The Influence of Nitrogen from Welding on Stainless Steel Weld Metal Microstructures

Soluble nitrogen is found to exert a major influence—particularly on the quantity and distribution of weld metal delta ferrite

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ABSTRACT. Small amounts of nitrogen were injected into Type 304L austenitic stainless steel weld metal. This was accomplished by using an argon-nitrogen shielding gas mixture on autogenous gas tungsten arc welds. Weld metal nitrogen as a function of nitrogen shielding gas content and applied pressure was examined.

Nitrogen shielding gas contents below 5% were found to have a major effect on the weld metal microstructure. The base metal nitrogen did not influence the nitrogen solubility reaction and solidification behavior during welding. For Type 304L austenitic stainless steel, a nitrogen coefficient was determined for the nickel equivalent expression.

Introduction

Small amounts of nitrogen in austenitic stainless steels have been known to alter microstructural-sensitive properties. Early investigators studied nitrogen as a solid solution strengthener and as a potential substitute for a certain amount of nickel in austenitic stainless steels (Ref. 1-7). Subsequent research has studied the nitrogen effect on mechanical properties, corrosion resistance and the delta ferrite-austenite duplex microstructure. This investigation was concerned with quantitatively determining the influence of nitrogen in a gas tungsten arc (GTA) shielding gas on austenitic Type 304L stainless steel weld metal. Particular emphasis was placed on weld metal microstructure and chemistry.

Literature Overview

Increased nitrogen content in wrought 18Cr-8Ni austenitic stainless steels has been reported to increase both yield and tensile strength (Ref. 8). It was determined that nitrogen acted as a solid solution strengthener similar to carbon; however, the nitrogen strengthening effect was temperature dependent.

At an ambient service temperature, a nitrogen concentration between 0.10 and 0.16 weight percent (wt-%) was found to produce optimum strength in wrought 18Cr-8Ni stainless steel (Ref. 9). At a temperature of 150°C (302°F), nitrogen also increased the yield and tensile strength (Ref. 10). However, above 700°C (1292°F), nitrogen strengthening was a short-lived phenomena, due to nitride formation. Nitride formation decreased the amount of nitrogen in solid solution causing a corresponding decrease in yield strength (Ref. 11,12).

Nitrogen strengthening of Type 316 austenitic stainless steel weld metal has also been investigated. A 9 ksi (62 MPa) increase in weld metal yield strength for each 0.01 wt-% increment of weld metal nitrogen was determined. Weldability, based on porosity, was reported to be impaired above a shielding gas nitrogen concentration of 15 volume percent (vol-%) (Ref. 13).

The influence of nitrogen in the range of 0.040 and 0.290 wt-% on intergranular and pitting corrosion of 18Cr-8Ni austenitic stainless steel was studied (Ref. 8,9). Early work found no increased tendency of intergranular corrosion (Ref. 8). More recent work has found that nitrogen retards carbide formation in heat-treated wrought stainless steel, thereby improving sensitization resistance (Ref. 9). The heat-affected zone of a high nitrogen (0.20 wt-%) nitrogen austenitic stainless steel weld has been found not to be sensitized (Ref. 14).

With respect to pitting, increased nitrogen content increased pitting resistance (Ref. 15). Pitting was observed to initiate at the ferrite-austenite interface. Nitrogen decreased the ferrite content, causing lower interfacial area, thus decreasing pitting initiation sites (Ref. 16). Increased nitrogen content increased stress corrosion cracking susceptibility of austenitic stainless steel weld metal (Ref. 17-19).

Solidification of austenitic stainless steel commonly results in a duplex microstructure of delta ferrite and austenite (Ref. 20-28). Small nitrogen variations alter delta ferrite content in weld metal microstructures (Ref. 17,29-32). These nitrogen variations affect weld metal integrity, because the amount, morphology and distribution of delta ferrite influence the mechanical properties and cracking susceptibility of stainless steel weld metal.

Delta ferrite amount, morphology and distribution required to produce optimal weld strength was determined to be service temperature dependent. At low service temperatures, delta ferrite has a ductile to brittle transition temperature (Ref. 33,34). Therefore, a weld metal microstructure containing a low ferrite content with a noncontinuous network is desired to limit brittle crack propagation. Less than 8 vol-% delta ferrite is required to insure a noncontinuous network.

