the ferrite and austenite displayed both a planar slow growth into one ferrite grain indicating that the nucleation is orientation related, and a non planar faster growth into the other ferrite grain. The planar phase boundary had an orientation relationship of the Kurdjumov Sachs type. In the modified material only non-planar growth of grain boundary austenite was observed with no orientation relation between the two phases which is characterised by a faster growth rate. The planar phase boundary had an orientation relationship of the Kurdjumov Sachs type. In the modified material only non-planar growth of grain boundary austenite was observed with no orientation relation between the two phases which is characterised by a faster growth rate. The theoretical analysis indicates that the increase in the nucleation rate leads to a limited increase in the reformation rate. The number of nucleation sites and the fact that the particles affect the nucleation, making it non-orientation dependent and thus having a faster dendritic growth, contribute to the increased austenite reformation. However the limited grain size and higher nitrogen content gave larger contributions to the final austenite fraction in the modified material than did the nucleation effects. This, again, show the importance of hindering nitrogen escape on welding of duplex grades.

5. Nitrogen Balance in Stainless Steel TIG Welds

Nitrogen absorption from welding arcs was reviewed in 1987 by Allum. Mechanistic experimental and theoretical investigations have been performed by Katz et al. who investigated the absorption and desorption of nitrogen in a specially-designed experimental chamber. The desorption process was strongly related to the surface availability, i.e. the sites on the surface available for nitrogen and thus not occupied by surface-active elements such as oxygen and sulphur. The higher the surface availability the higher the desorption of nitrogen. Bandopadhyay et al. investigated the influence of a glow discharge nitrogen–helium plasma on solid niobium and tantalum specimens in order to establish the nitrogen activity of the plasma. They found that the nitrogen content after saturation was a factor of three higher than after equilibration under non-plasma conditions. Mundra and Debroy developed a general model for the reactions in plasma–weld metal leading to the enhanced solubility of nitrogen in metals subjected to plasma. Emphasis was placed on the fact that the presence of atomic nitrogen at concentrations above equilibrium near the molten metal surface is responsible for the enhanced solubility. Palmer and Debroy subsequently applied this model and suggested that the steep temperature dependence of the solubility of atomic nitrogen, which increases with decreasing temperature, controls the nitrogen balance. They also mentioned the importance of plasma coverage of the weld pool because an incompletely covered weld pool gives rise to larger losses of nitrogen than a completely covered one. This is in accordance with the suggestions of Den Ouden and Griebling who performed tests using a non-travelling arc in various argon nitrogen mixtures on pure iron specimens of limited size in which the nitrogen content saturated after certain time. Hertzman investigated the influence of various TIG welding parameters and shielding gas compositions on nitrogen uptake on various stainless steels. The results showed that the nitrogen content...
approached the shielding gas-weld pool equilibrium after long times (120 s) but the shorter times (2.5 s) reflected the net nitrogen content of the weld metal in accordance with e.g. Kokawa.\textsuperscript{31)}

Cross et al.\textsuperscript{32)} found that 250 ppm contamination of oxygen in the shielding gas increased significantly the weld metal nitrogen content in welding of duplex stainless steels under hyperbaric conditions.

Hertzman and Wessman\textsuperscript{33)} investigated plates from five stainless steels including the duplex 2205 the super duplex SAF 2507 and the super austenitic 654 SMO. Chemical compositions are given in Table 3. The steels were TIG welded without filler with a stationary (non-travelling) arc for different times. The welding times were 0, 0.5, 2.5, 5, 10, and 20 s and the nitrogen content of the shielding gas was 100% Ar, Ar–2.5%N\textsubscript{2}, Ar–5%N\textsubscript{2} and Ar–10%N\textsubscript{2}. The arc length was 2.5 mm, the welding current 80 A and voltage between 9.6 and 11.2 V.

The nitrogen content and weld pool geometry were established and the dependence of weld top area and weld pool volume on time was assessed by regression analysis using expressions 1 and 2.

\[
\text{Weld top area} \quad A = a \cdot t^{2/3} \quad \text{..............(1)}
\]

\[
\text{Weld pool volume} \quad V = b \cdot t \quad \text{..............(2)}
\]

Based on a simple model of the flux of nitrogen in a stationary TIG weld with nitrogen-containing shielding gas without filler, a general expression giving the resulting net nitrogen content of a weld is presented below. The driving force for the nitrogen transport is the activity difference between the plasma, the weld pool and the shielding gas.

