Studies on Factors Affecting Carbon Content in Ferrochrome and Chromium Content in Slag

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Abstract

Based on the studies of experts both at home and abroad, in this paper the effects of characteristics of chrome ores and slags on the carbon content in alloy and chromium content in slag were analyzed from the statistical data in production practice

1. Introduction

Much work has been done on the carbon content in high carbon ferrochromium which affects the quality and use value of alloy and the chromium content in slag which is directly related to metal recovery during the production process. Just as pointed out by these studies, factors affecting C content in alloy and Cr content in slag are intricate and diversified. In our opinion, these two aspects mainly depend on the development of reduction process and refining process taking place in the furnace. Some discussions will be made from the characteristics of ores and slags influencing these processes.

2. Effect of ore characteristics

2.1 Characteristics of chrome ore

In order to understand the characteristics of chrome ores, mineralogical analyses of Cr ores from India, Kazakhstan, Iran and South Africa and also monocrystal separation for Iran and South Africa ores were carried out. See Table 1 and Table 2.

2.2 MgO/Al_2O_3 ratio of chrome ore and carbon content of alloy

Based on mineralogical analysis, we collected about 100 groups of data and analysed the relation between MgO/Al_2O_3 (in terms of MgO/Al_2O_3 in the slag) and carbon content in alloy. See Fig. 1

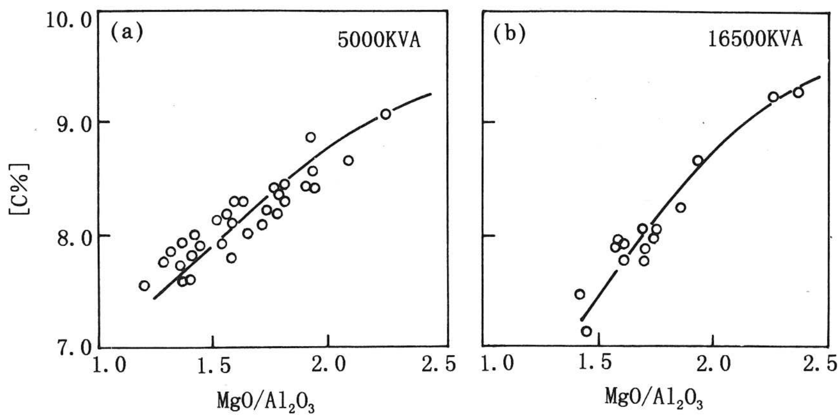

Fig. 1 Relation between MgO/Al_2O_3 in slag and carbon content in alloy in submerged arc furnaces of different capacity

Table 1 Mineralogical analysis for some kinds of chrome ores

Starting melting temp, ℃	Origin	Formation of ore	Structure of ore	Veinstone	Metallic minerals
1500	India	Medium fine grain	Lumpy, serious weathering, porous	Serpertine 10~15%	Autotype—halfauto, equiax granular cryst, minor allotype, size 0.1—1.8 mm, fine crackle growth, surface of gain oxidized
1595	South Africa	Remnant, medium /fine autotype half autotype, granular and embodied structure	Pisolitic and lumpy, the pisolitic about 25% of the ore	Bronzite and tremolit about 25%	Majority auto half autotype granular chrome spinel with iron, account for about 75%, big crystal 0.3—0.5mm, small crystal size 0.06~0.1mm, some small chrome spinel with iron, is covered by big pyroxene
1650—1660	Iran	Medium and fine half autotype—allotrioblast and granular Structure	Spotted, dense impregnation lumpy structure	Serpentine 30—50%	Majority fine allotrioblast black Mg —chromite, 65%, size 0.1—1mm, chromite ore distributed uneven, mainly dense impregnation, partly enriched to dense lumpy
	Kazakstan	Crypto—crystal structure	Impregnation lumpy structure	Serpentine about 15% Clay, shepar dite 15—20%	Half—autotype allotrio blast crystal 65—70%, size 0.5—2mm, change into morter or fragment structure under pressure

Table 2 Composition of Iran and South Africa crude ore and monocrystal

	Cr_2O_3	SFe	SiO_2	CaO	MgO	Al_2O_3
Iran crude ore	44.14	9.07	8.26	/	20.37	7.17
Iran monocrystal	54.17	11.08	2.0	1.1	15.12	11.53
South Africa Crude ore	18.80	18.61	7.74	/	11.36	14.73
South Africa monocrystal	42.27	19.1	6.6	1.7	8.5	16.25

2.3 Discussion

Chromite is the general name of chrome spinel whose chemical formula is $(Mg,Fe)(Cr,Fe,Al)_2O_4$ and which is a solid solution of five high melting point spinels actually.