At room temperature, austenitic stainless steel tensile strength is greater with a duplex structure. For each type of austenitic stainless steel, there is a specific volume-percent of delta ferrite which yields optimum strength.

At high temperatures, delta ferrite transforms to sigma phase which is brittle (Ref. 35,36), thus requiring control of the ferrite content. For Type 316 austenitic stainless steel, 5 vol-% delta ferrite provides a noncontinuous network and optimum high temperature creep strength (Ref. 37).

The hot cracking susceptibility of austenitic stainless steels is reduced with a duplex microstructure (Ref. 38-44). Investigators contend that 3 to 10 vol-% delta ferrite is required to reduce hot cracking susceptibility. However, ferrite is not a sufficient condition to prevent hot cracking. Recent investigations have shown that a primarily ferrite solidification mode
is also necessary (Ref. 26,27). To ensure primary ferrite solidification, alloy composition must lie on the effective chromium rich side of the liquidus projection line on the Fe-Cr-Ni phase diagram.

Investigators have empirically described the austenitizing strength of specific alloying elements relative to nickel (Ref. 45). A variety of nickel content have been determined for these specific alloying elements relative to nickel from 18.4 for high manganese austenitic stainless steels to 30 for the AISI 300 series austenitic stainless steels (Ref. 25,46,47).

The weld metal nitrogen content of austenitic stainless steel was found to be a function of the welding variables (Ref. 48). At constant current, an increase in the potential by 10 volts (V) can increase the weld metal nitrogen content by 0.10% nitrogen. Decreasing the current at constant voltage, the weld metal nitrogen content was also found to increase. Kotecki (Ref. 30), when studying open arc weld deposits made with self shielded flux-cored stainless steel electrodes, found a similar welding variable dependency and developed the following expression to estimate the weld metal nitrogen content:

$$\%N = 0.138 + 0.016V - 0.0005I - 0.004S$$

(1)

where $V$, $I$, and $S$ are the voltage, current and electrode extension, respectively.

Increasing the voltage and/or decreasing the current promotes a larger arc length and larger weld pool width, thus allowing the gas-metal reaction to proceed further as suggested in equation (1). The role of the electrode extension is not obvious. The dependency on welding variables may make it difficult to compare the reported nitrogen contents of the various investigators.

### Experimental Procedure

Autogenous gas tungsten arc welds were made on the surfaces of vacuum arc remelted Type 304L stainless steel plate specimens. The stainless steel composition is shown in Table 1. This material was chosen for the extremely low nitrogen content. Specimen size was 230 x 75 x 12.5 mm (9 x 3 x 1/2 in.).

The activity of nitrogen in the shielding gas was changed systematically by varying the shielding gas (Ar-$N_2$) composition and the applied pressure during GTA welding in a pressurized inert gas chamber. The shielding gas mixture was varied from 0 to 5 vol-% nitrogen. The low nitrogen concentration in the shielding gas mixture was used to inject nitrogen into the weld pool. These low concentrations of nitrogen in the shielding gas mixture simulated the nitrogen concentration expected from atmospheric contamination. The gas mixtures were made using a calibrated gas mixer. The chemical analysis of the argon and nitrogen used is given in Table 2. After each welding run, a 500 cubic centimeter (cc), i.e. (30.5 cu in.), gas specimen was taken from the shielding gas line and analyzed.

Automatic GTA welding was performed in a hyperbaric welding chamber which was pumped down and backfilled with argon prior to each welding run. A 300 ampere (A) DC welding supply with a high frequency arc start was used. All welds were made using the welding variables shown in Table 3. The torch angle was kept at 90 deg to the workpiece. The environmental gas pressure was varied from 0 to 4 bars above atmosphere.

Each weld metal specimen was chemically analyzed for carbon, oxygen, and nitrogen. All weld specimens were prepared for metallographic examination. A 10% oxalic acid electroetch was used to observe the nature of the delta ferrite. A special color etch was used to enhance solidification segregation of chromium and nickel. This etch was composed of 10 grams (g) ammonium bifluoride, 60 g potassium metabisulfite, and 200 cc water. The delta ferrite content was determined using a calibrated Forrester ferrite meter. Selected weld specimens were analyzed by microprobe to determine the distribution of the chromium, nickel and iron content across the dual phase microstructure.

