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LIQUID-PHASE SEPARATION OF SOLID-PHASE REDUCTION PRODUCTS OF RICH CHROMIUM ORES

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Annotation

The paper presents the results of the experimental study of the effect of solid-phase metallization time on the yield and composition of metal obtained by subsequent liquid-phase separation kempirsai, chrome, ore, fines (l ...2 mm) fluxed with quartzite were subjected to solid-phase metallization sintering at 1400°C in mixture with coal and then separated into metal and slag at 1850°C. It is found that 2 hours of metallization even at relatively low temperature 1400°C to reduce and extract more than 80% of chromium and 90% of iron, and the degree of extraction of both metals after 3 hours of metallization reaches 95%. The structure of the metal obtained after the liquid-phase separation of reduction products is similar to the structure of carbon ferrochrome. The metal contains carbides $(Cr,Fe)_{23}C_6$, and $(Cr,Fe)_7C_3$, and silicidesFeSi; and Cr_3Si. Increasing reduction sintering time enriched in chromium.

Keywords: chrome ore, pre-reduction, liquid-phase separation, carbothermal reduction, solid-phase reduction, selective reduction, degree of extraction, chrome spinel, ferrichrompicotite, carbon ferrochrome, chromium carbide, quartz shell.

Introduction

In the metallurgical industry, recovery processes play an important role. For the production of carbon grades of cast irons, ferroalloys, carbon is used as a reducing agent. In this regard, a lot of work has been devoted to studying the mechanism of the reduction of metals from oxides of ores and concentrates [1-7].

Due to the high melting point of chrome spinelide and host rocks of Kempirsay ore, represented mainly by serpentinite ($3MgO·2SiO_2·H_2O$), during the heating process it turns into forsterite $2MgO·2SiO_2$ with a melting point of ~1900°C. To obtain durable agglomerate from small things, sintering should be carried out at a temperature of 1400...1500°C and higher. To reduce the sintering temperature, fluxing additives are introduced into the mixture of sinter. The most widely used fluxes are materials containing silicon and aluminum.

Considering the high content of chromium in the tailings, it is also advisable to use them for further processing in order to extract this element. This becomes possible after pelletizing of dispersed particles and their metallization. In particular, the preliminary reduction of metals from chrome ore since 1977 has been carried out at the Xstrata Alloys ferroalloy plant in Ladenburg, South Africa [8,9]. By analogy with the pre-reduction of iron in iron ores, the preliminary metallization is carried out in ore-coal pellets or briquettes, using coke or coal as a reducing agent. At the same time, in addition to binder materials, such as bentonite, fluxing additives, in particular, borate ore or finely ground basalt, are also introduced into the composition of briquettes.

In the early 1980s,Mintek and Middelburg Steel&Alloys (South Africa) have developed a process for the production of ferrochrome in an open (type of steel-smelting) DC-smelting furnace in order to melt unprepared chromite ore fines. At the initial stage, ore fines in the form of particles about 2 mm in size were loaded onto the surface of the melt through a hollow electrode. However, at the end of the 1990s, after specially conducted comparative tests of batch feeding through a hollow electrode and a hole in the roof, Mintek concluded that there are no particular advantages to using hollow electrodes. A slight increase in the discharge was charged when loading through the arch opening completely compensated by the reduction in the cost of manufacturing solid electrodes and in comparison with the hollow and simplifying the charge supply system [10].

The successful experience of processing unprepared ore fines at the enterprises of the company Mintek is supposed to be used at Aktobe ferroalloy plant. In 2014, this company built a melting shop №4 with four ore-smelting direct-current furnaces with a capacity of 80 MBA each to extract chromium and iron from unprepared small ore supplied through the arch opening. Considering that the preliminary metallization with the use of coke breeze makes it possible to attain the degree of iron reduction up to 90% and chromium up to 50%, reducing the power consumption from 3.9 to 2.4 MWh/t, that is, by about 40% [11] It is advisable to assess the possibility of metallization of ore fines in order to extract metal by fusion in ore-smelting furnaces.

