RESEARCH OF REDUCING ABILITY OF CARBON REDUCTANTS FOR FERROALLOY PRODUCTION BY DILATOMETRIC METHOD

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ABSTRACT

In carbothermic method of ferroalloys production a nut coke is usually used as a reducing agent. Because of high prices and relatively high content of harmful impurities producers aspire to replace nut coke by cheaper carbon reductants, primarily by coal and semi-coke.These types of reductants have high reactive power and low content of sulfur and phosphorus. Disadvantages are high content of volatile and wetness (up to 40-45% in total) and low mechanical strength.

Hot durability and reactive power were determined by research of interaction of various lump carbon reductants with Kazakh chromium ore in resistance furnace with graphite heater using dilatometric method. Conditions of experiments simulated reduction processes in ferroalloy furnace, namely, heating of contacting chromium ore samples and reductant at the rate of 17 °C/min in reducing atmosphere under a load of 2 kg per sample (0,4 kg/cm^2).

Coke, semi-coke (produced by traditional and new technology), coal and graphite (for comparison) were selected as reductants. Semi-coke produced by new method with semi-dry quenching favorably differs from traditional semi-coke by noticeably lower wetness (minimum 1,5%) and content of volatile (minimum 2%) with satisfactory cold durability (15 kgf/cm^2).

Direct dilatometric measurements have shown that, according to degree of progress of reduction processes, coal has the most reactive power, then semi-coke and coke. The most inert is electrode graphite. But coal mechanically destroys at 500-700 °C at a standard load of 2 kg/briquette, while at the same load semi-coke keeps its shape over the whole range of temperatures. At the same time semi-coke starts active interaction with chromium ore at 1200 °C, coke - only at 1400 °C or more. Over 1600 °C reactive power of all types of carbon reductants is the same.

Thus, "new" semi-coke with low content of volatile and wetness can efficiently replace nut coke, which is usually used in ferroalloy production.

1. INTRODUCTION

There are various requirements to carbon reductants in ore-reducing processes [1]: high reactive power, which determines rate and low temperature of the beginning of reduction, developed pore structure, optimum ash value with low content of sulfur and phosphorus, low content of volatile and wetness; sufficient size and mechanical strength both in low and high temperatures, low cost, etc. A nut coke is mainly used as a carbon reductant, which is obtained during blast-furnace coke production. However, this coke is scarce and also its cost, reactive power, conductivity, and other indicators do not fully satisfy the requirements of electro thermal processes.

In connection with high requirements to reductant and few researches in this area, studies of interaction of various lump carbon reductants with Kazakh chromium ore were carried out. The purpose of the present work was to find the optimal carbon reductant, satisfying the requirements of ferroalloy smelting.

2. MATERIALS AND EXPERIMENTATION PROCEDURE

Determination of hot durability and reactive power of various lump carbon reductants was conducted by direct dilatometric method upon contact of reductants with chromium ore under a load [2]. Dilatometric method is detecting changes in length of samples during heating and cooling. Temporally length (or volume) measurement allows estimating degree of physical and chemical transformations, as degree of these transformations is proportional to changes in sizes of samples.

The investigated sample consisted of chromium briquette sandwiched between two discs of carbon reductant. Chromium briquettes always had the same sizes - diameter 24 mm, height - 24 mm. Briquettes were prepared from fine Kazakh chromium ore (table 1) with using sodium silicate (6 % from the weight of ore) as a binder by vibroimpact way in the steel moulding box. The finished briquettes were being dried at 110°C during 1 h and then were stored in air.

Table 1: The chemical compound of Kazakh chromium ore, % (mass)

Cr_2O_3	FeO	SiO_2	CaO	MgO	Al_2O_3	P
48	10	8	0,4	23	8	0,003

Two different brands of coke, semi-coke (produced by traditional and new technology), gas coal and for comparison - electrode graphite (table 2) were selected as carbon reductants.