Spinel	$FeO.Fe_2O_3$	$FeO.Al_2O_3$	$FeO.Cr_2O_3$	$MgO.Cr_2O_3$	$MgO.Al_2O_3$
Melting point ℃	1590	1750	1850	2000	2130

1. Thermodymically, FeO, Fe_2O_3, Cr_2O_3 are readily reducible, but not so when they are reduced from various spinels. It is thus evident that the reducibility is related to the existing forms and the

proportions of Fe and Cr oxides. See Table 3.

Table 3 Free energy formula, free energy value and lattice constant of some spinels

Formation reaction	Free energy formula	Free energy 1973 (KJ/mol)	Lattice constant(angstrom)
$MgO+Al_2O_3=MgO.Al_2O_3$	$\Delta G°=-35600-2.09T$	−39724	8.09
$FeO+Al_2O_3=FeO.Cr_2O_3$	$\Delta G°=-45144+8.36T$	−28650	8.37
$MgO+Cr_2O_3=MgO.Cr_2O_3$	$\Delta G°=-42840+7.11T$	−28817	8.32
$FeO+Al_2O_3=FeO.Al_2O_3$	$\Delta G°=-39710+7.11T$	−53738	8.14

It will be noted from Table 3 that:
(1) The presence of Al_2O_3 makes Fe quite difficult to be reduced;
(2) The presence of MgO makes Cr slightly difficult to be reduced;
(3) MgO and Al_2O_3 are easy to form dense reaction layer of $MgO.Al_2O_3$.
Hiroshi Katayama et al. [1~4] studied reducibilities of various forms of chromite ores and their constituents from Iran, Brazil and Kazankhstan. The studies proved that when the total amount of $MgO+Al_2O_3$ in chromite increases (especially when Al_2O_3 increases), the reducibility will be lowered.
In fact, Fe^{3+} is readily reduced to Fe^{2+} in chrome spinel mineral and causes a distortion of the crystal lattice of spinel which is advantageous to the reduction reaction. Accordingly, Shu Li and Dai Wei[5] put forward that for chrome spinel having a definite ratio of Cr/Fe, the proportion of trivalent Fe cation can be used to express the reducibility of chromite. From calculation, under the condition of definite Cr content and definite ratio of Cr/Fe, the proportion of Fe^{3+} in chrome spinel mineral will increase with the increase of MgO/Al_2O_3 ratio, namely, the reducibility will improve with the increase of MgO/Al_2O_3. It is reported[6] that the activation energy of reduction of chromite in the early stage (125kJ/mol) is far less than that in the later stage (238 kJ/mol). Thus, the effect of Cr/Fe on the reduction of chromite is only reflected in the early stage of reduction, after that MgO/Al_2O_3 ratio plays the main role. The formation of $MgO.Al_2O_3$ obstruction layer during the reduction process is inevitable. The studies of Katayama et al. showed that the addition is favorable to the melting and reduction of spinel minerals. During actual production practice, it has been found that the addition of certain amount of flux is indispensible due to the high melting point of both chrome ore and the natural slag produced.

Nevertheless, SiO_2, CaO (the main component of silica and lime) are easier to combine with MgO than with Al_2O_3. Therefore under reducing condition, the promoting action of flux is more remarkable for the chrome ore with relatively high MgO/Al_2O_3 ratio.
The initial products of reduction of chrome ore is the carbide of iron and chromium, $(Cr,Fe)_3C_2$ and $(Cr,Fe)_7C_3$. The relative amount of two carbides mainly depend on reduction temperature as well as the reducibility and grain size of chrome ore. Under the condition of same temperature and grain size, the alloy produced from chrome ore with good reducibility will have higher carbon content; on the contrary, chrome ore with poor reducibility will require higher temperature to reach the same extent of reaction. At this temperature, a certain amount of $(Cr,Fe)_{23}C_6$ will form together with $(Cr,Fe)_7C_3$, thereby lowering the carbon content in alloy.
It will be noted from the structure of mineral phase, starting melting temperature and composition of monocrystal of Iran and South Africa ores that the former belongs to picrochromite ore with larger grain size and lower Al_2O_3 content, difficult to melt but easy to be reduced; the latter belongs to rich-iron chrome spinel with smaller grain size and higher Al_2O_3 content, easy to melt but difficult to be reduced. In actual production practice, for smelting of high carbon ferrochromium using mainly Iran ore, the alloy will have higher carbon content; for smelting mainly using South African ore, the alloy will have lower carbon content, as shown in Fig. 1.

