

Carburization Phenomenon of ENiCrFe-7 Nickel-Based Alloy Covered Electrode

The relationship between the flux coating ingredients and carburization during shielded metal arc welding is presented

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ABSTRACT

The ENiCrFe-7 nickel-based alloy covered electrode is a key welding material for the construction of nuclear power plants. But this material is very susceptible to ductility dip cracking (DDC) at elevated temperatures. The carbon level in the weld has evidently shown its significance for the DDC susceptibility. However, it is practically difficult to decrease the carbon content in the deposited metal of this welding material. To clarify such carburization phenomenon, a systematic experiment was performed to investigate the controlling factors. It was found that the carburization was a universal phenomenon that occurred in the three different slag systems. The acidic (CaO-TiO₂-SiO₂ type) and neutral (CaO-CaF₂-TiO₂ type) slag systems exhibited relatively lower carburization; but the basic (CaO-CaF₂ type) slag demonstrated the largest carburization. It was confirmed that the carbon source was from the carbonates in the flux coating, which decomposed out carbon step by step and directly contributed to the carburization. The ferrosilicon and ferrotitanium could deoxidize the carbon from the carbon oxide at the welding temperature, thus indirectly contributing to the carburization. The larger welding current resulted in larger heat input and higher welding temperature that facilitated the decomposition of carbon oxide, therefore leading to the larger carburization.

KEYWORDS

- Carburization • ENiCrFe-7 • Covered Electrode • Nickel-Based Alloy
- Shielded Metal Arc Welding

Introduction

The ENiCrFe-7 nickel-based alloy covered electrode (specified by AWS A5.11, *Specification for Nickel and Nickel-Alloy Welding Electrodes for Shielded Metal Arc Welding*) has excellent welding usability, which can be used for joining nickel-based alloys (especially the Inconel 600 and 690 alloys) or dissimilar metals between stainless steels and low-alloy steels (Refs. 1, 2). The weld metals deposited from the covered electrode possess outstanding resistance to many corrosive aqueous

media, high-temperature oxidation, and irradiation, so ENiCrFe-7 has been widely used in the construction of nuclear power plants (Refs. 3–5).

However, from the 1990s, all kinds of welding materials of the nickel-based alloy Inconel 690 — including ENiCrFe-7 — have been found to be very susceptible to ductility dip cracking (DDC) at elevated temperatures (Refs. 6, 7). Since then, the mechanism of DDC and its possible controlling factors have been comprehensively investigated (Refs. 5–9). Among those factors, the carbon content in

the weld has evidently shown its significance and always played key roles in the precipitation or segregation of compounds to the grain boundaries, because carbon preferentially forms intense precipitation of carbides with chromium at grain boundaries in the nickel-based alloy (Refs. 10–13).

These carbides in the grain boundary may cause chromium depletion near the grain boundary and embrittle the grain boundary, and in turn reduce the DDC resistance. Consequently, controlling the carbon content to a relatively low level in the deposited metal of the ENiCrFe-7 covered electrode is believed to be helpful for reducing the DDC susceptibility. However, it is practically difficult to decrease the carbon content in the deposited metal of the ENiCrFe-7 covered electrode. It was found that the carbon content in the deposited metal of this covered electrode was always higher than that in the core wire after shielded metal arc welding (SMAW), although no graphite and any carbides were used in the flux coating (Ref. 14).

Such ‘carbon rise’ phenomenon during SMAW, defined as ‘carburization in the deposited metal of the covered electrode’ in this paper, is still open to determine the factors influencing the carbon transfer, and needs to establish the quantitative relationship between the ingredients of the flux coating and carbon composition in the deposited metal. The purpose of this study is to investigate the effects of the marble and deoxidizers content in the flux coating and the welding

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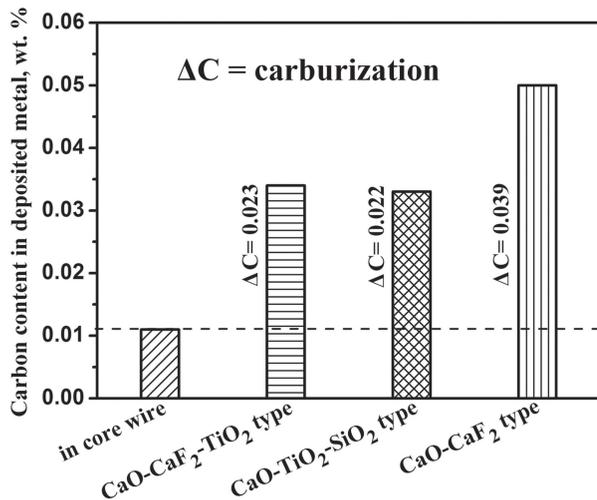


Fig. 1 — Carburization of the nickel-based Alloy ENiCrFe-7 covered electrodes with three different slag systems.

