Investigation of Influence of Silicon Carbide Phase and Chemical Composition on its Recovery

D A Boldyrev¹, L I Popova¹ and A A Tokarev²
¹Togliatti State University, 14, st. Belarusian, Togliatti, 445020, Russia
²South Ural State University, 76, Lenin av., Chelyabinsk, 454080, Russia.

E-mail: 151@nppgroup.ru

Abstract. When employing the cast iron manufacturing technology involving the use of silicon carbide, it was discovered that recovery of silicon carbide and that of its individual elements, viz., carbon and silicon varied. Based on the results obtained from a diffraction analysis and electron microscope investigation with electron microprobe analysis, the genuine structural and chemical features of industrial-grade silicon carbide were described. The phase composition of silicon carbide is inhomogeneous and consists of particles of the α-SiC crystalline silicon carbide and oxidized non-crystalline silicon carbide whose basis is a solid solution “carbon-silicon”. Recovery of silicon carbide by molten cast iron determined by the increase in the contents of carbon and silicon during the melting process is inversely on the content of the α-SiC phase.

1. Introduction
There is currently a tendency among cast iron foundries to use steel scrap as a replacement for expensive pig iron as part of charge materials to produce compacted graphite iron (CGI) products. In fact, pig iron being melted promotes formation of a larger amount of nucleation centers, or sites, in the base iron than molten steel scrap [1]. Therefore, when using steel scrap instead of pig iron, it is essential to monitor and adjust the chemical composition of the melt [2, 3]. For this purpose, metallurgical grade silicon carbide is used. It enriches the melt with silicon and carbon (it is believed that silicon carbide favors formation of a pure synthetic melt with nucleation sites (solidification centers)). Silicon carbide contributes to the increase in the amount of solidification centers as a result of which the amount of graphite nodules in the melt also increases, and the tendency of the cast iron to form cementite and ledeburite within its structure (also known as the chilling tendency of cast iron) decreases [4, 5]. The traditional charge materials used for manufacturing CGI products include fine-grain graphite and, normally, ferrosilicon of 45 per cent silicon (ФС/FS45 grade). These materials are primary products as they are manufactured from source materials and are used for the purpose specified which makes them relatively expensive. Notably, the graphite used for its intended purpose is delivered without being subjected preliminarily to activating treatment [6, 7] which explains its low recovery and the ferrosilicon has uncontrollable impurities transferring from the quartzite. Use of silicon carbide, as a source of carbon and silicon, in the iron foundry industry may constitute an advantageous alternative in terms of economy and technology to use of the traditional charge materials [8, 9]. In this case, carbon and silicon are decomposition pure products free of uncontrollable impurities. An additional technical effect resulting from its application is that the total weight and volume of the charge materials used with each ton of silicon carbide is less than those used with each ton of fine-grain graphite and ferrosilicon of 45 per cent silicon.
However, as silicon carbide is being tried out commercially, its recovery is found inconsistent which manifests itself case by case in the predominant recovery of either carbon or silicon [10, 11]. In order to establish the cause of such peculiar recovery of silicon carbide, one sample of fine-grain silicon carbide with a size of 0-10 mm and the content of SiC being 92–95% was taken from three batches of silicon carbide: 1. conventionally “good” sample; 2. conventionally “bad” sample (with poor recovery of carbon; 3. conventionally “bad” sample (with poor recovery of silicon).

The investigation methods used are presented in Table 1.

### Table 1. Investigation methods.

| Methods                      | Equipment                                      |
|------------------------------|-----------------------------------------------|
| Electron microscope investigation | LEO1455VP scanning electron microscope     |
| Electron microprobe analysis | EDX X-MAX80 energy dispersive spectrometer   |
| X-ray phase analysis         | ARL X'Tra X-ray diffractometer                |

### 2. Materials and experimental procedure

For an electron microprobe analysis to be performed, certain quantities of the samples have been deposited on a carbon-based substrate [12, 13]. SEM images are shown in figures 1–3, the element contents in the particle X-ray spectra are presented in Table 2.

