The welding of experimental low-nickel Cr–Mn–N stainless steels containing copper
by M. Coetzee* and P.G.H. Pistorius*

Synopsis
The susceptibility of experimental low-nickel Cr-Mn-N stainless steels to hot cracking, sensitization, and pitting corrosion in the as-welded condition was investigated. These steels were developed for deep-drawing applications and are similar in composition to type 201 stainless steel. In order to obtain good formability, the rapid rate of work-hardening (characteristic of the 200-series steels) was decreased by the addition of copper. The behaviour of two sets of alloys during fusion welding was investigated: 17Cr–7Mn–4Ni–0.5Cu steels containing 0.001 to 0.27 per cent nitrogen, and 17Cr–7Mn–2Ni–0.1N steels with copper contents varying between 0.01 and 3.11 per cent. All the steels in these two sets initially solidify as ferrite, which transforms partially to austenite during cooling. As the nitrogen level increases, the microstructure of an autogenous-weld metal ranges from large amounts of ferrite, martensite, and Widmanstätten austenite, to austenitic structures with small amounts of vermicular ferrite. The formation of ferrite during solidification and the presence of ferrite retained in the weld metal indicates that the experimental alloys will not be susceptible to hot cracking during welding. Except for the alloy with 0.27 per cent nitrogen, the resistance to pitting corrosion of the experimental steels in the as-welded condition is inferior to that of type 304 stainless steel. None of the experimental steels is susceptible to intergranular attack in the as-welded condition. The alloys with 0.19 and 0.27 per cent nitrogen have properties (corrosion and microstructure) similar to those of type 304 stainless steel in the as-welded condition.

Introduction
The comparatively high price of nickel in recent years has led to a situation in which the cost of this alloying element constitutes a significant part of the total cost in the production of stainless steels. For this reason, there is an incentive to produce an alloy that has properties similar to those of the 18Cr–8Ni stainless steels but with cheaper elements replacing most of the nickel. The primary function of nickel in the 18Cr–8Ni steels is to ensure that the alloys are austenitic at room temperature. Nickel is both an excellent austenite-former (it enlarges the austenite phase field at elevated temperatures) and an austenite-stabilizer (it stabilizes the austenite against the formation of martensite by lowering the Ms-temperature). In addition, nickel contributes to the corrosion resistance of these steels.

Nitrogen is a very effective substitute for nickel because it is both an excellent austenite-former and austenite stabilizer. Unfortunately, not all the nickel can be replaced by nitrogen; this is because of the limited solubility of nitrogen in iron alloys. Manganese is known to increase the solubility of nitrogen in molten and solid steels, and this constitutes the main reason for the addition of manganese as an alloying element to nitrogen-alloyed stainless steels.

The AISI-200 series stainless steels are well known examples of low-nickel austenitic stainless steels alloyed with manganese and nitrogen. In these steels, about half the nickel of the 500-series is replaced with manganese and nitrogen. Just enough nickel is added to form austenite at elevated temperatures and enough manganese to ensure that the austenite is stable at room temperature (the Ms-temperature is below room temperature). A possible drawback of these steels is that they exhibit a rapid rate of work-hardening, and are generally stronger than the nickel-containing alloys that they are intended to replace. This is primarily due to the decrease in nickel content, which leads to lower austenite stability and a decrease in stacking-fault energy (SFE), which, in turn, leads to higher rates of work-hardening, adversely affecting formability.

The increasing interest in a stainless steel that combines low cost with good formability has led to the development of a series of experimental Cr–Mn–N stainless steels at Mintek. The steels were designed as cheaper substitutes for the austenitic steels that are commonly used where good formability, and especially deep drawability, are important. Some envisaged applications include stainless-steel kitchen sinks, serving dishes, and cutlery. The experimental steels were designed to be similar in composition to type 201.
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stainless steel, with manganese and nitrogen replacing part of the nickel in the 300-series austenitic stainless steels. To decrease the rate of work-hardening inherent in these steels, copper was added. Copper is the only commercially available element other than nickel that is known to decrease the rate of work-hardening in austenite by raising the SFE5. It is also effective in stabilizing austenite against the formation of martensite5.