Table 2: The technical compound of carbon reductants

Type of carbon reductant	Ap, % (ash)	Vp, % (volatile)	Wp, % (wetness)
Coke, type A	12,0	3,5	1,5
Coke, type B	10,1	2,5	2,5
Semi-coke, type A (new technology)	14,1	4,1	2,8
Semi-coke, type B (traditional technology)	12,8	8,8	12,0
Gas coal	23,5	32	7,2

Semi-coke of Ltd. “Leninsk-Kuznetsk semicoking plant” produced by new technology with semi-dry quenching favorably differs from traditional semi-coke by noticeably lower wetness (minimum 1,5%) and content of volatile (minimum 2%) with satisfactory cold durability (15 kgf/cm^2). Semi-coke of Leninsk-Kuznetsk plant has also low content of phosphorus 0,01-0,03 % and sulfur to 0,3%. Discs (diameter - 29 mm and height - 15 mm) were cut from large lumps of carbon reductants by diamond tool.

Before the beginning of experiment dilatometric pair of chromium briquette and two carbon discs was placed in a high alundum crucible and was set in the isothermal zone of the furnace (figure 1). There was the load and the alundum index of movement on the top disc (the total weight 2 kg). The load corresponds to the pressure a column of briquettes (about 2 m height) on briquette (unit load 0,44 kg/cm^2). These conditions simulate conditions of a briquette in a melting stock column in ore-reducing electric furnaces. The furnace was closed, pumped out and filled with argon. During the line heating (heating rate about 17°C/min) the furnace was being outgassed and the pressure was equal to atmospheric. Changes of briquette sizes were fixed according to the movement of alundum index. After experiment metallographic sample was prepared from “crushed" briquette and the phase components formed in the briquette were analyzed.

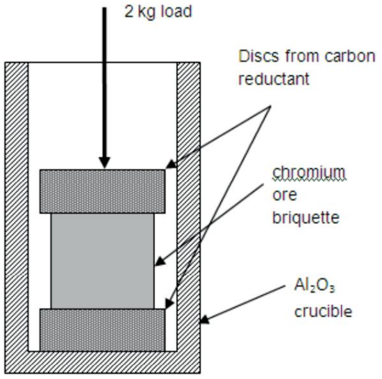


Figure 1: The scheme of dilatometric experiment

3. RESULTS AND DISCUSSION

Figure 2 shows the experimental dilatometric curves for different pairs "chromium briquette - carbon reductant." Correction for thermal expansion of samples and alundum equipment was deducted from the dilatometric curves. The correction was obtained from the "idle" experiment with the replacement of chromium briquette on quartz cylinder of the same size.

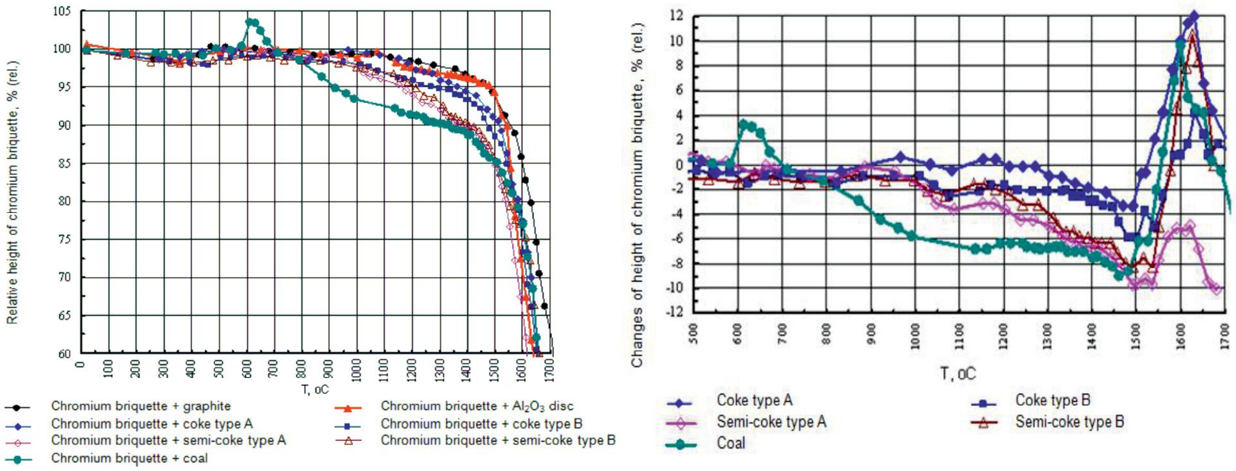
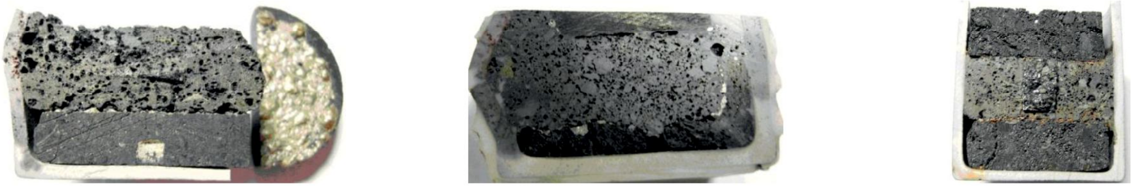