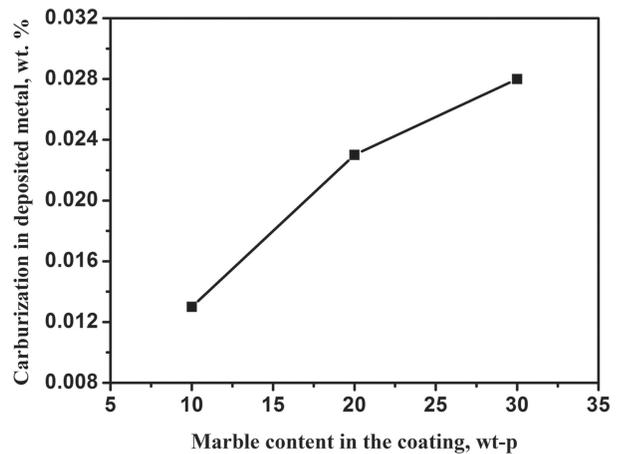


Fig. 2 — Effect of the marble content in the flux coating on the carburization for the ENiCrFe-7 covered electrode (CaO-CaF₂-TiO₂ type).

Table 1 — Chemical Compositions of the Nickel-Based Alloy Core Wire (wt-%)

No.	C	S	P	Si	Mn	Cr	Fe	Nb	Ni
CW1	0.011	0.006	0.019	0.10	1.0	29.01	7.30	1.82	Balance
CW2	0.025	0.005	0.015	0.11	0.90	29.20	4.40	2.10	Balance
CW3	0.030	0.006	0.016	0.21	0.92	29.35	10.39	1.62	Balance

Table 2 — The Compositions of the Mineral and Alloy Powders (wt-%)

Mineral or Alloy Powders	Chemical Compositions
Ferrocolumbium	Nb: 51.0, Fe: 48.8, C: 0.03, S: 0.006, P: 0.008
Ferrosilicon	Si: 44.9, Fe: 54.7, C: 0.025, S: 0.010, P: 0.015, C: 0.025
Ferrotitanium	Ti: 28.1, Fe: 71.6, C: 0.085, S: 0.010, P: 0.015
Fluorite	CaF ₂ : 97.8, S: 0.008, P: 0.010
Magnetite	Fe ₃ O ₄ : 97.9, S: 0.003, P: 0.015
Marble	CaCO ₃ : 98.6, S: 0.008, P: 0.006
Potassium fluoroaluminate	K: 45.3, Al: 10.5, F: 44.2
Pure chromium	Cr: 99.0, C: 0.02, S: 0.015, P: 0.010, Si + Fe ≤ 0.5
Pure manganese	Mn: 99.5, Si + Fe ≤ 0.25, C: 0.062, S: 0.005, P: 0.008
Rutile	TiO ₂ : 95.6, S: 0.010, P: 0.015
Sodium carbonate	Na ₂ CO ₃ : 98.5, NaCl ≤ 1.0, Na ₂ SO ₄ ≤ 0.1

current during SMAW on the carburization in the deposited metal of the ENiCrFe-7 covered electrode. The possible mechanism will also be discussed according to the general principles of the welding metallurgical reactions and chemical equilibrium.

Experimental

The nickel-based alloy covered electrodes, ENiCrFe-7, were fabricated in the lab with the standard processing technique that was commonly used in the welding material factory. The three batches of the nickel-base alloy core

wires with three different carbon levels (similar to the chemical composition of the Inconel 690 alloy) were manufactured in our partner factory. The dimension of the core wires was 3.2 mm diameter × 350 mm. The real chemical compositions of the core wires were re-inspected and listed in Table 1.

The flux coating was a uniform mixture of carbonates, fluorides, oxides, and metal powders that were bonded with water glass. In practice, many commercial mineral and alloy powders, such as marble, fluorite, rutile, feldspar, and magnetite, were used instead of the pure compounds,

oxides, and metal powders for reducing cost and imitating the mass production in the welding material factory. The compositions of these mineral and alloy powders are listed in Table 2.

The particle size of all the mineral and metal powders was controlled in the range of 100 to 250 μm. The carbon content in the mineral powders (except for the carbonates) was zero or lower than 0.01 wt-%, but in the metal/alloy powders was in the range of 0.018–0.085 wt-%. To investigate the carburization mechanism and its controlling factors, the flux coating ingredients of the ENiCrFe-7 covered electrodes were specially designed into different groups, as listed in Table 3, which included three typical types of the ENiCrFe-7 covered electrodes: CaO-CaF₂-TiO₂ (TC), CaO-TiO₂-SiO₂ (T-2), and CaO-CaF₂ (T-3) developed in our lab.