Chemical compositions of the experimental steels

A base alloy (723) was designed with a composition falling within the limits specified for type 201 stainless steel (Table I), except for the addition of 0.54 per cent copper to reduce the rate of work-hardening. Three reference steels were used, the chemical compositions of which are also shown in Table I. The first reference steel is a commercially available AISI type 304 stainless steel with more than 9 per cent nickel. The other two reference steels are laboratory melts with compositions falling within the range specified for type 201 stainless steel. Type 201A was designed to be similar in composition to the base alloy, but without the addition of copper. Type 201B is higher in nickel, but lower in manganese.

With the composition of the base alloy (723) as a basis, two further sets of alloys were produced. The first set, the nitrogen-containing steels, was designed to show the influence of nitrogen additions (0.001 to 0.27 per cent) on the properties of steels similar to the base alloy. The chemical compositions of the nitrogen-containing steels are shown in Table II. The second series of alloys, the copper-containing steels, was designed to show the influence of copper additions (0.01 to 3.11 per cent) to alloys similar to the base alloy except for the nickel content, which, in this case, was reduced to 2 per cent. The chemical compositions of these steels are given in Table III.

The mechanical properties and corrosion behaviour of the experimental alloys listed in Tables II and III have already been reported5–8. Copper additions to the experimental alloys result in a reduction in the proof stress and ultimate tensile strength5. Nitrogen additions raise the proof stress and the elongation, and depress the ultimate tensile stress (by about 30 MPa for each 0.1 per cent added) owing to the austenite-stabilizing effect of the nitrogen6. Copper and nitrogen additions reduce the rate of corrosion in 10 per cent H2SO4, but do not have any significant effect on the rate of corrosion in simulated minewater or synthetic seawater5,6.

The current study deals with the solidification behaviour of the experimental steels and their behaviour during autogenous fusion welding. As deep-drawn products are often welded by the use of autogenous processes (that is, without the use of a filler metal), it is important that such welding behaviour should be assessed. The aims of the project were as follows:

Table I

Composition range of AISI type 201 stainless steel, and the chemical compositions of the base alloy developed by Mintek and the three reference materials used in the investigation (percentage by mass)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>C</th>
<th>N</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AISI 304</td>
<td>17.2</td>
<td>6.9</td>
<td>4.0</td>
<td>0.04</td>
<td>0.07</td>
<td>0.036</td>
<td>0.067</td>
<td>0.19</td>
</tr>
<tr>
<td>Type 201A</td>
<td>17.2</td>
<td>7.1</td>
<td>4.1</td>
<td>0.04</td>
<td>0.05</td>
<td>0.034</td>
<td>0.079</td>
<td>0.51</td>
</tr>
<tr>
<td>Type 201B</td>
<td>17.2</td>
<td>5.6</td>
<td>0.02</td>
<td>0.07</td>
<td>0.047</td>
<td>0.119</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>Type 201C</td>
<td>17.0</td>
<td>7.1</td>
<td>4.2</td>
<td>0.04</td>
<td>0.05</td>
<td>0.036</td>
<td>0.001</td>
<td>0.44</td>
</tr>
<tr>
<td>Type 201D</td>
<td>17.1</td>
<td>7.2</td>
<td>4.1</td>
<td>0.04</td>
<td>0.05</td>
<td>0.035</td>
<td>0.047</td>
<td>0.46</td>
</tr>
<tr>
<td>Type 201E</td>
<td>17.5</td>
<td>7.1</td>
<td>4.1</td>
<td>0.04</td>
<td>0.05</td>
<td>0.034</td>
<td>0.270</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table II

Chemical compositions of the steels developed to show the influence of nitrogen additions (percentage by mass)

