Influence of Flux Composition on the Performance of a Nickel-Based Alloy Covered Electrode for 9% Ni Steel Welding

The effect of the flux coating ingredients on the welding performance, weld quality, mass transfer coefficient, and cryogenic impact energy is presented

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ABSTRACT

A nickel-based alloy covered electrode with two different types of flux coating was investigated in terms of weldability, weld quality, mass transfer, microstructure, and mechanical properties. It was found that the strong basic CaF₂-CaO-SiO₂ type electrode exhibited a larger deposition rate, smaller spatter loss and fumes, better fluidity of slag, and wider weld bead. The alkalies TiO₂-SiO₂-SrO type electrode exhibited larger penetration and excellent slag detachability. The metals had the larger mass transfer coefficients in the strong basic slag system if they could form basic oxides. However, the elements had the smaller mass transfer coefficients in the strong basic slag system if they could form acidic oxides. The impurities, S, P, and O, were in the relatively lower levels in the deposited metals of the CaF₂-CaO-SiO₂ type electrodes because of the higher contents of CaF₂ and CaO in the slag. The Charpy impact values of the CaF₂-CaO-SiO₂ type at 77 K were in the range of 81–83 J, but that of the TiO₂-SiO₂-SrO type were in the range of 66–70 J.

KEYWORDS

• Nickel-Based Alloy • Covered Electrode • Flux Coating • Cryogenic Impact
• 9% Ni Steel

Introduction

As one of the world’s three pillars of energy, liquefied natural gas (LNG) has occupied a very important position in the world energy pattern. The global demand for LNG has been increasing continuously in recent years. According to an energy report (Ref. 1), the global demand for LNG will reach 350 million tons in 2020. The storage and delivery of LNG will continue to increase. Because LNG is stored at or below its boiling temperature, the material for the inner walls of LNG storages should securely serve at the cryogenic temperature. Thus, it must have high strength and suitable fracture toughness at the cryogenic temperature. In 1942, 9% nickel steel was developed by an international nickel company as a structural material at cryogenic temperatures. Its low-temperature (77 K) impact value reached 200–300 J. It is the best ductile material that can serve in cryogenic conditions due to its high strength, large fatigue resistance, excellent corrosion resistance, small thermal expansion coefficient, and good weldability (Ref. 2). So far, 9% Ni steel has been comprehensively investigated. Its microstructure consists of fine martensite and retained austenite. The addition of 9% Ni keeps the unstable austenite from austenitization temperature to the room temperature. The existence of the retained austenite results in excellent mechanical properties at cryogenic temperature (Refs. 2–5).

As well known, the welding consumables are key factors affecting the quality of the weld joint. The covered electrode of a Ni-Cr-Fe alloy with a Ni content more than 55 wt-% can be used for 9% Ni steel welding (Refs. 6–8). Although the nickel-based alloy covered electrodes are expensive and show poor welding performance, their strength and low-temperature toughness are excellent. The thermal expansion coefficient of the nickel-based alloy is also similar to that of 9% Ni steel. In the industry, each welding consumable producer has its own flux ingredient that strongly affects the weld quality, mass transfer coefficient, bead geometry, slag detachability, and other welding performance. Generally, the flux coating composition includes gas formers, slag formers, binders, extrusion aids, alloy elements, and so on. The role of the flux coating includes protecting the weld metal from the invasion of air, keeping the arc stability, ensuring good slag detachability, and reducing spatter. In general, it is very difficult to take into account all these aspects when drawing up a flux ingredient. In recent years, several types of flux coatings have been investigated in our laboratory for developing high-level stainless steel and nickel-based alloy covered electrodes, such as E316L (Ref. 9), CaO-CaF₂, CaO-CaF₂-TiO₂,
and CaO-TiO₂-SiO₂ type ENiCrFe-7 (Refs. 8, 10, 11). Recently, a modified ENiCrFe-9 covered electrode has been developed that was designed especially for welding 9% Ni steel for construction of large-tonnage LNG ships. For improving the cryogenic impact toughness of the weld metal, both alkalescent and strong basic slag systems were adopted. In this paper, the modified ENiCrFe-9 covered electrodes with two different slag basicities were investigated in terms of the mass transfer coefficient, as-deposited microstructure, as well as the mechanical properties of the deposited metal. One of the objectives of this study was to evaluate the mass transfer coefficients of the key elements in two different flux coating systems for developing ENiCrFe-9 type covered electrode for welding 9% Ni steel. The results could also provide valuable data for developing other types of nickel-based covered electrodes with pure nickel core.