The aim of the work is an experimental study of the influence of the parameters of reductive roasting of small particles of chromic ore fluxed by quartzite on the yield of carbon ferrochrome during liquid-phase separation of the reduction products of uncombed ore fines

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Methods of experiments

The experiments were carried out in two stages. At the first stage, solid-phase reduction of metals from uncombed fine chrome ore was carried out, and at the second stage, liquid-phase separation of reduction firing products was carried out. The experiments were carried out in a resistance furnace with graphite heater. The original powdered Kempirsai ore in grains of 1...2 mm in size was moistened with a solution of liquid glass in water and rolled in a fine grinder (0…0,063 mm) quartzite. The resulting fluxed powder was dried by natural drying and mixed with ground (0,16...0,32 mm) Korkino coal. The materials were mixed, poured into a graphite crucible and placed in the working zone of the Tamman furnace. The reduction roasting was carried out at a temperature of 1400°C and a shutter speed of 60, 120, or 180 minutes. The temperature inside the reaction mixture was controlled by a tungsten-rhenium thermocouple BP5/20. The same experiment was repeated three times. A total of 12 experiments were conducted.

After isothermal aging, the crucibles with the reaction mixture were cooled to room temperature with the furnace. The resulting reduction products were divided by sieving. Sifted ore particles were melted to separate the metal and slag. Experiments on liquid-phase separation were carried out under the same conditions – at a temperature of 1850°C and an exposure of 4 min. To meet these conditions, an empty corundum crucible was heated in the furnace and without taking the crucible out of the furnace, the powder of regenerative ore fired was poured. The molten metal-slag mixture was stirred and the crucible removed from the furnace. The raw materials and the obtained slag and metal samples were carefully weighed to create a material balance. The type of the initial ore particles and the obtained products is shown in Fig.1. Metal samples were also investigated to X-ray diffraction analysis on a DRON-4 diffractometer.

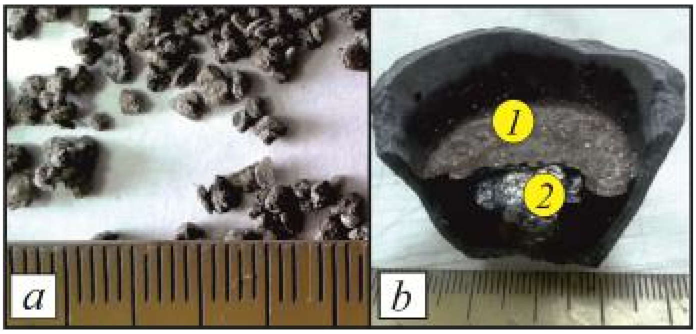


Figure 1. The initial fluxed ore powder (a), slag (1) and metal (2) after melting (b).

In the experiments used Kempirsay ore composition (wt.%):51,0 Cr_2O_3; 7,2 Al_2O_3; 0,40 CaO; 7,0 SiO_2; 19,16 MgO; 12,2 FeO; 0,033 P; 0,032 S. The composition of the coal of the Korkinsky deposit (wt.%): humidity W^r11,7%, coal ash A^c 25,0%, volatile components:V^r 41,6%, sulfur content 1,2%. The chemical composition of ash (mass%):47,0 SiO_2; 22,7 $A1_2O_3$; 12,6 Fe_2O_3; 5,30 CaO; 3,0 MgO; 5,60 SO_2; 0,90 TiO_2; 1,90 K_2O; 1,30 Na_2O; 4,6 P_2O_5; 0,30 MnO. As the fluxing material used silica composition (wt.%): 99,4 SiO_2, 0,14 Al_2O_3; 0,26 Fe_2O_3; 0,03 MgO; 0,01 TiO_2; 0,02 Na_2O.

Experimental results

The experimental results showed that the metal yield increases with increasing isothermal holding time during solid-phase reduction. It was 31, 38 and 43%, respectively, at 1, 2 and 3 hours of reduction. With the increase in the duration of this exposure, the degree of extraction of both chromium and iron increases, but iron regenerates somewhat faster – the degree of extraction of iron reaches 94% after 2 hour exposure, while the degree of extraction of chromium is only 84%. But after holding timefor 3 hours and the degree of extraction of chromium reaches 95 % (Fig.2).