In practice, the nickel-based alloy covered electrode with the CaO-TiO₂-SiO₂ slag system generally exhibits perfect welding performance (i.e., stable arc, good weld appearance, excellent slag detachability, and easy operation), but relatively lower mechanical properties, especially the impact toughness. It is converse for the CaO-

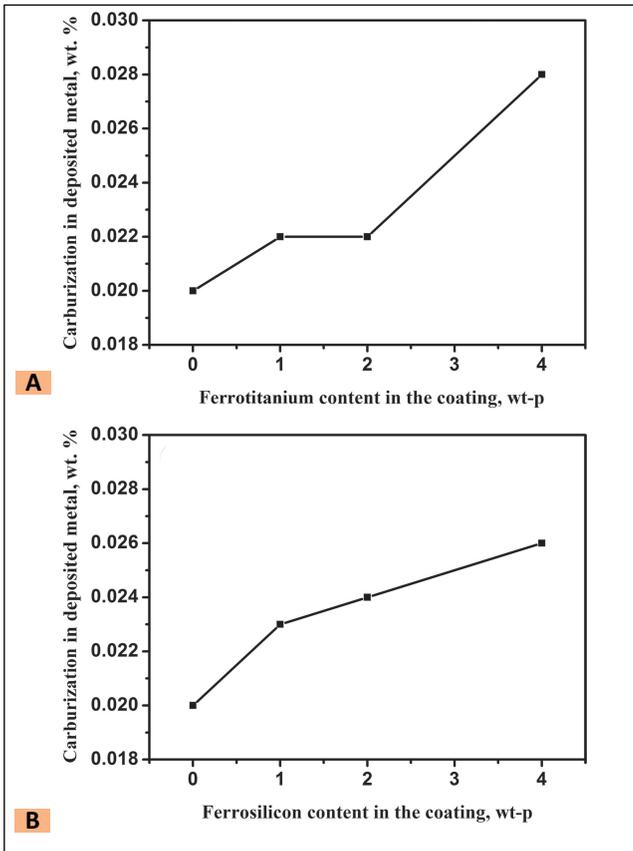


Fig. 3 — Effect of the deoxidizer content in the flux coating on the carburization for the ENiCrFe-7 covered electrode (CaO-CaF₂-TiO₂ type).

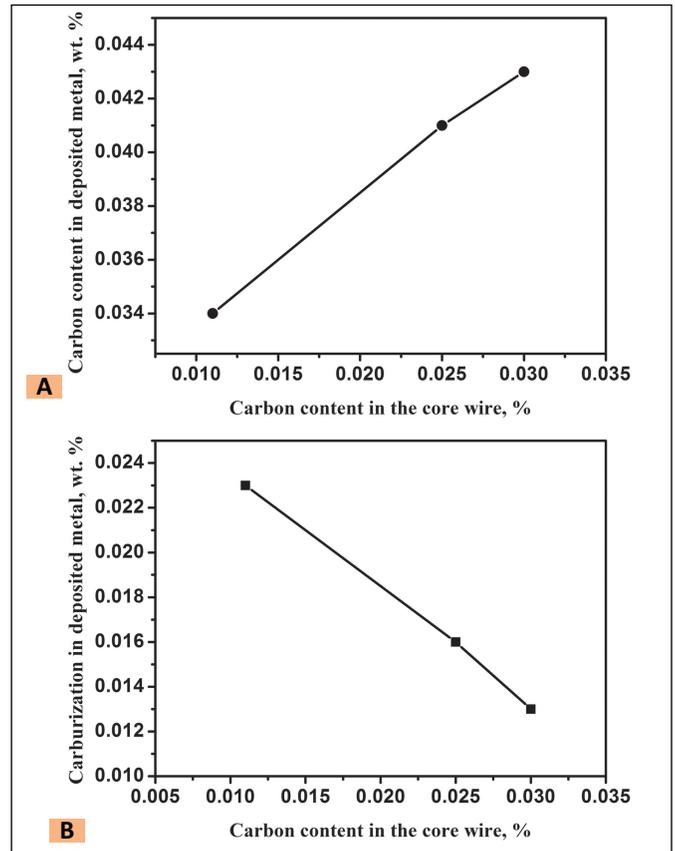


Fig. 4 — Effect of the carbon content in the core wire on the carburization for the ENiCrFe-7 covered electrode (CaO-CaF₂-TiO₂ type).

CaF₂ slag system. Only the CaO-CaF₂-TiO₂ slag system provides both the desired weldability and good weld quality. Hence, the covered electrodes with the CaO-CaF₂-TiO₂ slag system were selected for all the investigations except for the T-2 and T-3 ingredients (Table 3).

After coated with the designed flux, the ENiCrFe-7 covered electrodes were dried in turn at the temperature of

323 K for 1 h, 423 K for half an hour, and 623 K for 1 h. Such special procedure could decrease the water content in the coating and avoid welding porosity in the weld. The baking-step temperatures and times applied in this study have been optimized for avoiding cracking of the flux coating during and after drying. According to AWS standard A5.11-A5.11M, the weld pads prepared for the composition

analysis were clad using a Miller welding machine (Syncrowave 351 constant current AC/DC arc welding power source).