<table>
<thead>
<tr>
<th>Heat no.</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>C</th>
<th>N</th>
<th>Si</th>
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<tr>
<td>699</td>
<td>17.0</td>
<td>7.1</td>
<td>4.2</td>
<td>0.04</td>
<td>0.05</td>
<td>0.036</td>
<td>0.001</td>
<td>0.44</td>
</tr>
<tr>
<td>690</td>
<td>17.1</td>
<td>7.2</td>
<td>4.1</td>
<td>0.04</td>
<td>0.05</td>
<td>0.035</td>
<td>0.047</td>
<td>0.46</td>
</tr>
<tr>
<td>703</td>
<td>17.5</td>
<td>7.1</td>
<td>4.1</td>
<td>0.04</td>
<td>0.05</td>
<td>0.034</td>
<td>0.270</td>
<td>0.46</td>
</tr>
<tr>
<td>692</td>
<td>17.3</td>
<td>7.3</td>
<td>0.04</td>
<td>0.05</td>
<td>0.038</td>
<td>0.190</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>693</td>
<td>17.5</td>
<td>7.1</td>
<td>4.1</td>
<td>0.05</td>
<td>0.05</td>
<td>0.034</td>
<td>0.270</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table III

Chemical compositions of the steels developed to show the influence of copper additions (percentage by mass)

<table>
<thead>
<tr>
<th>Heat no.</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>C</th>
<th>N</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>713</td>
<td>17.1</td>
<td>7.0</td>
<td>2.0</td>
<td>0.05</td>
<td>0.01</td>
<td>0.046</td>
<td>0.10</td>
<td>0.40</td>
</tr>
<tr>
<td>714</td>
<td>16.9</td>
<td>7.1</td>
<td>2.2</td>
<td>0.06</td>
<td>0.03</td>
<td>0.048</td>
<td>0.10</td>
<td>0.42</td>
</tr>
<tr>
<td>715</td>
<td>17.1</td>
<td>7.1</td>
<td>2.1</td>
<td>0.05</td>
<td>0.05</td>
<td>0.037</td>
<td>0.09</td>
<td>0.42</td>
</tr>
<tr>
<td>716</td>
<td>17.1</td>
<td>7.1</td>
<td>2.1</td>
<td>0.05</td>
<td>0.05</td>
<td>0.034</td>
<td>0.09</td>
<td>0.42</td>
</tr>
<tr>
<td>717</td>
<td>17.0</td>
<td>6.9</td>
<td>2.1</td>
<td>0.05</td>
<td>3.11</td>
<td>0.034</td>
<td>0.10</td>
<td>0.39</td>
</tr>
</tbody>
</table>
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(1) to infer the susceptibility of the experimental steels to solidification cracking from an investigation of the weld-metal microstructures and the balance between austenite and δ-ferrite at elevated temperatures under equilibrium conditions
(2) to evaluate the corrosion properties of the steels in the as-welded condition and to compare the results with those obtained for the reference materials.

Susceptibility of the experimental steels to hot cracking during welding

Fully austenitic weldments are highly susceptible to hot cracking. Hot cracking, or solidification cracking, occurs during the final stages of solidification, at or above the solidus temperature of the lowest melting phase present. Owing to the over-critical presence of sulphur, phosphorus, or silicon, low-melting liquid films form at the grain boundaries, where segregation tends to be most extensive. When the material is subjected to thermal strains during cooling, its low strength, due to the presence of the liquid grain-boundary films, may result in the formation of hot cracks. It is generally recognized that a small amount of δ-ferrite retained in the weld metal, present as a non-continuous network, effectively limits the propagation of solidification cracks. More recent research indicates that the presence of ferrite is not a sufficient condition to decrease the susceptibility to hot cracking in austenitic stainless-steel welds. The most important condition for preventing hot cracking is primary ferritic solidification. If these two conditions are met, the steels should not be susceptible to hot cracking.

Experimental procedure

The chemical composition, specifically the balance between austenite- and ferrite-formers, is the principal factor determining the mechanism of solidification in austenitic stainless steels. Since chromium and nickel are the principal alloying elements in most austenitic stainless steels, the Creq/Nieq ratio is the dominant factor controlling the solidification mode. The chromium and nickel equivalent values for the experimental steels were calculated according to Espy's equations ([1] and [2]), which are expressed in percentage by mass:

\[
\text{Creq} = (\%\text{Cr}) + (\%\text{Mo}) + 1.5(\%\text{Si}) + 0.5(\%\text{Nb}) + 5(\%\text{V}) + 3(\%\text{Al})
\]

\[
\text{Nieq} = (\%\text{Ni}) + 30(\%\text{C}) + 0.87(\text{for Mn}) + 0.53(\%\text{Cu}) + 8(\%N - 0.045)X.
\]

where \(X = 0.0\) when N is between 0.0 and 0.2 per cent
\(X = 22\) when N is between 0.21 and 0.25 per cent
\(X = 20\) when N is between 0.26 and 0.35 per cent.