3. Effect of characteristics of slag

When studying reduction of chromite spinel by solid carbon and carbon dissolved in liquid alloy, R. H. Eric, O. Sykcan, E. Vlsu[10] found that chrome spinel will be reduced by carbon in alloy at the temperature of 1500～1680℃ and refining process will be intensified at the temperature of over 1700℃.

3. 1 Characteristics of slag

From the relationship among SiO_2 content in slag, MgO/Al_2O_3 in slag and melting point of slag (Table 4) and the relationship between viscosity of slag and temperatures[11] (Fig. 2), it will be noted that SiO_2 content and MgO/Al_2O_3 in slag are the key factors in determining the important characteristics— slag —melting point and viscosity.

Table 4 Relationship among SiO_2 content, MgO/Al_2O_3 and melting point of slag

MgO/Al_2O_3	$SiO_2$30%	$SiO_2$31%	$SiO_2$32%	SiO_2 33%	$SiO_2$34%	$SiO_2$35%	$SiO_2$36%	SiO_2%
0. 8	1841	1824	1813	1796	1780	1768	1739	1720
1. 0	1826	1810	1798	1781	1763	1745	1726	1709
1. 2	1809	1791	1779	1764	1746	1730	1712	1699
1. 4	1792	1776	1762	1748	1733	1717	1700	1683
1. 6	1772	1756	1744	1731	1717	1700	1682	1667
1. 8	1756	1741	1730	1716	1700	1686	1667	1651
2. 0	1736	1729	1716	1705	1688	1688	1685	1679
2. 2	1729	1717	1716	1714	1715	1714	1707	1704
2. 4	1704	1721	1727	1736	1742	1740	1735	1730
2. 6	1724	1740	1748	1756	1763	1763	1758	1753
2. 8	1745	1757	1769	1779	1781	1786	1783	1777

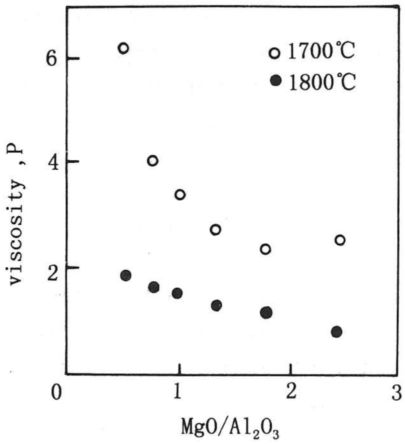

Fig.2 Effect of MgO/Al2O3 (in slag) on the viscosity of slag at SiO2 content of 30%

3. 2 Relationship between MgO/Al_2O_3 and Cr_2O_3 content in slag

Based on the knowledge of the characteristics of molten slag, we collected approximately 100 groups of data and analyzed the relation between MgO/Al_2O_3 and Cr_2O_3 content in slag, as shown in Fig. 3.

3. 3 Discussion

Summing up the above figures and tables, it will be noted that:

(1) The melting point of slag will always decrease with the increase of SiO_2 content at MgO/Al_2O_3 of less than 2. 2.

(2) When the SiO_2 content is fixed, the melting point of slag will first decrease with the increase of MgO/Al_2O_3 in slag; but when MgO/Al_2O_3 reaches a certain limit, the melting point will rise instead.

(3) When the SiO_2 content in slag is 30%, the relation between viscosity and MgO/Al_2O_3 in slag is similar to the relation between melting point and MgO/Al_2O_3 in slag; but at 1800℃, the viscosity will always decrease with the increase of MgO/Al_2O_3.