### Results and Discussion

The weld metal nitrogen concentration was measured as a function of the partial pressure of $N_2$ in the argon shielding gas and is illustrated in Fig. 1 for three different environmental pressures. The weld metal nitrogen content has an apparent parabolic relationship. The results of other investigators (Ref. 32,38,49) were plotted for comparison in Fig. 2. Shown are different curves for GTA autogenous weldments of similar chromium and nickel content. All curves have similar parabolic shapes with the final nitrogen content influenced by base metal nitrogen content. Apparently, the base metal nitrogen content is in a form which does not take part in the gas solubility reaction during welding. This observation develops from the fact that the weld metal nitrogen content is the same as the original base metal when a pure argon shielding gas is used. One normally expects nitrogen to be very mobile, with its content being changed by welding. The base metal nitrogen content for this investigation was low compared to that investigated by Cieslik, et al. (Ref. 38).

Additionally, the results of Arata, et al. (Ref. 49) also indicated that the total weld metal nitrogen content is the sum of the residual nitrogen content of the base metal and the nitrogen picked up from the shielding gas-metal interaction.

The weld metal nitrogen content was found to follow Sievert's Law for welds made at the three pressures studied in this investigation—Fig. 3. The curves for various environmental pressures exhibit the same slope over most of the range. Assuming temperature dependent solubility, this implies that the weld metal nitrogen was frozen in at the same effective reaction temperature in the welding thermal cycle for all externally applied pressures. Applying the law of mass action results in:

$$K = \frac{[N]}{P_{N_2}}$$

(2)

where $[N]$ is the weld metal nitrogen content, $P_{N_2}$ is the partial pressure of nitrogen in the shielding gas and $K$ is the temperature dependent equilibrium constant. The value of $K$ is known to have very weak applied pressure dependence and can be assumed for this case to be independent of the applied pressure.

Since the base metal nitrogen content apparently does not enter the gas-metal equilibrium during welding, the weld metal nitrogen concentration data from Fig. 2 were normalized by subtracting the...
base metal nitrogen concentration from the measured weld metal nitrogen concentration. Using the normalized weld metal nitrogen concentrations, Fig. 4 is a plot of normalized nitrogen concentrations squared as a function of nitrogen shielding gas partial pressure for welds made at 1 atmosphere environmental pressure. Also shown is the high pressure data for comparison. As seen in Fig. 4, all of the 1 atm data (with one exception) fall in a band showing that most investigators observed the same gas-metal reaction.

From equation (2) the slope of the curve in Fig. 4 is the equilibrium constant for the gas-metal reaction. Figure 4 shows two distinct equilibrium constants for the 1 atmosphere (*=1 bar) data. At low partial pressures, the slope of the curve is larger than at higher partial pressures. This suggests that the lower partial pressure produces a higher reaction temperature for the nitrogen solubility. Similar deviations have been reported for weld metal hydrogen in hyperbaric welds (Ref. 50). Apparently, increasing the nitrogen content to the welding arc reduces the reaction temperature of the welding arc plasma.

This change in effective equilibrium constant was not observed for the welds made at the higher applied pressures. The 3 and 5 bar results had the same slope as the higher partial pressure data from the 1 bar experiments. Increasing the applied pressure is known to increase the plasma density for a constant current (Ref. 53,54). Thus, it would be expected that the effective nitrogen concentration in the higher pressure plasma is greater than that in the 1 atmosphere plasma for the same nitrogen partial pressure (calculated from only the knowledge of shielding gas composition).

Nitrogen has a lower ionization potential than argon (Ref. 55). Therefore, the arc at the lower nitrogen concentrations may be controlled by the influence of argon. On the other hand, at higher nitrogen concentrations (caused by either increasing the nitrogen partial pressure or the applied pressure), the arc may be controlled by the influence of nitrogen. A nitrogen controlled arc would be expected to be cooler than an argon controlled arc. Hence the slope change indicates the transition from an argon to nitrogen controlled arc.