It is interesting to note that Espy makes use of a fixed number (0.87) to account for the influence of manganese, regardless of the actual manganese content. The weak austenite-forming ability of manganese results in having very little influence on the composition of the weld-metal phase.

Depending on the chemical composition, an austenitic stainless steel can solidify by primary separation of austenite or δ-ferrite from the liquid. The possible sequence of phase transformations during solidification under equilibrium conditions can be approximated by the selection of a vertical section at 70 per cent iron of the Fe–Cr–Ni ternary system. The pseudo-binary phase diagram is illustrated schematically in Figure 1. Although the experimental alloys are multi-component systems, the pseudo-binary phase diagram in Figure 1 gives a good approximation of the solidification process.

![Figure 1](image_url)

The ferrite–austenite phase distribution after annealing at a range of temperatures can be used to give an indication of the position on the pseudo-binary phase diagram (Figure 1) of a specific alloy relative to the δ/(δ+austenite) and (δ+austenite)/austenite phase boundaries. In order to determine the δ-ferrite content of the experimental alloys at different temperatures, samples of every alloy were annealed at temperatures ranging from 950 to 1390°C. An annealing time of 15 minutes was determined to be sufficient to reach equilibrium. After being annealed, the samples were quenched rapidly in water so that they would retain the high-temperature microstructures. The phase balance in each structure was determined by use of a point-counting technique.

Figure 1 indicates that the structure of the weld metal after autogenous welding (especially the δ-ferrite morphology) also gives an indication of the solidification mode and the position of the alloy relative to the phase boundaries. For the investigation of the ferrite morphology in welds, samples of each alloy were welded by an autogenous gas-tungsten arc-welding (GTAW) process. The process variables were adjusted to produce GTAW welds with partial penetration, and are shown in Table IV.
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Table IV
Welding process variables

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate thickness</td>
<td>1 mm</td>
</tr>
<tr>
<td>Electrode type</td>
<td>2% thoriated tungsten electrode</td>
</tr>
<tr>
<td>Classification</td>
<td>EWTh-2</td>
</tr>
<tr>
<td>Electrode diameter</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tip configuration</td>
<td>Ground to a 90° included angle</td>
</tr>
<tr>
<td>Arc length</td>
<td>2 mm</td>
</tr>
<tr>
<td>Polarity</td>
<td>Direct current, electrode negative (DCEN)</td>
</tr>
<tr>
<td>Torch travel speed</td>
<td>3.4 mm/s</td>
</tr>
<tr>
<td>Shielding gas</td>
<td>Argon, flow rate 30 l/min</td>
</tr>
<tr>
<td>Arc current</td>
<td>39 to 42 A</td>
</tr>
<tr>
<td>Arc voltage</td>
<td>8.4 to 10.1 V</td>
</tr>
<tr>
<td>Calculated heat input</td>
<td>47 to 54 J/mm</td>
</tr>
</tbody>
</table>

Results and discussion

Nitrogen-containing steels

The Creq/Nieq ratios of the nitrogen-containing experimental steels are shown in Table V. The alloys can be arranged in three distinct groups according to the Creq/Nieq values. Alloys 689 (0.001 per cent nitrogen) and 690 (0.047 per cent nitrogen) have similar Creq/Nieq values. For this reason, the amount of retained α-ferrite after annealing and the weld microstructures are similar. Alloys 723 (0.09 per cent nitrogen) and 703 (0.13 per cent nitrogen), and alloys 692 (0.19 per cent nitrogen) and 693 (0.27 per cent nitrogen) can be grouped together for the same reason.