Experimental Procedure

Because the alloy core wire was more difficult to produce, and had a higher electric resistance that could result in a quick temperature rise during welding (Refs. 7, 12), the commercial pure nickel with diameter of 3.2 mm and length of 350 mm was used as the core wire in this paper. In the pure nickel, the C is less than 0.05 wt-%, and the S and P are less than 0.015 wt-%, respectively. The other impurities are less than 0.5 wt-%. Some appropriate mineral powders used in the flux coating were selected in accordance with our own proprietary technology. Ingredients of the flux coating are listed in Table 1.

The production process of the covered electrodes was carried out by using the conventional extrusion method. The as-extruded covered electrodes were baked at 423 K for 1 h and then 573 K for 1 h. The appearance of the core wires and the covered electrodes are shown in Fig. 1A.

Prior to welding, the base metal
was polished with a grinding wheel and then cleaned with acetone. Butt joint welding in the flat position was performed by using shielded metal arc welding (SMAW). The alternating current was set to 125–130 A, the welding voltage was 23–25 V, the welding speed was 3.5–4.0 mm/s, and the interpass temperature was controlled below 393 K. To keep both ends of the weld at the same height, the welding of the next pass began at the end of the previous pass. Between passes, the weld bead was cleaned with a chipping hammer and stainless steel brush. Radiography was conducted to detect welding defects, and the results indicated that all the deposited metals were qualified. The appearance of the as-welded plate and the macro morphology of the deposited metal with about 45–50 passes were shown — Fig. 1B and C.

The spatter loss coefficient, melting and deposited rates, slag detachability, and bead geometry were evaluated by using the methods described in Refs. 12–18. To collect the spatter, a 9% Ni plate with the thickness of 3 mm was erected on a copper plate with the thickness of 3 mm. Both the 9% Ni steel and the copper plate were put in a cylindrical box of copper with the height of 400 mm, diameter of 600 mm, and thickness of 1 mm for avoiding spatter loss. The spatter deposited on the plate in the box could be easily collected. The spatter loss coefficient, SLC was defined as

\[ \text{SLC} = \frac{M_c}{M_w} \times 100\% \]  

where \( M_c \) indicates the weight of the core wire of the electrode, \( M_w \) indicates the mass loss of the electrode. For each type electrode, three tests were conducted. The reported SLC is the average value of the three tests.

The melting rate, MR, and the deposited rate, DR, are defined as the following equations:

\[ \text{MR} = \frac{M_c}{At} \]  

\[ \text{DR} = \frac{M_d}{At} \]  

where \( M_c \) indicates the mass loss of the core wire, \( M_d \) indicates the weight of the deposited metal, \( A \) indicates the welding current, and \( t \) indicates the duration of the welding process. \( A \) and \( t \) were recorded during the experiments. Both \( M_c \) and \( M_d \) could be directly measured. \( M_c \) is the mass difference of the core wire of the electrode before and after welding. \( M_d \) is the mass increment of the 9% Ni steel plate, which could be measured by weighing the steel plate before and after welding (slag was removed before weighing). Because the mass loss during welding includes spattering, evaporating at welding temperature (in the form of welding fumes), oxidizing/burning (in the form of oxides mixed with the slag), and residual metal particles embedded in the slag (Refs. 10, 12), the coefficient of loss, CL, was defined as

\[ \text{CL} = 1 - \frac{\text{DR}}{\text{MR}} \]  

For quantitatively measuring the slag detachability, the images of the weld joint with the residual slag were analyzed by using the commercial Image-Pro Plus software to determine the relative fraction of the slag adhesion area. Then the slag detachability rate, SDR, could be defined as

\[ \text{SDR} = \frac{A_0 - A_1}{A_0} \times 100\% \]  

where \( A_0 \) and \( A_1 \) indicate the slag adhesion area and the total area of the weld joint in the image, respectively.

In addition, all the welding operations in this study were done by a professional welder. Some subjective judgments on the operating properties of the electrodes, such as slag fluidity and fumes, were made by the welder.