Figure 20 shows schematically how the nitrogen from the shielding gas enters the arc column. From the arc nitrogen is transported into the weld metal and the rate of this transport is controlled by a mass transfer coefficient, here called \( R_{pw} \). The escape of nitrogen from the weld pool occurs primarily at the weld top area, which increases as the welding proceeds. The controlling mass transfer coefficient is denoted \( R_{wg} \) (wg=weld/shielding gas).

If the activity differences are assumed to control the nitrogen flux, the following expression can be used Eq. (3).

\[
\frac{dm}{dt} = A_{pw} \cdot R_{pw} (a_p - a_{w}^0) - A_{wg} \cdot R_{wg} (a_w - a_g) \quad \text{...........(3)}
\]

Here \( dm \) represents the net nitrogen content, \( A_{pw} \) is the weld top area, \( a_p \) is the nitrogen activity of the plasma, \( a_{w}^0 \) the activity of nitrogen in the weld just under the plasma, \( A_{wg} \) the weld top area, \( a_w \) the activity of nitrogen in the weld metal and \( a_g \) the activity of nitrogen in the shielding gas. The nitrogen activity for gas (4), and weld metal (5) are given by:

\[
a_p = k_1 \cdot \sqrt{N} \quad \text{...............(4)}
\]

\[
a_{w}^0 = a_w = \gamma \cdot \text{[%N]} \quad \text{...............(5)}
\]

\[
a_g = k_2 \cdot \sqrt{N} \quad \text{...............(5)}
\]

where \( \gamma \) refers to the activity coefficient for the steel and [\%N] the nitrogen content in the weld pool. For simplification the nitrogen activity is assumed to be constant in the weld pool. This assumption seems reasonable since the weld pool undergoes strong convection and moreover nitrogen diffuses rapidly in the molten metal.

6. Calculation of Mass Transfer and Plasma Nitriding Coefficients

After integration of Eq. (3) values for the coefficients \( R_{pw}, R_{wg} \) and \( k_1 \) were assessed using non-linear regression. Values for the activity coefficient for nitrogen in the different materials were calculated using Thermocalc.\textsuperscript{16)} A value of \( k_1 = 10 \) gave a good fit to the experimental results. Support for this value was also given by Bandopadhay et al.\textsuperscript{27,31)} The nitriding capacity of the plasma is thus about ten times larger than a molecular gas of the same composition.

Using the assessed parameter values for \( R_{pw}, R_{wg} \) the net nitrogen content can be calculated. Figures 21 and 22 show the fit to the experimental results for 2205 and 654SMO. Note that the solubility limit of nitrogen is exceeded for the shorter times and higher nitrogen partial pressures which explains why experimental data are lower than the calculated line. This occurs since the nitrogen solubility was not included in the model. The reason for this was that under welding conditions the liquid may be supersaturated and if this occurs, the nitrogen content at supersaturation could provide useful data in the parameter assessments.

Figures. 23 and 24 show the predicted effect of weld geometry and nitrogen activity of the shielding gas.

7. Application to Real Welds

In order to apply the developed model to real welds, some experiments were performed with autogenous TIG welding on plate material with chemical composition given in Table 4.

\( \text{Ar–2.5%N}_2 \) was used with a flow rate of 12 l/min and travel speeds of 2.5 and 10 mm/s were chosen.

| Steel | Charge | %C | %N | %Si | %Mn | %Cr | %Ni | %Mo | %N | %Cu |
|-------|--------|----|----|-----|-----|-----|-----|-----|----|-----|
| 2205  | 382984 | 0.019 | 0.001 | 0.024 | 1.46 | 21.98 | 5.73 | 3.05 | 0.144 | 0.27 |
| SAF 2507 | 802694 | 0.023 | 0.0004 | 0.021 | 0.27 | 24.93 | 6.91 | 3.83 | 0.258 | 0.15 |
| 654 SMO | 820791 | 0.016 | 0.0003 | 0.017 | 3.65 | 24.41 | 21.91 | 7.26 | 0.528 | 0.44 |
Figure 25 shows the fit to experimental results concerning the influence of travel speed, obtained with constant heat input.