Figure 2: Dilatometric measurements of interaction between lump carbon reductants and chromium briquettes under 2 kg. load during heating to 1700°C

This figure also shows the dilatometric curve for another "idle" experiment - "chromium briquette - Al_2O_3 disc”. To 1500°C dilatometric curve for this pair is almost identical to the results of heating of the pair "chromium briquette - graphite discs", the interaction between graphite and chromium ore begins only in high temperatures during the softening and the beginning of melting of chromium ore itself. At the same time the formation of metal phase is observed only on the boundary "briquette - graphite" (figure 3a).

In contrast to graphite, intensive interaction between coke and chromium briquette begins at significantly lower temperatures (figure 2a). Dilatometric curve obtained by subtracting from the dilatometric curve for pair "chromium briquette - coke" curve for pair "chromium briquette - Al_2O_3 discs" clearly shows that the temperature of the beginning of solidphase reduction strongly depends on the type of coke. For coke type A temperature of the beginning of interaction is 1300-1400°C, and for coke type B - 1000°C (figure 2b). Occurrence of metal phase takes place not only on the boundary of chromium briquette and coke, but some quantity of metal inclusions occurs inside of chromium briquette. After the end of the experiment coke discs hold their shape without significant cracking (figure 3 b, c).



a - Graphite, section, top disc of graphite is separated

b – Coke, type A, sample

c - Coke, type B, section

Figure 3: Appearance of chromium ore briquettes in contact with reductant (graphite and coke) after the experiment

Dilatometric curves for pair "chromium briquette – semi-coke" point to that the interaction of reductant with the ore begins as early as for the best coke grade (type B), but it develops considerably more intense with increasing of temperature. It is true for both semi-coke produced by wet quenching (semi-coke type B), and semi-coke produced by new technology of dry quenching (semi-coke type A) (figure 2). Intensive occurrence of metal phase is observed not only on the boundary between semi-coke and briquette, but also many metallic inclusions are present in the whole volume of chromium briquette (figure 4a, b and figure 5). This points to more intensive development of solid phase reduction of chromium ore by solid carbon in the case of semi-coke in comparison with coke and especially graphite.

a – Semi-coke, type A, section

b - Semi-coke, type B, sample

c - Coal, section, top coal disc dispersed

Figure 4: Appearance of chromium ore briquettes in contact with reductant (semi-coke and coal) after the experiment

There are some through-cracks in semi-coke briquettes, which appeared after the experiment. But at the same time semi-coke briquettes keep the original dimensions. However, it is noted that cracks were in the original lumps of semi-coke, new cracks don't appear and further crush of semi-coke pieces doesn't occur. According to dilatometric curve for pair "chromium briquette – coal" coal has the best reactive power from the studied reductants (figure 2). The interaction in this pair begins with a temperature of 800°C and further proceeds even stronger than with semi-coke. But earlier in the temperature range 550-700°C It was detected that coal discs swelled due to the intense devolatilization. As a result, coal discs lost their continuity and during making of metallographic samples they usually dispersed into powder.