The chemical compositions of the welding slag were analyzed by a Thermo Fisher ARL9900 x-ray fluorescence spectrometer (XRF). Considering that the slag was a mixture of oxides and fluoride, the analyzed result could be expressed in terms of calcium fluoride, basic oxides, and acidic oxides (Refs. 8, 9, 12, 13, 17–20). The chemical compositions of the welding slag were presented in Table 2. The basicity of each

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**Table 2 — Compositions of Slags for the Nickel-Based Alloy Covered Electrodes (wt-%)**

<table>
<thead>
<tr>
<th>Type</th>
<th>CaO</th>
<th>CaF₂</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>MnO</th>
<th>Nb₂O₅</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>FeO</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
<th>MoO</th>
<th>MgO</th>
<th>NiO</th>
<th>WO₃</th>
<th>SrO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF₂-CaO-SiO₂</td>
<td>23.40</td>
<td>39.98</td>
<td>12.84</td>
<td>4.44</td>
<td>2.92</td>
<td>2.32</td>
<td>2.23</td>
<td>1.72</td>
<td>1.17</td>
<td>3.01</td>
<td>2.87</td>
<td>1.06</td>
<td>0.79</td>
<td>1.07</td>
<td>0.18</td>
<td>—</td>
</tr>
<tr>
<td>TiO₂-SiO₂-SrO</td>
<td>3.18</td>
<td>17.16</td>
<td>13.38</td>
<td>23.27</td>
<td>5.04</td>
<td>1.70</td>
<td>3.67</td>
<td>8.14</td>
<td>0.92</td>
<td>2.98</td>
<td>7.96</td>
<td>0.53</td>
<td>1.93</td>
<td>1.01</td>
<td>0.13</td>
<td>9.00</td>
</tr>
</tbody>
</table>
flux coating could be evaluated by the following equation (Refs. 17, 18) that has been widely used in evaluating the basicity index of flux coating. 

\[
\text{B.I.} = \frac{\text{CaO} + \text{MgO} + \text{MnO} + \text{FeO} + \text{Fe}_{2}\text{O}_3 + \text{ZrO}_2}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + 0.5 (\text{TiO}_2 + \text{ZrO}_2)}
\]

where each chemical composition of the slag is expressed in weight percent. When the B.I. for a given flux coating is less than 1.0, the flux coating is regarded as neutral. A B.I. greater than 1.2 is regarded as basic. When the B.I. is between 1.0 and 1.2, the flux coating is considered as acidic. When the B.I. is between 0.8 and 1.0, the flux coating is regarded as acid. When the B.I. is less than 0.8, the flux coating is regarded as basic.

Assessment of the Weldability and Weld Quality

The weldability and weld bead quality, including arc stability, deposition rate, spattering, fumes, slag detachability, penetration, and bead geometry, are especially influenced by the flux composition of the covered electrodes. Considering that clean weld metals (i.e., ultra low hydrogen, low oxygen, low sulphur, and phosphorus) are extremely important for the cryogenic application, an alkalessent TiO₂-SiO₂-SrO type and a strong basic CaF₂-CaO-SiO₂ type slag

<table>
<thead>
<tr>
<th>Table 3 — Chemical Compositions of the Deposited Metals for the Nickel-Based Alloy Covered Electrodes (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
</tr>
<tr>
<td>CaF₂-CaO-SiO₂</td>
</tr>
<tr>
<td>TiO₂-SiO₂-SrO</td>
</tr>
<tr>
<td>AWS A5.11 ENiCrFe-9</td>
</tr>
</tbody>
</table>

Fig. 3 — Macro morphologies of the welds with and without slag: A and B — CaF₂-CaO-SiO₂ type; C and D — TiO₂-CaF₂-SiO₂ type.
systems were established in this study. Through a large number of experimental selections, the flux ingredients of these two slag systems were optimized and fixed (as listed in Table 1), which ensured acceptable operationality (stable arc, small spattering and fumes, good slag detachability) and good weld bead quality (good appearance, no porosity, no cracks, appropriate weld geometry). Comparing the two slag systems, the CaF$_2$-CaO-SiO$_2$ type exhibited a larger deposition rate, smaller spatter loss, smaller fumes, and better fluidity of slag during welding, while the TiO$_2$-SiO$_2$-SrO type exhibited better slag detachability. The weldability of these two types of flux-coated electrodes was summarized in Table 4 for comparison.

Figure 3 shows the appearance of the weld beads for the two types of electrodes. The slag of the CaF$_2$-CaO-SiO$_2$ type was dark brown, but that of the TiO$_2$-SiO$_2$-SrO type was light brown — Fig. 3A and C. After removing the slag, both beads exhibited fine ripples on the surface of the welds. Some small burnt-on slags could be found — Fig. 3B. This indicated that the slag detachability of the CaF$_2$-CaO-SiO$_2$ type flux was not as good as that of the TiO$_2$-SiO$_2$-SrO type flux — Fig. 3D.