The results show that welding with nitrogen-containing shielding gas will lead to nitrogen ingress into the arc. The plasma will increase the nitrogen activity and act as a nitrogen pump and thus increase the nitrogen content of the weld metal. In the case of highly nitrogen alloyed steels an increased welding speed, in combination with balanced nitrogen containing shielding gas, is predicted to decrease the nitrogen losses, in line with experimental findings.

Also the geometry of the weld pool strongly influences the net nitrogen content of the weld e.g. a large weld pool surface area will enhance the nitrogen escape i.e. if the weld pool arc coverage is low. A similar effect can be predicted by an increase in heat input and keeping constant weld geometry, due to the increased nitrogen escape area. Since the shape of the weld pool is strongly related to the presence of surface active elements such as sulphur, oxygen and nitrogen, it is suggested that the lack of reproducibility reported in welding of nitrogen alloyed grades is connected to the batch to batch variation of surfactants.

8. Concluding Remarks

Nitrogen as an alloying element in high alloy stainless steels is gaining in importance and along with the metallurgical advances in the manufacturing processes, this development will continue. This paper has concerned only a few of the aspects regarding the utilisation of nitrogen as an alloying element: 1) The different effect on the tendency to formation of intermetallic phases for the duplex grades as compared to the austenitic and the greater importance of

| Table 4. Chemical composition of the 2205 steel used in travelling arc welds. |
|-----------------|-------|------|------|------|------|------|------|-------|
| Steel           | Batch | % C  | % Si | % P  | % Mn | % Cr | % Ni | % Mo  |
| 2205            | 802174| 0.017| 0.002| 0.021| 1.50 | 22.14| 5.68 | 2.99  |
| % N             |       | 1.77 |      |      |      |      |      | 0.24  |

Fig. 21. 2205 stationary arc weld with Ar–2.5/5/10%N2 shielding gas. The lines are calculated values and symbols represent the experimental results: × Ar–2.5%N2, ◇ Ar–5%N2, □ Ar–10%N2.

Fig. 22. 654 SMO stationary arc weld with Ar–2.5/5/10%N2 shielding gas. Nitrogen content [%N] versus time [s]. The lines are calculated and symbols represent the experimental results: × Ar–2.5%N2, ◇ Ar–5%N2, □ Ar–10%N2.

Fig. 23. Effect of weld pool shape (at a constant weld pool volume) on net nitrogen content in a stationary TIG weld with a 2.5%N–bal.Ar shielding gas.

Fig. 24. Predicted effect of shielding gas nitrogen partial pressure on weld pool nitrogen content. Stationary arc, time 1s.

Fig. 25. 2205 welded with Ar–2.5%N2 shielding gas. Nitrogen content [%N] versus travel speed [mm/s]. The crosses represent experimental values for 0.5 kJ/mm heat input.
balancing metallic elements in case of the duplex steels. 2) The importance in maintaining a correct nitrogen content in the steel in view of the positive effects on microstructure evolution, mechanical properties and corrosion resistance and finally aspects on the control of the nitrogen content in the weld pool and thus to indicate ways to avoid losses during welding.

Many of the results presented are achieved by the use of thermodynamic databases which facilitate modelling work. They also makes it possible to interpret experimental results, to extrapolate in temperature and composition and to investigate the effect of individual alloying elements in a way that would otherwise require unrealistic experimental efforts. The future material development and optimisation of materials properties will to an increasing extent rely on theoretical considerations in combination with verifying critical experiments. This places demands on the precision of the predictive capability of the databases, which must be subject to continuous efforts. In terms of modelling of nitrogen effects, the list of new knowledge needed is very long: e.g. nitrogen reactions in plasma, surface reactions such as nitrogen uptake and release in oxidising media and in combination with other gaseous species, solubility information and other phase diagram information, nucleation and growth of gaseous pore formation in welding just to mention just a few.

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