Table V
Chromium and nickel equivalents for the experimental steels calculated from Espy’s equations

<table>
<thead>
<tr>
<th>Heat no.</th>
<th>Creq (Creq/Nieq)</th>
<th>Nieq</th>
<th>Creq/Nieq</th>
</tr>
</thead>
<tbody>
<tr>
<td>689 (0.001% N)</td>
<td>17.74</td>
<td>6.32</td>
<td>2.8</td>
</tr>
<tr>
<td>690 (0.047% N)</td>
<td>17.90</td>
<td>6.25</td>
<td>2.9</td>
</tr>
<tr>
<td>723 (0.090% N)</td>
<td>17.94</td>
<td>7.66</td>
<td>2.3</td>
</tr>
<tr>
<td>703 (0.130% N)</td>
<td>18.24</td>
<td>8.68</td>
<td>2.1</td>
</tr>
<tr>
<td>692 (0.190% N)</td>
<td>18.10</td>
<td>10.50</td>
<td>1.7</td>
</tr>
<tr>
<td>693 (0.270% N)</td>
<td>18.31</td>
<td>10.70</td>
<td>1.7</td>
</tr>
<tr>
<td>713 (0.019% Cu)</td>
<td>17.78</td>
<td>5.90</td>
<td>3.0</td>
</tr>
<tr>
<td>714 (0.059% Cu)</td>
<td>17.74</td>
<td>6.03</td>
<td>2.9</td>
</tr>
<tr>
<td>716 (0.10% Cu)</td>
<td>17.82</td>
<td>5.66</td>
<td>3.1</td>
</tr>
<tr>
<td>717 (0.11% Cu)</td>
<td>17.82</td>
<td>6.03</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The amount of δ-ferrite present in alloys 689 and 690 at specific annealing temperatures is shown in Figure 2. Even after having been annealed at temperatures as low as 950°C, alloys 689 and 690 still contain a small amount of δ-ferrite. The composition of these steels seem to fall within the dual-phase ferrite-plus-austenite region of the phase diagram (Figure 1) at these lower temperatures. At temperatures higher than 1250°C, there is an abrupt increase in the ferrite content. Owing to the position of the austenite/δ-austenite plus ferrite boundary on the phase diagram (Figure 1), an increase in the ferrite content with increasing temperature precludes the possibility of primary austenitic solidification. At temperatures as high as 1350 and 1390°C, the structures still contain appreciable amounts of austenite, and are probably still within the austenite-δ-ferrite phase field.
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δ-ferrite increases, indicating that primary austenitic solidification does not take place. At 1390°C, the steels contain less than 20 per cent ferrite and are probably still within the dual-phase austenite-plus-ferrite region. This indicates that the compositions of the alloys must lie close to the eutectic triangle (Figure 1), as expected from the low Cr<sub>eq</sub>/Ni<sub>eq</sub> ratios. The conclusion can be drawn that the alloys solidify in region 2 of the phase diagram (Figure 1), δ-ferrite being the leading phase. The weld microstructures (a typical example is shown in Figure 7) confirm this conclusion in that they consist predominantly of austenite with a small amount of vermicular ferrite (black).

Copper-containing steels

The amounts of strong austenite-forming elements (nickel, carbon, and nitrogen) are similar for all the alloys in this series of copper-containing steels. The only element that varies significantly is copper, which is known to be a weak austenite-former<sup>2</sup>. For this reason, copper is not expected to influence the solidification behaviour and weld-metal microstructures of the steels to any large extent. This is confirmed by the data given in Figure 8 in which the amount of δ-ferrite present at different temperatures is shown for the alloys with the minimum (0.01...}

Figure 3—The microstructure of the weld metal in alloy 689 (0.001 per cent N) after autogenous welding

Figure 4—The amount of δ-ferrite after the annealing of alloys 723 (0.09 per cent N) and 703 (0.13 per cent N) at specific temperatures

Figure 5—The microstructure of the weld metal in alloy 703 (0.13 per cent N) after autogenous welding
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Figure 6—The amount of δ-ferrite after the annealing of alloys 692 (0.19 per cent N) and 693 (0.27 per cent N) at specific temperatures

Figure 7—The microstructure of the weld metal in alloy 693 (0.27 per cent N) after autogenous welding

Figure 8—The amount of δ-ferrite in alloys 713 (0.01 per cent C) and 717 (3.11 per cent Cu) after autogenous welding

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per cent) and maximum (3.11 per cent) copper contents. The δ-ferrite content of the two alloys is almost identical, emphasizing the weak austenite-forming ability of copper.