The nitrogen influence on delta ferrite content was determined by making autogenous GTA welds. Autogenous welds kept the nickel and chromium concentrations constant with the only variable being nitrogen injected into the weld metal from the shielding gas. The delta ferrite content was measured as a function of weld metal nitrogen concentration and is shown in Fig. 5. The nitrogen austenite stabilization is apparent by a significant decrease in delta ferrite content with an increase in weld metal nitrogen.

Figure 6 includes the ferrite content measurements of Cieslak, et al. (Ref. 38) and Espy (Ref. 47) as a function of normalized weld metal nitrogen content. Their data agrees with the results of this investigation. This agreement suggests that the ferrite content is not a function of the total weld metal nitrogen but only a function of that part which is in solution. These findings again suggest that the base metal nitrogen is in a form which does not influence weld metal solidification.
behavior during the short period of the welding cycle.

The base metal chemistry was used to define a constant chromium equivalent line on the DeLong diagram (Ref. 25). Then the ferrite number obtained for different weld metal nitrogen contents was used to determine a corresponding nickel equivalent from the diagram. The resulting nickel equivalents are shown in Fig. 7 vs. the corresponding weld metal nitrogen contents. The slope of the straight line fit of the data (Fig. 7) is then the nitrogen coefficient in the DeLong nickel equivalent diagram. The data show that nitrogen influences the nickel equivalent. The nitrogen coefficient was determined to be 13.4. This value is considerably lower than the value of 30 reported by DeLong. However, the new coefficient is closer to the values of 14.2, 18.4, and 20 reported by Suutala (Ref. 51), Hull (Ref. 46) and Mel'kumor and Topilin (Ref. 52), respectively.

Séferian (Ref. 53) developed an expression for predicting the delta ferrite amount from nickel and chromium equivalent expressions. This expression is given as:

$$\% \text{ferrite} = 3 \left[ \text{Cr}_{\text{eq}} - 0.93 \text{Ni}_{\text{eq}} - 6.7 \right]$$ (3)

where the nickel and chromium equivalents are calculated from the Schaeffler equations:

$$\text{Ni}_{\text{eq}} = \% \text{Ni} + 0.5 \left( \% \text{Mn} \right) + 30 \left( \% \text{C} \right)$$ (4)

$$\text{Cr}_{\text{eq}} = \% \text{Cr} + 1.5 \left( \% \text{Mo} \right) + 0.5 \left( \% \text{Nb} \right)$$ (5)

Modifying equation (4) to include the weld metal nitrogen concentration and using our determined nitrogen coefficient of 13.4 yields a coefficient for nitrogen in the Séferian equation of $-37.4$. This coefficient can be found from the slope of delta ferrite content as a function of weld metal nitrogen concentration—Fig. 6. The slope of the experimental data shown in Fig. 6 is $-36.4$, which corresponds very well to the calculated slope of $-37.4$.

Nitrogen had a marked effect on weld metal microstructure between 0.086 to 0.105 wt-% nitrogen. Below 0.086 wt-% nitrogen, the weld metal contained dendritic ferrite. Above 0.105 wt-% nitrogen, the weld metal contained a dendritic austenitic structure. The austenitic dendrites were coarse in structure, consisting of primary dendrites with retarded secondary arms. Between these two bounds, a mixed dendritic ferrite/dendritic austenite weld metal microstructure was observed and is shown in Fig. 8.

The weld bead shown in Fig. 8 was made with a shielding gas composition of 4.5 vol-% nitrogen and 95.44+% argon. The weld metal nitrogen concentration was determined to be 0.101 wt-%. Etching helped to reveal a striking microstructural change across the weld bead. At the weld interface, proeutectic ferrite solidification pattern is seen. In an area between the fusion line and center line, a microstructural change occurs from ferritic dendrites to retarded austenitic dendrites. At the center line, a stabilized microstructure of retarded austenite dendrites is seen.

A suggested explanation for the observed microstructural change is nitrogen rejection at the solidification interface. The solidification reaction starts with a proeutectic ferrite mode which would reject any austenitic stabilizer at the solidification front. This solidification mode would continue until the liquid was rich in austenite stabilizers. At this point, a solidification change would occur from proeutectic ferrite to proeutectic austenite resulting in a corresponding micro-structural change.