Additionally, the welding parameters were set as follows according to the operating requirement of the nickel-based alloy covered electrodes: welding current = 85 A, welding voltage = 26–28 V, welding speed = 3 mm/s, and arc length = 1–3 mm. TC-

Table 3 — Flux Coating Ingredients of the Nickel-Based Alloy ENiCrFe-7 Covered Electrodes (in weight proportions)

No.	CaCO ₃	Na ₂ CO ₃	CaF ₂	K ₃ AlF ₆	Na ₂ O + K ₂ O	SiO ₂	TiO ₂	Nb50% + Fe50%	Si45% + Fe55%	Ti28% + Fe72%	Fe ₃ O ₄	Mn	Cr
TC	20.0	0.6	28.5		3.1	8.9	26.0	4.0			2.4	8.5	8.0
T-2	18.0	0.6	8.0	3.0	4.1	16.9	33.4	3.0		5.0		9.0	9.0
T-3	44.0	0.6	22.0	7.7	3.4	9.8		4.0	3.5	4.5		6.5	4.0
CaCO ₃ -1	30.0	0.6	28.5		3.1	8.9	26.0	4.0			2.4	8.5	8.0
CaCO ₃ -3	10.0	0.6	28.5		3.1	8.9	26.0	4.0			2.4	8.5	8.0
ST-1	20.0	0.6	28.5		3.1	8.9	26.0	4.0			2.4	4.5	8.0
Si-2	20.0	0.6	28.5		3.1	8.9	26.0	4.0	1.0		2.4	4.5	8.0
Si-3	20.0	0.6	28.5		3.1	8.9	26.0	4.0	2.0		2.4	4.5	8.0
Si-4	20.0	0.6	28.5		3.1	8.9	26.0	4.0	4.0		2.4	4.5	8.0
Ti-2	20.0	0.6	28.5		3.1	8.9	26.0	4.0		1.0	2.4	4.5	8.0
Ti-3	20.0	0.6	28.5		3.1	8.9	26.0	4.0		2.0	2.4	4.5	8.0
Ti-4	20.0	0.6	28.5		3.1	8.9	26.0	4.0		4.0	2.4	4.5	8.0

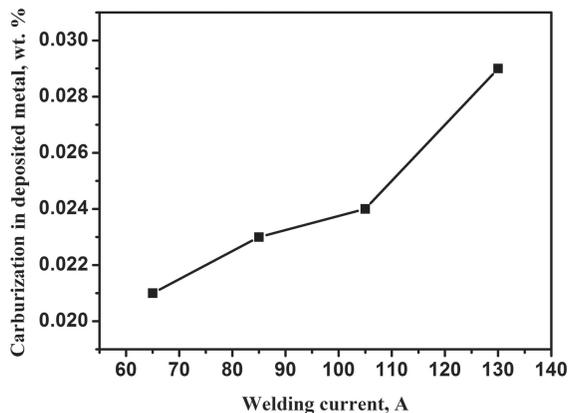


Fig. 5 — Effect of the welding current on the carburization for the ENiCrFe-7 covered electrode (CaO-CaF₂-TiO₂ type).

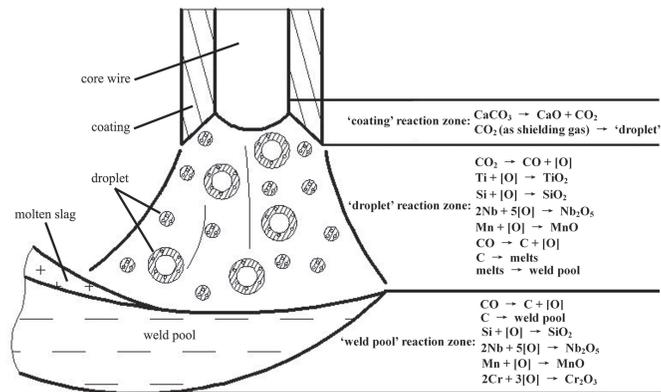


Fig. 6 — Illustration of the carburization behavior and mechanism of the ENiCrFe-7 covered electrode during SMAW.

65, TC-105, and TC-130 were exceptions welded with different currents, referring to the notes in Table 4. The covered electrodes in this group were specially designed for investigation of the welding current effect on the carburization in the deposited metal. All the three samples TC-65, TC-105, and TC-130 had the same ingredient of the flux coating TC as listed in Table 3.

The carbon and sulfur content in each deposited metal was specially measured from the undiluted weld metal by using the high-frequency infrared carbon/sulfur analyzer (CS-206). The measuring accuracy of this method was about 0.001%. The other elements in the deposited metal were measured by using the Thermo Scientific inductively coupled plasma emission spectrometer (iCAP 6300 ICP). The measuring accuracy was about 0.01%. All measured compositions of the deposited metals of the ENiCrFe-7 covered electrodes with different flux coatings are summarized in Table 4. To quantitatively indicate the 'carbon rise' in the deposited metal, the real carbon content in the deposited metal after deducting the carbon content in the core wire was defined as 'carburization' in this study.

For quantitatively measuring the carbon transfer behavior, three different mass transfer coefficients were defined as follows (Ref. 14): 1) The total mass transfer coefficient is defined as the ratio of the wt-% of the metal/element in the deposited metal to its wt-% in the covered electrode; 2) the mass transfer coefficient from the core wire to the deposited metal is defined as the ratio of the wt-% of the

metal/element in the deposited metal to its wt-% in the core wire (its wt-% in the coating is zero); and 3) the mass transfer coefficient from the coating to the deposited metal is defined as the ratio of the wt-% of the metal/element in the deposited metal to its wt-% in the coating (its wt-% in the core wire is zero). Generally, the mass transfer coefficient from the core wire is significantly larger than from the coating.