On cooling, the copper-containing steels retain dual-phase austenite-ferrite microstructures down to very low temperatures, suggesting that these alloys remain in the austenite-plus-ferrite phase field down to ambient temperature without being transformed to fully austenitic structures. The amount of δ-ferrite in all the steels increases significantly at annealing temperatures higher than about 1300°C, the structures being almost fully ferritic at a temperature of 1350°C. The conclusion can be drawn that, at 1350°C, the compositions of these steels are in the single-phase ferrite region located on the chromium-rich side of the ferrite solvus line (Figure 1). The results indicate that the high Crreq/Nireq values shift the positions of the copper-containing steels into region 4 of the pseudo-binary phase diagram, with δ-ferrite the primary phase during solidification. The microstructures of the welds, of which a typical example is shown in Figure 9, confirm this conclusion. The structures are all essentially similar owing to the weak austenite-forming ability of copper. The weld metal contains δ-ferrite (grey etching phase), and some martensite and austenite (light etching phase) in the form of Widmanstätten needles growing into the ferrite.

Pitting corrosion of welded joints

Experimental procedure

Electrochemical pitting-corrosion tests of welded samples were carried out according to ASTM Standard G61-86 for the conducting of cyclic potentiodynamic measurements\textsuperscript{18}. The samples examined were chosen in such a way that the weld, the heat-affected zone (HAZ), and the surrounding base metal were exposed simultaneously to the solution. At least two tests were performed for each alloy. The samples were immersed in a de-aerated 3.56 per cent NaCl solution for one hour before scanning commenced. After one hour, the corrosion potential ($E_{corr}$) was noted, and the scan proceeded from the corrosion potential in the noble direction at a scanning rate of 0.6 V/h. The onset of pitting is indicated by

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Figure 9—The microstructure of the weld metal in alloy 713 (0.01 per cent Cu) after autogenous welding

an abrupt increase in the corrosion rate that occurs above a certain potential, the pitting potential ($E_{\text{pit}}$). The scanning direction is reversed when the current reaches 5 mA/cm$^2$, and the scan continues until the corrosion potential is reached or the hysteresis loop closes. The potential where the hysteresis loop closes is termed the protection potential ($E_{\text{prot}}$). An example of a typical cyclic polarization diagram with $E_{\text{corr}}$, $E_{\text{pit}}$, and $E_{\text{prot}}$ indicated is shown in Figure 10. The pitting potential ($E_{\text{pit}}$) is used to characterize the pitting behaviour of an alloy. Because a wide range of alloys was used and both $E_{\text{corr}}$ and $E_{\text{pit}}$ vary depending on the type of alloy, the difference ($E_{\text{pit}} - E_{\text{corr}}$) gives a better indication of the resistance of the alloys to pitting. The larger the difference between these potentials, the higher the resistance to pitting corrosion.

Results and discussion

Nitrogen-containing steels

The influence of increasing nitrogen contents on the pitting corrosion behaviour of the nitrogen-containing steels as given by the ($E_{\text{pit}} - E_{\text{corr}}$) values is shown in Figure 11. The average ($E_{\text{pit}} - E_{\text{corr}}$) values obtained for type 304 and the two type 201 stainless steels are also indicated. (All values for the electrode potential are given relative to the Ag/AgCl reference electrode.)

The nitrogen-containing steels show an increase in resistance to pitting with increasing nitrogen content. This is consistent with the findings of other investigations, which showed that the presence of nitrogen appreciably increases the resistance of manganese-containing steels to pitting. The mechanism responsible for this greater resistance to pitting could not be identified. It is known that pitting represents a localized breakdown of the passive film. Apparently the passive film contains more chromium and molybdenum when nitrogen is present, reducing the rate of breakdown. With these reduced rates, an increase in effective potential is needed to initiate pitting corrosion. After pit initiation, nitrogen also plays a role in retarding pit growth. As the metal dissolves in the pitting solution, the dissolved nitrogen consumes an H$^+$ ion in the pit to form an ammonium ion. This prevents the lowering of the pH in the pit and helps to passivate the pit in the earlier stages of pit formation. Nitrogen also plays a small role in reducing the rate of active corrosion in a pit. If the experimental steels in the as-welded condition are compared with type 304 stainless steel, it is evident that very high nitrogen levels are required for the
The welding of experimental low-nickel Cr–Mn–N stainless steels resistance to pitting of the experimental steels to be comparable with that of type 304. (An average value for \( E_{\text{pit}} - E_{\text{corr}} \) of 455 mV was obtained for type 304 in the same test.) Except for the alloys containing less than 0.1 per cent nitrogen, the steels compare well with type 201 stainless steel, where average values for \( E_{\text{pit}} - E_{\text{corr}} \) of 363 mV for type 201A, and 273 mV for type 201B were obtained.