To evaluate the weld geometry, the two weld beads were sectioned — Fig. 4. It was evident that the height and penetration, as defined in Fig. 4A, of the weld bead of the TiO$_2$-SiO$_2$-SrO type were obviously larger than that of the CaF$_2$-CaO-SiO$_2$ type — Fig. 4B and C. The CaF$_2$-CaO-SiO$_2$ flux resulted in a wider weld bead because of its better fluidity of slag during welding (Table 4). Generally, the fluidity of slag depends on its viscosity at the welding temperature, which influences the bead profile and the weld quality via affecting the metallurgical reactions and metal transfer during welding (Ref. 21). The appropriate slag viscosity provides effective protection of the welding pool from atmospheric gases. In the flux ingredients, the titanates, silicates, and other acidic oxides are commonly used to enhance the viscosity of slag. For example, the basic unit in the silica network is the silicate tetrahedron made up of a small silicon atom surrounded by four close-packed oxygen atoms. The two- or three-dimensional network forms by the close connection between these SiO$_4^{4-}$ silicate tetrahedrons, which increases the viscosity of slag. On the other hand, the fluoride and the basic oxides (such as CaO) can decrease the viscosity of slag due to the breakdown of the network structure (Ref. 22). Because the atomic size of F$^-$(1.33 Å) is similar to the O$^-$(1.36 Å), the F$^-$ replaces the O$^-$ in the -O-Si-O- to form the -Si-F- structure. The basic oxides break down the network stemming from the cations (such as the Ca$^{2+}$ introduced by the CaO) that were inserted into a spatial structure created by the -Si-O- liaison, forming the -Si-O-Ca-O- structure. For the TiO$_2$-SiO$_2$-SrO type, there is a higher level of SiO$_2$ and TiO$_2$ that contribute to a higher viscosity of slag. The network structure built by the SiO$_2$ (and/or TiO$_2$) confines the fluidity of the weld pool and the transverse diffusion of heat, resulting in the deeper penetration and smaller bead width (Refs. 16, 17, 20–23).

<table>
<thead>
<tr>
<th>Type</th>
<th>Melting Rate (g/amp·h)</th>
<th>Deposition Rate (g/amp·h)</th>
<th>Coefficient of Loss</th>
<th>Spatter Loss Coefficient (%)</th>
<th>Slag Detachability (%)</th>
<th>Fluidity of Slag during Welding</th>
<th>Fumes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$-CaO-SiO$_2$</td>
<td>14.70</td>
<td>14.20</td>
<td>3.40</td>
<td>1.21</td>
<td>95%</td>
<td>Better</td>
<td>Better</td>
</tr>
<tr>
<td>TiO$_2$-SiO$_2$-SrO</td>
<td>13.60</td>
<td>13.06</td>
<td>3.97</td>
<td>1.39</td>
<td>100%</td>
<td>Not good</td>
<td>Not good enough</td>
</tr>
</tbody>
</table>

Fig. 4 — Cross-sectional images of the weld metals: A — Sketch map of the weld metal; B — CaF$_2$-CaO-SiO$_2$ type; C — TiO$_2$-CaF$_2$-SiO$_2$ type.
of CaO and CaF₂ leads to a lower viscosity of slag, which results in a reverse effect, i.e., smaller penetration but larger bead width — Fig. 4B.

Chemical Composition of the Deposited Metals and Mass Transfer

Although the chemical compositions of the deposited metals of the two types of electrodes met the requirements of the AWS A5.11 ENiCrFe-9 standard (Table 3), some apparent differences in the main alloy elements between the two types could be found. The Mo, W, Cr, Mn, and Si in the deposited metals of the TiO₂-SiO₂-SrO type electrode were a little higher than those of the CaF₂-CaO-SiO₂ type. The impurities, S, P, and O, were also higher in the TiO₂-SiO₂-SrO type. However, the C behaved differently. Considering different flux coating compositions, the real behaviors of each alloying element can be implied by their mass transfer coefficients that were defined by the following equation (Refs. 8, 13):

\[ \eta = \frac{W_{\text{depo}}}{W_{\text{wire}}} + \lambda W_{\text{coat}} \]  

where \( \eta \) indicates mass transfer coefficient, \( W_{\text{depo}} \) indicates the weight percent of the element in the deposited metal, \( W_{\text{wire}} \) indicates the weight percent of the element in the core wire, \( W_{\text{coat}} \) indicates the weight percent of the element in the coating, and \( \lambda \) is the ratio of the coating weight to the core wire weight.