The resulting change to primary austenite would then possess a microstructure that would absorb nitrogen and other austenite stabilizing elements. It would be expected that this rejection-absorption behavior would result in a banded structure of primary ferrite, primary austenite, and primary ferrite, respectively. However, Fig. 8 shows no such banding. A possible explanation is that the stirring of the weld pool is sufficient to cause a high level of nitrogen in the remaining weld pool. The nitrogen content would be sufficient enough to stabilize the remaining liquid for primary austenite solidification.

Increasing the weld metal nitrogen content has two effects:

1. Increasing nitrogen shifts the composition of the weld pool to the proeutectic austenite side of the liquidus projection line—Fig. 9.

2. The solidification structure changes from ferritic dendrites to austenitic retarded dendrites.

The weld pool chemical composition change can be explained by the classical nonequilibrium solidification equation for a constant distribution coefficient (Ref. 57):

$$C_d^* = C_d \left( k_d - 1 \right)$$ (6)

Applying the nonequilibrium solidification equation to weld metal nitrogen, $C_d^*$ is the nitrogen composition of the liquid at the solid-liquid interface, $C_d$ is the weld pool nitrogen composition, $f_l$ is the weight fraction of liquid in the fusion zone, and $k_d$ is a distribution coefficient:

$$k_d = \frac{C_d}{C_l}.$$
For proeutectic ferrite solidification, \( k_0 \) is less than one. As the weld pool solidifies in a proeutectic ferrite solidification mode, the \( f(k_{eq}) \) term becomes larger with time. Equation (6) predicts a nitrogen increase in the liquid composition \( C_{eq}^* \). Thus, nitrogen rejection increases weld pool austenitic stability, which effectively moves the nickel equivalent across the eutectic composition. This promotes a change in solidification behavior from primary ferrite to primary austenite.

The microstructural behavior appears to be consistent with the experimentally determined criteria for dendritic-cellular transformation put forward by Plaskett and Vineyard (Ref. 58). This criterion states that dendritic growth occurs if:

\[
\frac{C_l}{R^{1/2}} < A \frac{C_0}{k_0}
\]

where \( C_l \) is the thermal gradient in the liquid ahead of the solidification interface and \( R \) is the solidification rate.

Both quantities are assumed constant in this investigation, since the welding variables were held constant. In this case, \( C_0 \) is the weld metal nitrogen content, \( k_0 \) is the distribution coefficient and \( A \) is a constant. For proeutectic austenite solidification, \( k_0 \) is greater than one. For proeutectic ferrite solidification, \( k_0 \) is less than one.

It becomes apparent from equation (7) that the shift from dendritic to retarded dendritic growth could be expected with increasing nitrogen content if \( k_0 \) increases faster than \( C_0 \). From equation (7), it can be seen that an increase in the \( k_0 \) value (from a value less than one to a value greater than one) may promote a condition which reverses the inequality and thus causes a change from a dendritic to a cellular microstructure. The observed retarded dendrites may be early evidence of this transition.

**Summary**

Small nitrogen contamination levels—5% \( N_2 \) and below—in the argon shielding gas will have an effect on Type 304L stainless steel weld metal microstructure and properties. The nitrogen absorption by the weld metal from the shielding gas appears to be independent of the initial base metal nitrogen content. The resulting total weld metal nitrogen content is the sum of the nitrogen absorbed by the gas-metal interaction and the base metal nitrogen content.

Two distinct effective equilibrium constants (effective reaction temperatures) exist for the solubility of weld metal nitrogen for 1 atmosphere applied pressure. Higher applied pressures—3 and 5 bar—produced weld metal nitrogen contents that indicated only one effective equilibrium constant which can be related to one of the constants determined for 1 atmosphere.

Soluble nitrogen was found to have a major influence on the weld metal microstructure—in particular, the quantity and distribution of delta ferrite. The base metal nitrogen is apparently in a form which does not influence the weld metal solidification behavior. For Type 304L austenitic stainless steel, a nitrogen coefficient of 13.4 was determined for the nickel equivalent expression used to calculate the amount of delta ferrite. This value is lower than the value, 30, which is presently used. The new coefficient is closer to the values of 14.1, 18.4 and 20 reported by other investigators (Ref. 46, 51, 52).

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**References**

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