Results

Effect of the Flux Coating Type on the Carbon Transfer in the Deposited Metal of the ENiCrFe-7 Covered Electrodes

The flux coating for the ENiCrFe-7 covered electrodes could be classified as neutral CaO-CaF₂-TiO₂, acidic CaO-TiO₂-SiO₂, and basic CaO-CaF₂ types according to the main components in the ingredients. All the three types exhibited good welding usability and high weld quality. The chemical compositions of their deposited metals were all in accord with the specification of grade ENiCrFe-7 in AWS A5.11-A5.11M, as shown in Table 4 (TC, T-2, and T-3). However, it was obvious that the carbon contents in the deposited metals of the three type covered electrodes were all much higher than that in the core wire, suggesting that 'carburization' phenomenon occurred during SMAW.

Figure 1 clearly shows the difference in the carbon contents in the deposited metals among the three type

covered electrodes. The carbon content in the core wire was also shown in the figure for comparison.

It was evident that the basic slag system (i.e., CaO-CaF₂ type) exhibited the maximum 'carbon rise.' If deducting the carbon from the core wire (i.e., 0.011%), the carbon content increased 0.039 wt-%. For the acidic and neutral slag systems (i.e., CaO-TiO₂-SiO₂ and CaO-CaF₂-TiO₂ types), the carbon contents increased 0.022 and 0.023 wt-%, respectively. These results suggested that the basic slag system induced a larger 'carburization' phenomenon than the acidic and neutral slag systems for the nickel-based Alloy ENiCrFe-7 covered electrode.

Effect of the Marble in the Flux Coating on the Carbon Transfer in the Deposited Metal

The carbonate is an essential constituent in the flux ingredients for most of the covered electrodes, which can stabilize the arc and decompose out CO₂ during SMAW to protect the molten droplets against atmospheric contamination. The marble, a common carbonate, is cheap and easy to get, and has always been used in flux coating. To distinguish the effect of the marble content in flux coating on the carburization, the three ingredients CaCO₃-1, TC, and CaCO₃-3 with different amounts of marble (Table 3), were investigated.

For all three ingredients, a remarkable carbon 'rise' in the deposited metals could be observed as listed in Table 4. It was evident that the

Table 4 — Chemical Compositions (wt-%) of the Deposited Metals of the Nickel-Based Alloy ENiCrFe-7 Covered Electrodes. (All the covered electrodes were fabricated with core wire CW1 as indicated in Table 1, and with CaO-CaF₂-TiO₂ slag system as indicated in Table 2, and were welded with the welding current of 85 A except the special explanatory notes.)

No.	C	S	P	Mn	Si	Cr	Fe	Nb	Ni	Carbon 'rise'	Notes (difference in the flux coating ingredient, or in the core wire, or in the welding current)
TC	0.034	0.010	0.018	3.71	0.36	29.10	8.41	1.56	Balance	0.023	CaO-CaF ₂ -TiO ₂ type; C = 0.011% in the core wire; CaCO ₃ = 20.0 wt-% in the coating; Welding current = 85 A
T-2	0.033	0.011	0.018	3.51	0.59	28.92	8.85	1.75	Balance	0.022	CaO-TiO ₂ -SiO ₂ type
T-3	0.050	0.012	0.019	3.69	0.45	29.03	10.34	1.51	Balance	0.039	CaO-CaF ₂ type
TC-CW2	0.041	0.006	0.015	3.65	0.38	29.18	5.72	1.87	Balance	0.016	C = 0.025% in the core wire (CW2)
TC-CW3	0.043	0.008	0.021	3.72	0.41	29.35	11.26	1.41	Balance	0.013	C = 0.030% in the core wire (CW3)
CaCO ₃ -1	0.039	0.009	0.018	3.88	0.23	29.08	8.58	1.29	Balance	0.028	CaCO ₃ = 30.0 wt-% in the coating
CaCO ₃ -3	0.024	0.008	0.017	3.35	0.58	28.67	8.07	1.81	Balance	0.013	CaCO ₃ = 10.0 wt-% in the coating
ST-1	0.031	0.013	0.020	2.21	0.32	29.06	8.35	1.44	Balance	0.020	Ferrosilicon = 0; Ferrotitanium = 0 in the coating
Si-2	0.034	0.010	0.019	2.24	0.51	29.08	8.73	1.47	Balance	0.023	Ferrosilicon = 1.0 wt-% in the coating
Si-3	0.035	0.006	0.015	2.30	0.58	29.13	9.14	1.52	Balance	0.024	Ferrosilicon = 2.0 wt-% in the coating
Si-4	0.037	0.008	0.016	2.36	0.89	29.18	9.90	1.73	Balance	0.026	Ferrosilicon = 4.0 wt-% in the coating
Ti-2	0.033	0.009	0.020	2.29	0.39	29.11	8.86	1.49	Balance	0.022	Ferrotitanium = 1.0 wt-% in the coating
Ti-3	0.033	0.009	0.017	2.37	0.40	29.18	9.41	1.58	Balance	0.022	Ferrotitanium = 2.0 wt-% in the coating
Ti-4	0.039	0.009	0.016	2.46	0.49	29.30	10.42	1.78	Balance	0.028	Ferrotitanium = 4.0 wt-% in the coating
TC-65	0.032	0.009	0.020	3.71	0.36	29.06	8.37	1.58	Balance	0.021	Welding current = 65 A
TC-105	0.035	0.010	0.019	3.68	0.37	29.12	8.46	1.53	Balance	0.024	Welding current = 105 A
TC-130	0.040	0.008	0.020	3.60	0.39	29.15	8.48	1.43	Balance	0.029	Welding current = 130 A