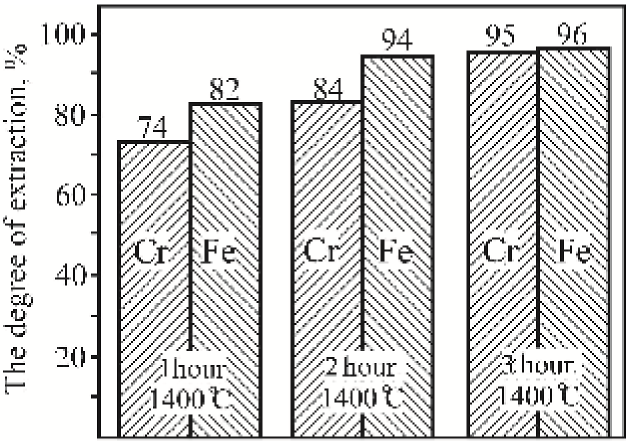
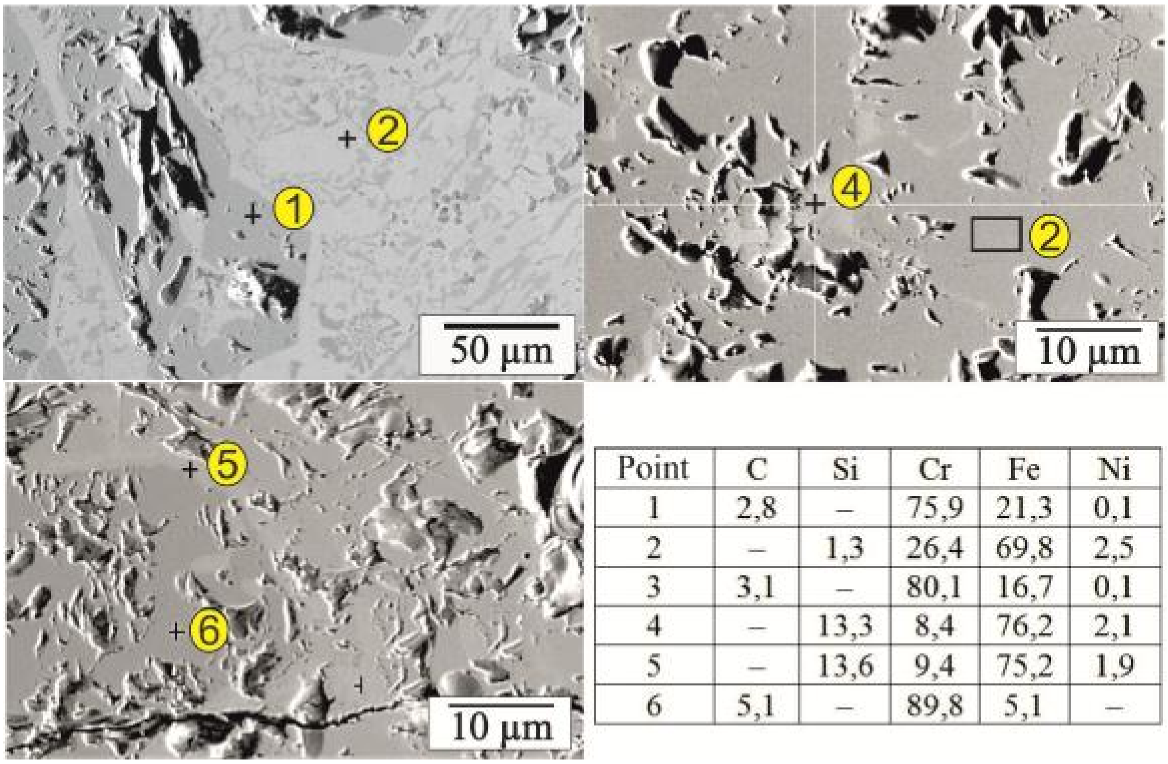


Figure 2.The Degree of extraction of metals by a two-stage process with different duration of reduction firing



Point	C	Si	Cr	Fe	Ni
1	2,8	–	75,9	21,3	0,1
2	–	1,3	26,4	69,8	2,5
3	3,1	–	80,1	16,7	0,1
4	–	13,3	8,4	76,2	2,1
5	–	13,6	9,4	75,2	1,9
6	5,1	–	89,8	5,1	–

Figure 3. Content of elements (wt. %) in metal after liquid-phase separation of solid-phase reduction products for 1 h (t. 1 and 2), 2 h (t. 3 and 4) and 3 h (t. 5 and 6)