In this study, the average weight of the core wire is about 24.50 g, and the average weight of the coating is about 21.58 g for the CaF₂-CaO-SiO₂ type and about 22.17 g for the TiO₂-SiO₂-SrO type. Thus, \( \lambda \) is 88.07% for the CaF₂-CaO-SiO₂ type but 90.48% for the TiO₂-SiO₂-SrO type. The high ratios are because the large amounts of alloying metals were added in the coating. According to the flux coating ingredients (Table 1) and the chemical compositions of the deposited metals (Table 3), the mass transfer coefficients of the main alloying elements could be calculated by using Equation 7 — Fig. 5.

It could be found that the mass transfer coefficients of Ni, W, Mo, Fe, Cr, and Mn in the CaF₂-CaO-SiO₂ type are slightly higher than in the TiO₂-SiO₂-SrO type. However, that of Nb and Si are in the reverse manner. The higher mass transfer coefficients suggest the smaller loss during welding, while the lower mass transfer coefficients indicate the larger loss via the oxidation, evaporation, spattering, and fumes during welding. According to the data shown in Fig. 5, one could conclude that the loss of Ni, W, Mo, Fe, Cr, and Mn in the CaF₂-CaO-SiO₂ type was smaller than in the TiO₂-SiO₂-SrO type. But the loss of Nb and Si in the CaF₂-CaO-SiO₂ type was larger than in the TiO₂-SiO₂-SrO type.

The loss of metals during welding mainly depends on their oxygen affinity and boiling points. The higher oxygen affinity of metals and a stronger oxidizing environment would lead to forming more oxides that enter into the slag. The lower boiling point of the metals increases evaporation loss (e.g., Mn in this study). The oxygen affinity of the metals was roughly ranked in the order Si > Nb > Mn > Cr > Fe > Mo > W > Ni through all the welding processes (including the droplet reaction, weld pool reaction, and weld metal solidification stages) (Ref. 24). This order just matches the value sequence of the mass transfer coefficients of these elements as shown in Fig. 5.

It was noteworthy that the ratio of the coating weight to the core wire weight was very high in this study (much higher than that in the reported research [Refs. 7–10, 12]) because the alloy elements were added from the coating. When the flux coating contained too many metallic powders, the molten slag became viscous during welding. Some small metal droplets might be enveloped by the viscous slag and detained in the slag after welding (Refs. 10, 12), resulting in the larger loss of the metals. Such a phenomenon was confirmed by the observation as shown in Fig. 6.

The size of the solidified droplets was in the range of 0.1–2.0 mm. One of the droplets was analyzed by EDS analysis, which contained Cr: 26.39, Ni: 21.22, Fe: 18.22, Mo: 13.60, W: 9.27, Nb: 6.25, Mn: 4.36, and Si: 0.69 (wt-%). Obviously, the detached metal particles were part of the metals transferred from the covered electrode. As the amount of the detached metal particles increased, the mass transfer coefficients of these metals were re-
duced. Due to this reason, some refractory elements, e.g., W, Mo, and Ni, exhibited relatively lower mass transfer coefficients — Fig. 5.

In general, the basic oxides (such as CaO and MnO) in the slag preferred to react with the acidic oxides (such as SiO₂, TiO₂, and Nb₂O₅) during welding to form complexes (Refs. 12, 13, 17, 18, 20, 25):

\[(\text{CaO}) + (\text{SiO}_2) \text{ (or TiO}_2\text{)} = (\text{CaO}\cdot\text{SiO}_2) \text{ (or CaO}\cdot\text{TiO}_2) \quad (8)\]

\[(\text{MnO}_2) + (\text{SiO}_2) \text{ (or TiO}_2\text{)} = (\text{MnO}\cdot\text{SiO}_2) \text{ (or MnO}\cdot\text{TiO}_2) \quad (9)\]

For strong basic flux coating, the strong basic oxides were dominant, which consumed more acidic oxides (such as SiO₂, TiO₂, and Nb₂O₅) during welding. This drove the following oxidation reaction and led to smaller mass transfer coefficients of these metals — Fig. 5.

\[[\text{M}] + [\text{xO}] = (\text{MO}_x) \quad (M = \text{Si, Nb}) \quad (10)\]

This is why the mass transfer coefficients of Si and Nb in the CaF₂-CaO-SiO₂ type are smaller than in the TiO₂-SiO₂-SrO type.

For the TiO₂-SiO₂-SrO type flux coating, the strong acidic oxides were dominant, which consumed more basic oxides (such as CaO, MnO, and FeO) during welding. This drove the following oxidation reaction and led to the following mass transfer coefficients of these metals — Fig. 5.

\[[\text{M}] + [\text{O}] = (\text{MO}) \quad (M = \text{Mn, Fe}, \text{etc.}) \quad (11)\]

According to the tested results in Fig. 5 and the above discussions, one can immediately conclude that the metals have a larger mass transfer coefficient in the strong basic slag system if they can form basic oxides (e.g., Mn, Fe). In contrary, the elements have a smaller mass transfer coefficient in the strong basic slag system if they can form acidic oxides (e.g., Si, Nb).