a – Boundary between chromium briquette and Semi-coke, type A, x200
Light-coloured inclusions - metal

b – Center of chromium briquette - Semi-coke, type A, x200
Light-coloured inclusions - metal

Figure 5: Samples of chromium briquettes after heating in contact with semi-coke type A

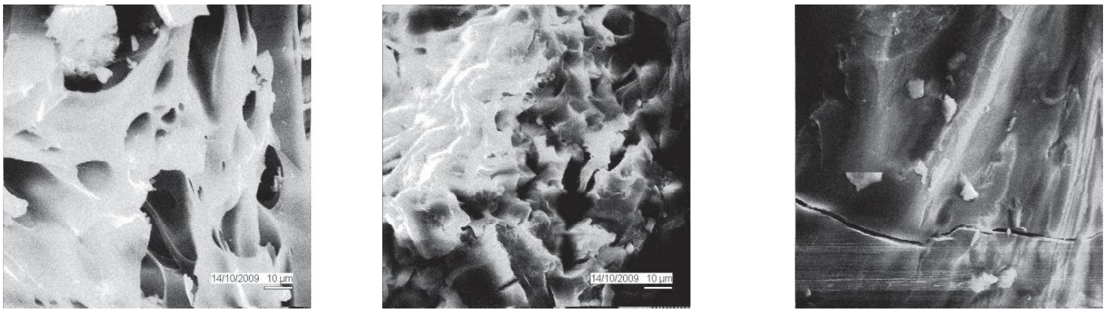
Over 1600 °C reactive power of all types of carbon reductants is the same.

Recently developed a new model of reduction of thermodynamically stable oxides by solid carbonaceous materials allows explaining the results [3]. It is known that most of oxides of basic ferroalloy elements (such as chromium, manganese, silicon, etc.) can be reduced to metal only by solid carbon. Reducing ability of gaseous carbon oxide is not enough to reduce such oxides. And, indeed, reduction parameters observed in practice, such as the temperature of the beginning of reduction, reductant consumption, the degree of reduction, agree with "solid phase" interaction of oxides with carbon and supported by appropriate thermodynamic calculations. On the other hand, this model does not explain high reaction rates, which are more consistent with "gas phase" reduction mechanism. The matter is that the point contact of lump carbon reductant and lumps of ore gives insignificant surface area of reaction that is clearly not enough for the observed reaction rates of reduction process.

Combined "gas phase-solid phase" reduction mechanism is accepted for this model. The following conception is in the basis of the reduction mechanism: direct reductant is solid carbon deposited on the surface of oxide grains as the result of dissolution of unstable gaseous carbon molecules and radicals such as CR_X, where R - oxygen and (or) hydrogen. Hydrogen and oxygen released by dissolution of such molecules realize a new gasification of solid carbonaceous material with the formation of a new gas molecules CR_X type. Then by contact of new carbonaceous gas with ore lumps carbon atoms again deposit on their surfaces in the form of soot and released hydrogen atoms again react with lump reductant to form gas molecules such as CR_X.

Thus, high reactive power of semi-coke is explained by larger porosity and internal specific surface area of the material in comparison with coke and especially graphite. Semi-coke has strongly branched internal structure even more than the original coal (figure 6). Due to blowout of volatiles coal over breaks and gets more reactive power than semi-coke. However, formation of large amount of reductant fines in packing of ore-smelting electric furnace decreases gas permeability and disturbs the normal flow of the reduction process [4].

Semi-coke produced by traditional technology is stricken by microcracks across the grains, presumably because of thermal shock during wet quenching (figure 6). There are no such cracks in semi-coke produced by new method with semi-dry quenching and therefore its crushing during heating happens to a small extent.



a - original coal b – semi-coke c – microcrack in semi-coke

Figure 6: Microstructure of coal and semi-coke (scanning electron microscope)

4. CONCLUSIONS

Semi-coke with low content of volatile and wetness can efficiently replace nut coke, which is usually used in ferroalloy production. Low cold durability of semi-coke in relation to coke doesn't lead to overgrinding of semi-coke in high-temperature conditions of ore-reducing melting.

5. REFERENCES

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