High temperature and slag of good flowability are the keys to the progress of refining reaction. During the smelting of high C FeCr, the slag temperature is usually controlled at 1650～1730℃. Therefore all types of slag that favor the raising of temperature and the lowering of slag viscosity will have a good refining effect. Accordingly, it is obvious that the Cr_2O_3 content in slag should be related to MgO/Al_2O_3 in slag.

In fact , in terms of the existing forms , the

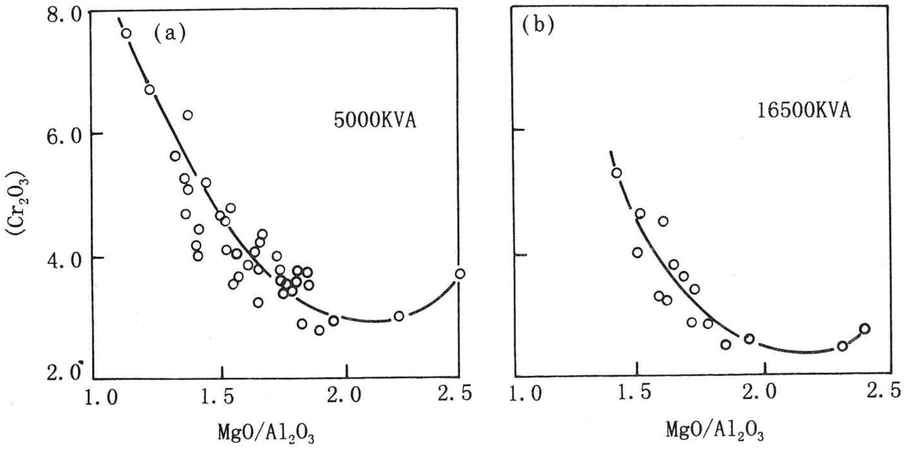

Fig. 3 Relation between MgO/Al_2O_3 content and Cr_2O_3 in slag in submerged arc furnaces of different capacity

chromium in slag comprises Cr in floating particles of chrome spinel, Cr dissolved in slag and Cr in metallic particles included in slag. When the variation in the composition of slag is not too large, the variation of Cr finally dissolved in slag will also not be too large and so is the amount. For this reason, use of ore that is difficult to melt but easy to be reduced for smelting will generally result in a final slag of quite low Cr_2O_3 content, unless the MgO/Al_2O_3 is high enough to raise the viscosity of the slag and thus some of chrome spinel are held up in slag. On the contrary, use of ore that is difficult to melt and difficult to be reduced or easy to melt but difficult to be reduced will result in a final slag of quite high Cr_2O_3 content since the presence of many spinel particles or sticky molten Cr_2O_3 in slag will cause a distinct rise of the viscosity of slag.

The tendencies of the curves in Fig. 3 verified the above analysis that the Cr_2O_3 content in slag decreases with the increase of MgO/Al_2O_3, but when MgO/Al_2O_3 increases beyond a certain value, the Cr_2O_3 content will rise instead due to the increase of the viscosity of slag and the worsening of the refining effect.

Reaction between slag and alloy in molten bath can be approximately expressed by the following formula:

$$(Cr_2O_3) + 3[C] = 2[Cr] + 3CO$$

When the reaction reaches equilibrium, the Cr_2O_3 content in slag is quite low ($<0.5\%$), and will still be lower at a higher carbon content in alloy. Studies in molten—state reduction[12] have shown that it is possible to decrease the Cr content in slag to 1—2% at the later stage of reduction. In our actual production, the Cr content in the final slag can be really reduced to 1—2%.

Conclusion

(1) During high carbon ferrochromium production, the characteristics of ore and slag have decisive influences on the carbon content in alloy and Cr content in slag.

(2) The reducibility of chrome ore with high MgO/Al_2O_3 is better than ore with low MgO/Al_2O_3. Therefore, using ore with higher MgO/Al_2O_3 for smelting will correspondingly result in an alloy with higher carbon content.

(3) A lowest point exists in the relation between Cr_2O_3 content and MgO/Al_2O_3 in slag due to the influence of the viscosity of slag. When MgO/Al_2O_3 in slag exceeds this value, the Cr_2O_3 content in slag will increase with the increase of MgO/Al_2O_3 in slag.

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