In addition, the values of S, P, and O in the deposited metals exhibited similar behaviors, i.e., they all were in a relatively lower level in the CaF₂-CaO-SiO₂ type, while in a relatively higher level in the TiO₂-SiO₂-SrO type (Table 3). However, each has itself a mechanism. The desulfurization and dephosphorization during welding were realized by adding Mn and basic oxides/fluorides in the flux. The metallurgical processing involves the following main chemical reactions (Refs. 12, 13, 22):

\[[\text{NiS}] + [\text{Mn}] = (\text{MnS}) + [\text{Ni}] \quad (12)\]
\[
\text{[NiS]} + (\text{MnO}) \text{ (or/and CaO)} = (\text{MnS}) \\
\text{(or/and CaS)} + (\text{NiO}) \quad (13)
\]

\[
3(\text{CaF}_2) + 4[\text{NiS}] = 3(\text{CaS}) + 4[\text{Ni}] + \text{SF}_6 \quad \uparrow \quad (14)
\]

\[
2[\text{Ni}_3\text{P}] + 5(\text{NiO}) + 3(\text{CaO}) = ((\text{CaO})_3\cdot\text{P}_2\text{O}_5) + 11[\text{Ni}] \quad (15)
\]

\[
2[\text{Ni}_3\text{P}] + 5(\text{NiO}) + 4(\text{CaO}) = ((\text{CaO})_4\cdot\text{P}_2\text{O}_5) + 11[\text{Ni}] \quad (16)
\]

The reaction products MnS, CaS, (CaO)₃·P₂O₅, and (CaO)₄·P₂O₅ entered into the slag. Because CaF₂ and basic oxides decreased slag viscosity (Ref. 22), they could improve floating of these sulfides and complex oxides in the welding pool. As the reactions progress, the sulfur and phosphorus were expelled from the melted metals. It was reasonable that the higher contents of Mn and basic oxides/fluorides in the flux (Table 1) would eliminate more sulfur and phosphorus, decreasing the sulfur and phosphorus level in the deposited metals (Table 3).

Since the maximum solubility of oxygen in nickel at 1573 K is 200 ppm (Ref. 26), the oxygen in the deposited metals basically existed in the forms of oxides. In the flux, the deoxidizer (i.e., 45% Si + 55% Fe, 28% Ti + 72% Fe, Mn and 50% Al + 50% Mg, as listed in Table 1) predominantly reacts with oxygen to form oxides in the metallurgical processing. These oxides could float in the weld pool and gather together to form slag. Due to fast solidification of the welding pool melt, there were some residual oxides retained in the weld metal, which were the main source of the oxygen in the deposited metal. Previously, the acidic oxides (e.g., FeO, SiO₂, MnO₂, TiO₂, and Al₂O₃ are generally the products of the deoxidation reactions) were found to increase oxygen in the deposited metals, but the basic oxide/fluoride (e.g., CaF₂ and CaO) decreased oxygen (Refs. 8, 22, 27). Those findings are well consistent with the results of this study, i.e., the CaF₂-CaO-SiO₂ type flux with higher contents of CaF₂ and CaO maintained relatively lower oxygen concentration, while the TiO₂-SiO₂-SrO type flux with more TiO₂ and SrO generated a relatively higher level of oxygen (Table 3).

The C in the deposited metal was mainly transferred from the core wire and the decomposition of the carbonates in the flux coating during SMAW. According to the previous research (Ref. 11), the increase of carbonates in the flux coating promoted carburization in the deposited metal. It is obvious that the higher contents of CaCO₃ in the CaF₂-CaO-SiO₂ type flux coating generated a higher C content in the deposited metal (Table 3), but the lower contents of carbonates (i.e., CaF₂ and SrCO₃) in the TiO₂-SiO₂-SrO type flux coating resulted in a lower C content (Table 3).

### Microstructure Characterization

As expected, the as-solidified weld metals exhibited dendritic morphologies that were composed of face-centered cubic-structured nickel solid solution along with some small interdendritic precipitates and grain boundary phases. Under an optical microscope, there was no obvious difference between the deposited metals of the two types of electrodes — Fig. 7.

To reveal the distribution of the main alloying metals, some EDS line scanning profiles across dendrites and grain boundary were recorded. It was found that the Fe and Cr preferred to aggregate in the dendrite core, but the Mo and Nb tended to accumulate in the interdendritic zone — Fig. 8.