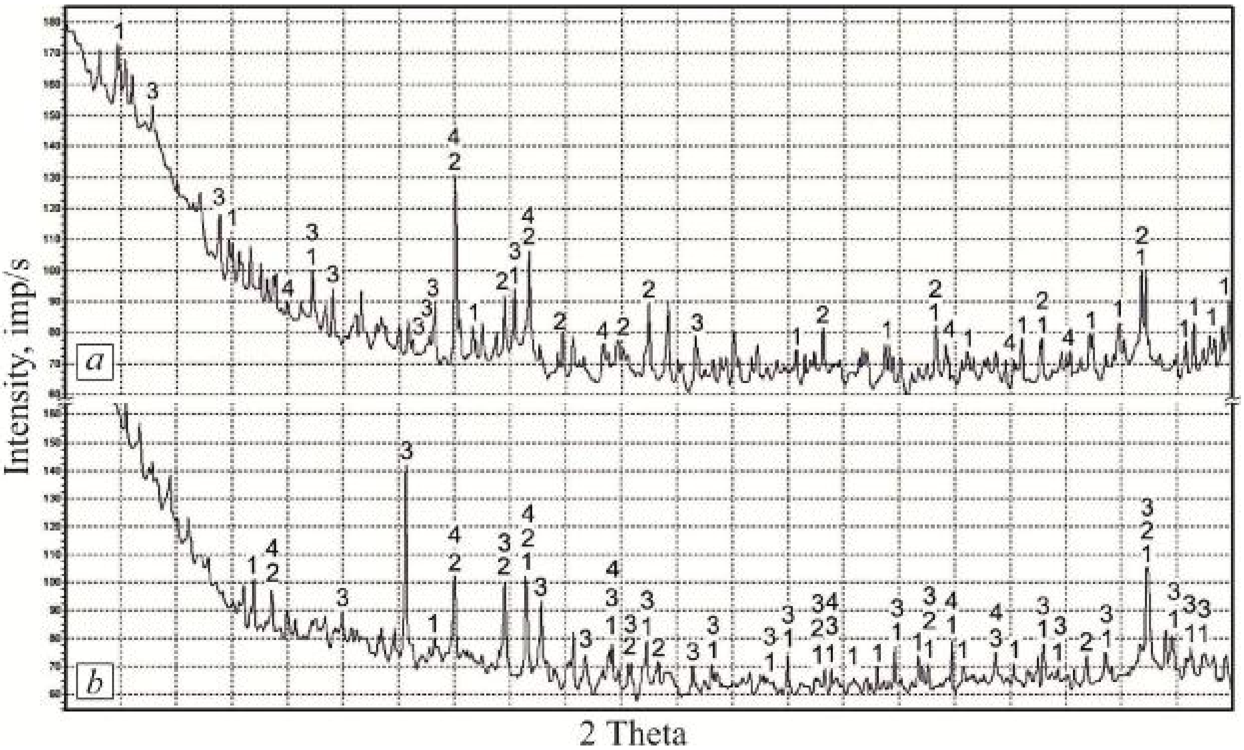


Figure 4. X-ray of ferrochrome after separation of reduction products for 1 h (a) and 3 h (b): 1 - $(Cr,Fe)_{23}C_6$ [12], 2 - $(Cr, Fe)_7C_3$ [13], 3 - $FeSi_2$ [14], 4 - Cr_3Si [15]

Table 1 – Composition of slag after separation

Sampleofslag	Contentofcomponents, mass. %				
Reductionwithin 1 hour					
1	Cr_2O_3	FeO	SiO_2	MgO	$A1_2O_3$
2	13,64	1,85	37,71	26,39	20,41
3	13,27	0,62	38,21	27,20	20,70
4	12,29	2,79	39,50	23,72	21,69
5	15,36	2,15	35,41	28,26	18,83
Average	**13,64**	**1,85**	**37,71**	**26,39**	**20,41**
Reductionwithin 2 hours					
6	9,12	1,24	37,19	30,89	21,57
7	9,09	0,34	36,75	28,72	25,11
8	6,04	0,05	40,14	32,88	20,88
9	8,08	0,54	38,03	30,83	22,52
Average	**7,85**	**0,53**	**38,48**	**30,21**	**22,53**
Reductionwithin3hours					
10	3,81	0,62	35,94	32,59	27,04
11	2,31	0,28	27,09	25,93	44,39
12	0,94	–	35,1	36,28	27,68
13	3,41	0,54	34,04	36,07	25,94
Average	**2,50**	**0,48**	**33,04**	**32,71**	**31,26**

The structure of the metal obtained as a result of the separation of the reduction products corresponds to the structure of carbon ferrochrome. The metal always found a carbide phase and silicides, and increasing the length of the reduction extracts the contents of silicon and, consequently, the quantity of silicides increases. In this case, the concentration of iron in the composition of silicides increases and decreases significantly in the composition of carbides (Fig. 3).

According to the results of x-ray spectral analysis, the main phases in the alloy are carbides $(Cr,Fe)_{23}C_6$ and $(Cr, Fe)_7C_3$. In addition to the carbide phases, silicides are present $FeSi_2$ and Cr_3Si (Fig. 4).