carburization was very sensitive to the marble content in the flux coating, which increased from 0.013 to 0.028 wt-% as the marble content increased from 10 to 30 wt-%. Such a distinct relationship between the carburization and marble content in the flux coating could be illustrated in

Fig. 2.

Effect of the Deoxidizer in the Flux Coating on the Carbon Transfer in the Deposited Metal

The deoxidizers usually added in the flux coating are purposive for deoxidizing in the weld metallurgical re-

actions and improving the mass-transfer coefficient of some key elements, especially for the metal elements with a low mass-transfer coefficient. However, the deoxidizers may also induce the carburization in the deposited metal.

In this study, the Si-Fe group (ST-1,

Si-2 to Si-4 in Table 3) and Ti-Fe group (ST-1, Ti-2 to Ti-4 in Table 3) were designed with very similar flux ingredients but with different ferrosilicon and ferrotitanium contents for exploring their effect on the carburization. It was found that the carburization in the deposited metal increased in a similar tendency as the ferrosilicon or the ferrotitanium contents increased in the flux coating as shown in Fig. 3.

Effect of the Carbon Content in the Core Wire on the Carbon Transfer in the Deposited Metal

Since the mass transfer coefficient from the core wire to the deposited metal is much higher than that from the flux coating to the deposited metal (Ref. 14), it is meaningful to examine the carbon transfer behavior from the different core wires. The group (TC, TC-CW2, and TC-CW3) was prepared with the same flux coating ingredient (TC) but with three different core wires (each had a different carbon content). Due to only one variable (the carbon content in the core wire) in this group, it was easy to relate the carbon content and carburization in the deposited metal to the carbon content in the core wire as shown in Fig. 4. There was no suspense that the carbon content in the deposited metal increased from 0.034 to 0.043 wt-% as the carbon in the core wire increased from 0.011 to 0.030 wt-% (Fig. 4A). However, the carburization decreased from 0.023 to 0.013 wt-% as the carbon in the core wire increased to the same level (Fig. 4B).

Influence of the Welding Current on the Carbon Transfer in the Deposited Metal

In practice, the welding current influenced not only the weld appearance and welding quality, but also the chemical composition of the weld. The carbon transfer from the covered electrode (including from the core wire and flux coating) to the deposited metal during SMAW could be affected by changing the welding current (i.e., changing the metallurgical temperature).

In this study, the TC flux ingredient (Table 3) was designed for estimating the effect of the welding current on

the carburization because of its very good electrode weldability. The covered electrodes with the flux coating TC were deposited under four different welding currents: 65, 85, 105, and 130 A. The results indicated that the carbon content and carburization in the deposited metals were significantly dependent on the welding current as listed in Table 4. The carburization increased from 0.021 to 0.029 wt-% as the welding current increased from 65 to 130 A as shown in Fig. 5.

Discussion

Carbon Transfer Behavior and Mechanism of the ENiCrFe-7 Covered Electrodes during SMAW

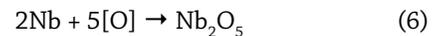
Shielded metal arc welding experiences a complicated metallurgical process, in which the weld metallurgical reactions occur in three different zones — flux coating melting, droplet transfer, and weld pool (Ref. 15). According to general weld metallurgical knowledge (Refs. 15–17) and data listed in Table 3, one could outline the possible metallurgical reactions related to the carburization during SMAW for the ENiCrFe-7 covered electrodes.

In the flux coating melting reaction zone, the marble began to decompose into CaO and CO₂ when the flux coating was heated up to 1171 K by the welding arc (Ref. 17). The CaO was then compounded with other acidic oxides to form the molten slag, while the CO₂ acted as the shielded gas to protect the droplets and weld pool against the surrounding air. In the droplet reaction zone, the mixture of the droplets and CO₂ gas could be heated up to 2800 K by the welding arc (Refs. 15, 17). Such a high temperature greatly promoted the following endothermic reactions:



Obviously, as these reactions proceeded, a quantity of oxygen decomposed out and entered into the droplets and weld pool, greatly in-

creasing the oxidability. On the other hand, there were many strong oxyphilic elements in the melts. They would immensely consume the reactive oxygen to form various oxides entering into the slag, such as Ti, Si, Nb, and Mn.



Apparently, these reactions would greatly reduce the oxygen content in the shielding gases and alloy melts, which should promote the above reactions (1)–(3). As more [O] was decomposed out and consumed, more CO was gradually generated in the shielding gas. Since the CO decomposition into carbon and [O] was also an endothermic reaction, it could be promoted by the high arc temperature and lack of [O] in the droplet reaction zone.