On the grain boundaries, Nb and Mo were obviously aggregated, but Ni and Cr were reasonably depleted — Fig. 9.

The equilibrium distribution coefficient, \( k \), which was defined as the ratio of the concentration of the element in the dendrite core to the nominal composition of this element, could indicate segregation behavior. The \( k \) values of Fe and Cr were larger than one, suggesting that they aggregate in the dendrite core, while the values of Mo, Mn, and Nb were less than one, indicating that they aggregate in the interdendritic zone. Special emphasis should be put on the Nb, of which the \( k \) value...
was far smaller than one, suggesting its significant segregation behavior. For easy reference, all the $k$ values were summarized in Table 5.

The segregation behavior of several key elements in various nickel-based alloys has been reported in many published literatures (Refs. 28–32). DuPont et al. collected and summarized those equilibrium distribution coefficients in a table (Ref. 33), where one can find that the $k$ values of Ni, Fe, and Cr are larger than one for many nickel-based alloys. The $k$ value of Mo is in a range of 0.71–0.97, but that of Nb is in a range of 0.42–0.58. It is as expected that these metals in the deposited metals investigated in this study, shown in Fig. 8 and Table 5, behaved very similarly to those observed in other nickel-based alloys (Refs. 28–33).

The interdendritic precipitates often exhibited in granular forms. Their sizes are mostly less than 1 μm — Fig. 9A and B. The grain boundary phases frequently appeared with continuous or discontinuous fashion — Fig. 9A, C, and D.

There is no suspense that those precipitates and grain boundary phases are carbides, oxides, and/or their mixtures. Their types could be roughly identified by the EDS analysis as listed in Table 6. The titanium oxides were found in both deposited metals — marked as 3, 4, 7, and 8 in Fig. 9 — while the aluminum oxide was found only in the deposited metal of the TiO$_2$-SiO$_2$-SrO type — marked as 8 in Fig. 9. The titanium and aluminum were introduced from the flux coatings (Table 1). A fact should be emphasized that all the particles investigated by EDS revealed very high niobium and carbon concentrations as shown in Table 6. It was reasonable to believe that they all included NbC. Previous research confirmed that (Nb, Ti) carbides and/or oxides independently nucleated and grew on the surface of the oxides (TiO$_2$ and/or Al$_2$O$_3$) in different orientations, forming a complex compound in which the (Nb, Ti) carbides appeared as a rim around the core oxides (Refs. 34, 35). The grain boundary phases could be speculated to be Nb(Mo, Cr)C according to the EDS results (Table 6) — Fig. 9C—F.

### Table 5 — Chemical Compositions (wt-%) and the Equilibrium Distribution Coefficients

<table>
<thead>
<tr>
<th>Element</th>
<th>CaF$_2$-CaO-SiO$_2$ Type</th>
<th>TiO$_2$-SiO$_2$-SrO Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_c$</td>
<td>$C_{core}$</td>
</tr>
<tr>
<td>Ni</td>
<td>68.78</td>
<td>69.98</td>
</tr>
<tr>
<td>Cr</td>
<td>14.77</td>
<td>15.64</td>
</tr>
<tr>
<td>Fe</td>
<td>6.60</td>
<td>6.92</td>
</tr>
<tr>
<td>Mo</td>
<td>4.11</td>
<td>3.33</td>
</tr>
<tr>
<td>Mn</td>
<td>3.62</td>
<td>3.22</td>
</tr>
<tr>
<td>Nb</td>
<td>2.12</td>
<td>0.91</td>
</tr>
</tbody>
</table>