In the composition of the slag with increasing the length of the reduction extract the content of oxides of iron and chromium is reduced. As expected, the iron oxide content decreases more rapidly at the beginning. After 2-hour aging in the slag contains about 0.5 % of iron oxides. The content of chromium oxides decreases more slowly and reaches 2.5 % after exposure for 3 h (see table 1).

Conclusion

The quantitative characteristics of the metal and slag yield in the process of liquid-phase separation depending on the parameters of solid-phase metallization of uncoated ore fines are established. It is shown that as a result of solid-phase metallization within 3 hours of ore particles, even at relatively low (1400 ° C) temperature, it is possible to ensure a high (about 95%) degree of extraction of iron and chromium.

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АЛДЫН АЛА ТОТЫҚСЫЗДАНҒАНҰСАҚ ХРОМ КЕНДЕРДІ БӨЛУ

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Түйін

Зерттелетін объект ретінде кемпірсай хром кені (1...2 мм)алынған. Хром кенді ұсақталған кварцит бар материалды алдын ала сыртқы түйіршіктердің беттеріне қапталған. Кварцитпен қапталған кеңдерді көмірмен 1400°С температурасында жеке-жеке уақыт ұзақтылығымен 1,2 және 3 сағат бойытотықсыздану процестерді жүргізілді. Алынған металлданған кеңдерді жоғары температурада1850°Сжеке-жеке балқытылып, металл мен қож өнімдерін алынған. Алынған нәтежелері бойынша 1400°С температурасында 1 сағат аралығында темір мен хромның шығуы 72% және 82%, ал үш сағаттық изотермиялық уақытында хромның шығуы 95% дейін жетті. Тотықсыздану өнімдерін бөлу нәтижесінде алынған металдың құрылымы көміртекті феррохром құрылымына сәйкес келеді. Рентгенфазалық әдісімен қорытпада$Cr_{23}C_6$ және $(Cr,Fe)_7C_3$ карбидтерді және FeSi және Cr_3Si силицидтерді мен жеке α-(Cr,Fe) фазаларды анықталған. Тотықсыздануuaқыты ұзақтығы арттырумен байланысты ондағы темір силицид фазасы ұлғаюна және керісінше карбид хром кемеуіне әкеп соқтырады. Пайдаланған 3 сағаттық металданған хром кендері бөліну нәтежесінде қождағы темір мен хром оксидтердің минималды концентрациялары 0,5%FeO және 2,5% Cr_2O_3 дейін төмендейді.

Кілттік сөздер:хром кеңі, алдын ала тотықсыздану, сұйықфазалы бөліп алу, карботермиялық тотықсыздану, қатты-фазалы тотықсыздану, селективті тотықсыздану, алу дәрежесі, хромшпинелид, феррихромпикотит, көміртекті феррохром, хром карбиді, кварц қабықшасы.

ЖИДКОФАЗНОЕ РАЗДЕЛЕНИЕ ПРОДУКТОВ ТВЕРДОФАЗНОГО ВОССТАНОВЛЕНИЯ БОГАТЫХ ХРОМОВЫХ РУД

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Аннотация

Экспериментально изучено влияние продолжительности твердофазной металлизации при 1400°С офлюсованных кварцитом частиц кемпирсайской хромовой руды размером 1...2 мм в смеси с углем на состав и выход металла при последующем жидкофазном разделении продуктов металлизации на металл и шлак при 1850°С. Установлено, что металлизация в течение 2 ч даже при использованной относительно низкой температуре 1400°С

позволяет восстановить и извлечь более 80 % хрома и более 90 % железа, а при металлизации в течение 3 ч степень извлечения обоих металлов достигает 95%. Структура металла, полученного в результате разделения продуктов восстановления, соответствует структуре углеродистого феррохрома. В металле содержатся карбиды $(Cr,Fe)_{23}C_6$и $(Cr,Fe)_7C_3$и силициды FeSi, и Cr_3Si, причем с увеличением продолжительности восстановительной выдержки возрастает количество силицидов и содержание железа в них, а карбиды обогащаются хромом. Получаемый в результате разделения шлак по мере роста продолжительности выдержки при обжиге обедняется оксидами железа и хрома; их среднее содержание в случае после твердофазного обжига в течение 3 ч снижается до 0,5 и 2,5% соответственно.

Ключевые слова: хромовая руда, предварительное восстановление, жидкофазное разделение, карботермическое восстановление, твердофазное восстановление,селективное восстановление, степень извлечения, хромшпинелид, феррихромпикотит, углеродистый феррохром, карбид хрома, кварцевая оболочка.