**Copper-containing steels**

The influence of increases in copper content on the tendency of the experimental steels to pitting corrosion as given by \( E_{\text{pit}} - E_{\text{corr}} \) is shown in Figure 12.

![Figure 12](image)

**Figure 12**—The influence of copper on the resistance to pitting corrosion (as given by \( E_{\text{pit}} - E_{\text{corr}} \)) of the copper-containing steels

The addition of copper to stainless steels is known to have a beneficial effect on their resistance to pitting corrosion. This is due to a reduction in the rate of active corrosion in the presence of copper. Up to a copper level of 1 per cent, the copper-containing alloys also show this tendency. An increase in the copper content of the experimental steels to levels higher than 1 per cent seems to have a slight negative effect on their resistance to pitting corrosion. Even the maximum value of \( E_{\text{pit}} - E_{\text{corr}} \) at 1 per cent copper does not compare well with the average value of 455 mV for type 304 in the same test. Except for the alloys containing 0.5 and 1 per cent copper, the steels do not perform well compared with type 201 stainless steel.

The decrease in resistance to pitting at higher copper levels (more than 1 per cent) is probably the result of a significant surface enrichment of metallic copper, which has been detected in both copper-containing ferritic and austenitic stainless steels exposed to chloride-containing solutions. The metallic surface layer of copper dissolves as cupric ions \( (\text{Cu}^2+ + 2e^-) \) in the passive potential range. This dissolution of metallic copper has a detrimental effect on the stability of the passive film by producing a number of active sites from which local dissolution of the passive film starts. As a result, the presence of significant amounts of copper (more than 1 per cent) in the experimental steels may result in a decrease in resistance to pitting corrosion.

**Susceptibility to sensitization and intergranular corrosion in the as-welded condition**

**Experimental procedure**

Stainless steels are potentially susceptible to sensitization and intergranular attack. The susceptibility of welded samples to these phenomena was evaluated according to Practice B of ASTM Standard A262-93A for the detection of the susceptibility to intergranular attack in austenitic stainless steels. The more commonly used oxalic acid test (Practice A) could not be used because of the presence of large amounts of b-ferrite in the weld metal of most specimens. Practice B describes the procedure for the ferric sulphate–sulphuric acid test. It detects susceptibility to intergranular attack associated with the precipitation of chromium carbides in unstabilized austenitic stainless steels. This method was selected because it is suitable for small specimens, and the quantitative nature of the results facilitates comparison between different alloys. The samples tested contained welds, but were cut in such a way that no more than a 13 mm width of base metal was included on either side of the weld.

**Results and discussion**

**Nitrogen-containing steels**

The influence of increasing nitrogen levels on the corrosion rate of the experimental steels during testing in a boiling ferric sulphate–sulphuric acid solution is shown in Figure 13. The average corrosion rates measured for type 304, 210A, and 201B stainless steels are also indicated.

It is generally recognized that the presence of nitrogen in stainless steels decreases their susceptibility to sensitization by retarding the growth of \( \text{M}_{23}\text{C}_6 \) precipitates. This is probably due to an increase in the concentration of chromium at the carbide interface, which lowers the concentration gradient between the austenite matrix and the grain boundaries. Since the diffusion of chromium in austenite is rate controlling, sensitization is retarded. The expected
The welding of experimental low-nickel Cr–Mn–N stainless steels

beneficial effect of nitrogen is not evident in the experimental steels, probably because the samples display general corrosion but are unsensitized. The differences in corrosion rate merely reflect differences in passive current density. This conclusion is based on the following observations.