It was undoubted that the decomposed carbon would partially enter into the melts, leading to the carburization in the deposited metal of the nickel-based alloy ENiCrFe-7 covered electrode, and might partially react with CO₂ gas.



The latter reaction would consume the carbon and partially counteract the carburization in the deposited metal.

In the weld pool reaction zone, the above carburization mechanism was still effective, although the temperature in this reaction zone was relatively lower (about 2000 K (Ref. 17)). This was because the CO decomposition could still occur at this temperature (Refs. 15, 17). Furthermore, compared to the other two reaction zones, the weld pool had more chance to receive the decomposed carbon, because there were longer reaction times and more CO gas around the weld pool. All these conditions promoted the CO decomposition and led to more carbon enter-

ing into the weld pool.

Although the carbon transfer mechanism discussed above could not be observed directly, the consideration on the basic metallurgical reactions involving carbon and the carburization is evident. For example, when the marble in the coating increased from 10 to 30 wt-%, the carbon in the deposited metal increased from 0.024 to 0.039%, while the silicon in the deposited metal decreased from 0.58 to 0.23%, suggesting that the carbon in the CO was deoxidized by Si, and the Si was consumed. The effect of the deoxidizers on the carburization (Fig. 3) also supported the basic metallurgical reactions and above discussions. To more intuitively understand the carburization mechanism in the deposited metal for the ENiCrFe-7 covered electrodes, the SMAW process and related chemical reactions were summarized and illustrated in Fig. 6.

In addition, the oxidizing loss of the carbon in the core wire was also possible during SMAW. But such a loss was relatively very small compared to the carburization from the flux coating. For easily treating, the oxidizing loss of the carbon in the core wire was not considered when calculating the carburization values in this study.

Controlling Factors for the Carbon Transfer in the Deposited Metal

Apparently, the carbon in the deposited metal was transferred from the core wire and flux coating. The carbon in the core wire was relatively low (0.011 wt-%). If the oxidizing loss of the carbon in the core wire was considered, the carbon transferred from the core wire became not worth mentioning compared to the amount of carbon from the flux coating. The carbon source in the flux coating came mainly from the carbonates and some carbon-contained metal/alloy powders. The carbon contents in the ferrotitanium, ferrosilicon, ferroniobium, manganese, and chromium powders used in this study were measured to be about 0.085, 0.020, 0.018, 0.018, and 0.018 (all in wt-%), respectively.

Considering that the weight proportions of these metal/alloy powders in the flux ingredients were small

(Table 3), the contribution of the carbon in the metal/alloy powders to the carburization in the deposited metal should be very limited (one could simply calculate the total carbon content from the metal/alloy powders according to the data in Table 3; it should be less than about 0.01 wt-%).

This again suggested that the carburization in the deposited metal mainly came from the carbonates in the flux coating. And then, it was without any doubts that the carburization in the deposited metal increased as the carbonates (e.g., marble in this study) increased in the flux coating (see CaCO_3 -1, TC, and CaCO_3 -3 in Tables 3 and 4, plus Fig. 2). This was because more carbonates in the flux coating provided more carbon source.

The remaining question is how much carbon in the carbonates in the flux coating can be transferred into the deposited metal. As discussed in last section, the carbon transferred into the deposited metal via the carbonate decomposition, CO_2 decomposition, and then the CO decomposition. To maintain these decomposition reactions, in addition to the sufficiently high-temperature conditions, the decomposed [O] must be continuously consumed by other metals via forming oxides entering the slag. According to the Ellingham diagram (Ref. 18), the oxygen affinity of elements at about 1800 K (being comparable to the temperature in the weld pool (Refs. 18, 19)) can be ranked from strong to weak in following sequence: $\text{Ca} > \text{Ti} > \text{Si} > \text{C} > \text{Nb} > \text{Mn} > \text{Cr} > \text{P} > \text{Fe} > \text{H} > \text{S} > \text{Ni}$.

It is clear that Ti and Si can preferentially combine with the decomposed [O], promoting the carbon reduction reaction, so that the carburization in the deposited metal can be enhanced by increasing the deoxidizers (e.g., ferrotitanium or ferrosilicon) in the flux coating (Fig. 3).

It should be mentioned that a unilateral increase in carbonate in the flux coating would significantly increase the basicity of the slag system, and might affect the stability of the arc and metal transfer mode. These changes might influence the CO_2 and CO decomposition reactions, and in turn, influence the carbon transfer from the coating into the deposited metal. It is well known that the welding arc can be stabilized by providing easily ionized elements in the

flux. Although the role of each flux component in more complex systems is not completely understood (Ref. 20), the contribution of marble to the arc stability generally is relatively small according to the welding arc physics (Ref. 21) and observation in this study.

However, more carbonate in the flux coating might release more CO_2 gas that improved gas-generating chemical reactions in the metal droplets leading to pressure buildup, then affecting the size of droplets, rate of transfer, amount of spatter, etc. (Ref. 22). These changes might indirectly affect the carbon transfer to the deposit metal.