**Mechanical Properties**

The tensile properties of the deposited metals of the two types of electrodes at room temperature did not exhibit a substantial difference — Fig. 10A. The two were above the minimum values listed in the standard AWS A5.11 ENiCrFe-9 (where the minimum tensile strength is 650 MPa, and the minimum elongation is 25%).
In addition, the impact value at 77 K of the CaF$_2$-CaO-SiO$_2$ type was above 80 J, which was distinctly larger than that of the TiO$_2$-SiO$_2$-SrO type, the latter was below 70 J in the impact value — Fig. 9B. Such a difference in the cryogenic impact properties were believed to be contributed from the impurities, e.g., S, P, and O, in the deposited metals. Since the S, P, and O were in relatively lower levels in the deposited metal of the CaF$_2$-CaO-SiO$_2$ type than in that of the TiO$_2$-SiO$_2$-SrO type (as shown in Table 3), the impact value at 77 K of the former was reasonably larger than that of the latter. Although the impurities are generally in very low levels, they are detrimental to the impact properties. For example, the S can easily form a low-melting-point eutectic Ni$_3$P + Ni (melting point about 917 K); and the P can easily form a low-melting-point eutectic Ni + NiS (melting point about 1153 K). These low-melting-point eutectic phases tend to distribute along grain boundaries, which deteriorate the grain boundary strength and increase cracking susceptibility (Refs. 12, 13). The weak grain boundaries should more easily initiate and propagate cracks, leading to the lower cryogenic impact values. The S and O could also be trapped in the deposited metal in the form of sulfides and oxides due to fast solidification during welding. The higher contents of S and O led to the larger volume fractions and number densities of the inclusions. It was determined that these inclusions were the sulfides and/or oxides of Al, Ti, and Mn as indicated — Fig. 8. Although there was no direct evidence to show the effect of these inclusions in this study, it was believed that they were detrimental to the toughness due to their easily debonding from the metal matrix (Refs. 36–39). Because the TiO$_2$-SiO$_2$-SrO type has higher S and O (Table 3), it is reasonable that the deposited metal of this type of electrode exhibits lower cryogenic impact values — Fig. 10B.

Although both deposited metals exhibited cryogenic impact values in different levels, their fractographies all reveal the typical dimple fracture mode — Fig. 11.

The plastic fracture mode at 77 K is generally favorable to the cryogenic application. Since the two electrodes (all are in accordance with the ENiCrFe-9 Standard) investigated were developed for welding 9% Ni steel for construction of the LNG tanks, the matching in cryogenic mechanical properties between the weld metal and the 9% Ni steel should be considered. Nowadays, the Charpy impact values at 77 K of the 9% Ni steel are almost above 200 J (Refs. 40–42). The heat-affected zones of the 9% Ni steel can generally reach above 100 J (Refs. 41, 42). However, the deposited metals of the TiO$_2$-SiO$_2$-SrO type electrodes exhibited only 66–70 J of the cryogenic impact value.
values. In view of this consideration, the CaF$_2$-CaO-SiO$_2$ type electrodes should be recommended for welding 9% Ni steel.

**Conclusions**

The nickel-based alloy covered electrodes (in accordance with the ENiCrFe-9 Standard) with two different types of flux coatings were investigated in terms of their weldability, weld quality, mass transfer, microstructure, and mechanical properties. According to the experimental results, the following conclusions could be made:

1) In comparison, the strong basic CaF$_2$-CaO-SiO$_2$ type exhibited a larger deposition rate, smaller spatter loss and fumes, and better slag fluidity that resulted in a wider weld bead but smaller penetration. The alkalescent TiO$_2$-SiO$_2$-SrO type exhibited better slag detachability.

2) The mass transfer coefficients (from the covered electrode to the deposited metal) of Ni, Cr, Fe, Mo, W, and Mn of the CaF$_2$-CaO-SiO$_2$ type were evidently larger than that of the TiO$_2$-SiO$_2$-SrO type, but that of Nb and Si were in a reverse manner. The metals exhibited the larger mass transfer coefficients in the strong basic slag system if they could form basic oxides. In contrast, the elements exhibited the smaller mass transfer coefficients in the strong basic slag system if they could form acidic oxides. In addition, the impurities S, P, and O were in the relatively lower levels in the deposited metals of the CaF$_2$-CaO-SiO$_2$ type electrodes because of the higher contents of CaF$_2$ and CaO in the slag. However, the C behaved differently due to the higher contents of CaCO$_3$ in the CaF$_2$-CaO-SiO$_2$ type flux coating.

3) The as-solidified microstructures of the deposited metals of the two types of electrodes were very similar. The equilibrium distribution coefficients of Ni, Fe, and Cr were larger than one, while that of Mo, Mn, and Nb were less than one. In particular, that of Nb was only 0.43 (for CaF$_2$-CaO-SiO$_2$ type) or 0.37 (for TiO$_2$-SiO$_2$-SrO type). These findings were very similar to those observed in other nickel-based alloys.

4) The tensile properties of the deposited metals of the two types of electrodes at room temperature were very close. The Charpy impact values at 77 K for the CaF$_2$-CaO-SiO$_2$ type were in the range of 81–83 J, but that for the TiO$_2$-SiO$_2$-SrO type were in the range of 66–70 J.

![Fig. 11 — Fracture morphologies of the impact specimens: A and C — CaF$_2$-CaO-SiO$_2$ type; B and D — TiO$_2$-CaF$_2$-SiO$_2$ type.](image)

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**References**