The average corrosion rate obtained for type 304 stainless steel during testing was 0.69 mm/year. This value is less than the maximum corrosion rate generally used in the case of type 304 as a criterion to determine whether sensitization took place, which is 1.2 mm/year. The conclusion can be drawn that autogenous welding of type 304 does not render the structure susceptible to intergranular corrosion. This was confirmed by examination of the corroded samples under a scanning electron microscope (SEM), which revealed some evidence of carbide precipitation at the grain boundaries, but no evidence of intergranular corrosion. The nitrogen-containing experimental steels show low corrosion rates of the same order as that of type 304 stainless steel, and SEM investigation confirmed that these steels are not sensitized in the as-welded condition. Hence, the differences in corrosion rate between the alloys are probably due to differences in passive current density. Although the experimental alloys perform slightly worse than type 304, the corrosion rates during testing compare well with that of type 201 stainless steel.

Copper-containing steels

The influence of increasing copper levels on the corrosion rate in a boiling ferric sulphate–sulphuric acid solution is shown in Figure 14.

Copper does not seem to have a significant influence on the resistance of the experimental alloys to intergranular corrosion. The low corrosion rates of the alloys indicate that the steels are not sensitized in the as-welded condition. The results obtained for alloy 717 (3.11 per cent copper) are not included in Figure 14 since an incorrectly performed solution heat treatment prior to welding resulted in severe sensitization and intergranular corrosion of the base-metal structure.

Hardness profiles across welds

Hardness profiles across autogenous welds indicate that the difference in hardness between the base material and the weld metal of the experimental steels is much less pronounced than in the case of type 304 stainless steel. The difference in hardness between the base material and the weld metal of type 304 stainless steel is around 20 Vickers, while in most cases the difference is less than 12 Vickers in the case of the experimental steels. The conclusion can be drawn that autogenous welding does not have a significant influence on those mechanical properties which are related to hardness.

Practical implications

The nitrogen-containing experimental steels are not particularly susceptible to hot cracking or sensitization during welding. Autogenous welding does not influence the mechanical properties of the alloys to the same extent as in the case of type 304 stainless steel. The alloys with lower nitrogen contents (689, 690, 723, and 703) will be suitable in applications where excellent corrosion resistance is not an important requirement. The high-nitrogen steels (692 and 693) are very suitable for welding. These steels display pitting-corrosion resistance comparable with that of type 304 stainless steel, fine weld microstructures similar to that of type 304 (which will make the steels especially resistant to hot cracking), and mechanical properties in the weld similar to that of the base metal. The high-nitrogen alloys should be excellent low-cost substitutes for type 304 stainless steel.

The weldability of the copper-containing steels is not as good as that of the nitrogen-containing steels. Although the steels have good resistance to hot cracking due to the presence of δ-ferrite and primary ferritic solidification, the coarser microstructures and large amounts of δ-ferrite in the weld metal will to some extent decrease the resistance to hot cracking. Autogenous welding does not render the steels susceptible to sensitization, and the mechanical properties of the welds are similar to those of the base metal. These steels will be suitable for applications where low cost is important and corrosion resistance inferior to that of type 304 can be tolerated.

A portion of the Espy diagram for the prediction of weld microstructures is shown in Figure 15. The positions of the base alloy (725), the alloys with the minimum and maximum nitrogen levels (689 and 693), and the alloys with the minimum and maximum copper levels (713 and 717) are shown on the diagram, as well as the positions of some commercially available filler metals. Most of the commercially available filler metals for austenitic stainless steels are suitable for the welding of the experimental steels. Types 316L and 309L stainless steel can be used successfully as filler metals, but 308L should be avoided in the steels with lower nitrogen levels (689, 690, 723, 703, and the copper-containing steels) because it could result in the presence of martensite in the weld metal. Although the position of type 310 stainless steel is not shown on the diagram because of the reduced scale, it should be avoided as a filler metal since it will result in fully austenitic weld microstructures, which will be susceptible to hot cracking.

Conclusions

(1) All the nitrogen-containing steels solidify primarily as δ-ferrite. The morphology of the δ-ferrite retained in the
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