In practice, the droplet transfer mode during SMAW for the $\text{CaO-CaF}_2\text{-TiO}_2$ type flux depended mainly on the fluorite amount in the coating. Although the marble increased from 10 to 30 wt-% in this study, the welding arc stability and droplet transfer mode did not change significantly. According to the welding practice, the carbon transfer was less affected by the droplet transfer mode, but strongly affected by the deoxidizing metals, such as Si and Ti. This could be confirmed by the change in the Si contents in the deposited metal (Table 4), i.e., as the marble increased from 10 to 30 wt-%, the Si in the deposited metal decreased from 0.58 to 0.23 wt-% (Table 4).

Regarding to the difference in the carburization among the three different slag systems (acidic, neutral, and basic) as shown in Fig. 1, its essence is the difference in the amounts of the carbonate and deoxidizers in the flux coating (Table 3). The neutral slag system (i.e., TC: $\text{CaO-CaF}_2\text{-TiO}_2$ type, Table 3, and Fig. 1) and the acidic slag system (i.e., T-2: $\text{CaO-TiO}_2\text{-SiO}_2$ type) include relatively lower carbonates and without or with little deoxidizer, so that they have a relatively smaller carburization effect (Fig. 1). The basic slag system (i.e., T-3: CaO-CaF_2 type) contains a high concentration of carbonates and about 8 wt-% deoxidizer, thus it exhibits a relatively larger carburization effect — Fig. 1.

Effect of the Carbon Content in the Core Wire on the Carbon Transfer

It is no doubt that the carbon content in the core wire significantly af-

fects its content in the deposited metal, because the mass transfer coefficients from the core wire are always larger than that from the flux coating (Ref. 14). The increase in the carbon content in the core wire results in its increase in the deposited metal as indicated in Fig. 4A.

On the other hand, the oxidation-reduction reaction: $\text{CO} \rightarrow \text{C} + [\text{O}]$ is a reversible reaction. The increase of the carbon in the melts can decelerate the CO decomposition, then reducing the carburization. In addition, the relatively larger amount of carbon in the melts will increase its chance to contact with [O] in the slag or shielded gas, then increasing its oxidizing loss. Consequently, the dual effects lead to the decrease in the carburization as carbon content increases in the core wire as shown in Fig. 4B.

Based on the discussions above, one can make a bold inference, that is, if the carbon content in the core wire is high enough (e.g., more than 0.1%), the carburization phenomenon in the deposited metal of the nickel-based Alloy ENiCrFe-7 covered electrode will become negligible.

Effect of the Welding Current on the Carbon Transfer

The welding current determines the heat input during SMAW, which significantly influences the welding metallurgical reactions (e.g., the CO_2 decomposition, carbon deoxidation from the CO, oxidizing loss of the metals, etc.), and in turn affects the composition of the deposited metal of the covered electrodes (Refs. 14, 23). Generally, welding at a larger current results in a larger heat input and higher welding temperature that facilitates the CO_2 and CO decompositions, plus accelerates the oxidation reactions in the welding metallurgical process.

The former directly contributes to the carburization (via CO_2 and CO decompose out [O] and C). The latter improves the CO decomposition by consuming more [O] by the Ti, Nb, and Mn in the covered electrodes, because these metals have stronger oxygen affinity than carbon at the welding temperature according to the Ellingham diagram (Ref. 18), thus indirectly contributing to the carburization.

In addition, welding at a larger cur-

rent leads to a streaming spray mode by which the melt droplets become very small (Refs. 24, 25). The smaller droplets greatly increase the interface between the melts and CO_2/CO , thus promoting the carbon deoxidation from the CO_2 and CO, and increasing the carburization.

Conclusions

The carburization in the deposited metal of the ENiCrFe-7 nickel-based alloy covered electrodes during SMAW was investigated. The following conclusions could be drawn from the experimental results:

1) The flux coating with different slag systems exhibited different carburization effects. The basic slag system (i.e., CaO-CaF₂ type) exhibited the maximum carburization effect with the 'carbon rise' of 0.039 wt-%. The acidic and neutral slag systems (i.e., CaO-TiO₂-SiO₂ and CaO-CaF₂-TiO₂ types) exhibited relatively lower carburization effects with the 'carbon rise' of 0.022 and 0.023 wt-%, respectively.

2) The carbon source was confirmed to be from the carbonates in the flux coating, which decomposed out carbon and directly contributed to the carburization. For the neutral slag system, the 'carbon rise' increased from 0.013 to 0.028 in percent when the marble content in the coating increased from 10 to 30 wt-%.

3) The deoxidizers in the flux coating could increase the carburization in the deposited metal. As the ferrotitanium or ferrosilicon increased in the flux coating from zero to 4 wt-%, the 'carbon rise' increased about 0.008 and 0.006 in percent, respectively.

4) As the carbon in the core wire increased from 0.011 to 0.030%, the carbon in the deposited metal increased from 0.034 to 0.043%, but the 'carbon rise' decreased from 0.023 to 0.013%.

5) As the welding current increased, the 'carbon rise' in the deposited metal

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increased significantly.

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