### Table 2. Contents of silicon carbide sample elements in particle X-ray spectra, Wt%.

| Sample No. | Spectrum No. | Element, Wt% |
|------------|--------------|--------------|
|            | C    | Si    | O     |
| 1          | 16   | 59.2  | 36.2  | 4.6   |
|            | 17   | 71.5  | 24.4  | 4.2   |
|            | 18   | 52.0  | 44.4  | 3.6   |
|            | 19   | 52.3  | 28.6  | 19.2  |
|            | 20   | 34.7  | 33.0  | 32.3  |
|            | 21   | 68.9  | 18.8  | 12.3  |
|            | 22   | 81.8  | 13.4  | 4.8   |
| 2          | 1    | 35.1  | 33.0  | 31.8  |
|            | 2    | 58.2  | 36.2  | 5.6   |
|            | 3    | 69.8  | 18.0  | 12.2  |
| 3          | 4    | 55.8  | 32.2  | 12.0  |
|            | 5    | 76.7  | 17.8  | 5.5   |
|            | 6    | 51.1  | 35.8  | 13.0  |
|            | 7    | 48.5  | 38.6  | 12.8  |
|            | 8    | 35.8  | 34.7  | 29.5  |
|            | 10   | 53.5  | 40.5  | 6.0   |
|            | 11   | 51.3  | 32.9  | 15.9  |
|            | 13   | 42.9  | 35.0  | 22.1  |
|            | 14   | 92.3  | 4.2   | 3.5   |
|            | 15   | 62.2  | 27.6  | 10.2  |
Figure 1. (Scanning) electron microscopic images of a fragment of sample No.1; marked with rectangle is an area subjected to a local electron microprobe analysis.

Figure 2. (Scanning) electron microscopic images of a fragment of sample No.2; marked with rectangle is an area subjected to a local electron microprobe analysis.
Only carbon, silicon and oxygen have been analyzed, the impurities have been left out. The SEM images were obtained with the help of a back-scatter detector. The intensity of the grey color in these images indicates the positions of the above elements in the periodic table (the lighter the grey color, the higher number in the periodic table the element has). The weight percentage values of the elements in the above table are qualitative [14, 15]. The electron microprobe analysis has shown that the samples being investigated have the following four phases: hexagonal silicon carbide (its amount was so insignificant that it was not taken into account further in the analysis process), rhombohedral silicon carbide (α-SiC), graphite, and silicon. Diagrams showing the contents of carbon, silicon and rhombohedral silicon carbide (α-SiC) are depicted in Figure 4.

The morphological types of the particles in each of the three samples analyzed are identical. They are represented by two major types. The first type is characterized by monolithic (solid), homogeneous and less oxidized particles with a higher content of silicon relative to carbon; the second type is distinct for a predominant content of carbon, more oxidized small particles forming agglomerations being bonded by loose and porous carbon compound. The weight stoichiometric 7:3 silicon-to-carbon ratio for both types of the particles is not observed [16]. The actual ratio values are either higher or lower than the above value. The samples differ from each other in terms of the quantitative relationship between the particles of both types and their dimensions. Particles of the second type and particles of the petcoke that have failed to react mainly find themselves in the pores and cavities of the particles of the first type.

The morphological types of the particles in each of the three samples analyzed are identical. They are represented by two major types. The first type is characterized by monolithic (solid), homogeneous and less oxidized particles with a higher content of silicon relative to carbon; the second type is distinct for a predominant content of carbon, more oxidized small particles forming agglomerations being bonded by loose and porous carbon compound. The weight stoichiometric 7:3 silicon-to-carbon ratio for both types of the particles is not observed [16]. The actual ratio values are either higher or lower than the above value. The samples differ from each other in terms of the quantitative relationship between the particles of both types and their dimensions. Particles of the second type and particles of the petcoke that have failed to react mainly find themselves in the pores and cavities of the particles of the first type.

3. Conclusion

Sample No. 1 is predominantly represented by the largest particles of the first type. The particles of the first type are oxidized less as compared to the similar particles of the other samples. In sample No. 2 more oxidized particles of the second type prevail over the rest of the particles with the content of carbon being higher than that of silicon. Conversely, in sample No. 3 more oxidized particles of the second type prevail over the rest of the particles with the content of silicon being higher than that of carbon. Based on the results obtained from a combination of qualitative electron microprobe analysis and x-ray phase analysis, it is safe to conclude that industrial-grade silicon carbide is an inhomogeneous material made up of particles of crystalline silicon carbide α-SiC and amorphous silicon oxycarbide. This is corroborated by the absence of an identified crystalline lattice of the silicon-carbon phase of the permanent composition discovered when the x-ray phase analysis was performed. An x-ray phase analysis visualizes it not as a unified phase but as an individual combination of carbon and silicon. The overall deterioration of recovery of the samples of silicon carbide Nos. 2 and 3 by the molten metal as compared to that of sample No. 1 directly results from the fact that the content of the crystalline silicon carbide α-SiC in them increased by 2.5–4.5 times as compared to the amorphous silicon carbide[17, 18]. The analysis of the contents of the carbon and silicon and their recovery by the molten metal from samples Nos. 2 and 3 indicates that despite the highest contents of the carbon and silicon in sample No.3 only the carbon is recovered from it, and consequently, it is mainly the silicon that is oxidized which prevents its content from increasing; the decline in the growth of the carbon (recovery of the carbon) when sample No. 2 was used was caused by its combined minimum content in this sample.

Based on the results obtained from the analyses performed, augmented industrial tests were carried out in the cast iron foundry of AO Avtovaz where grey and compacted graphite iron products were cast in 40-ton AC electric arc furnaces. Silicon carbide in the 0 to 2.5 mm size range with a composition from 88% to 92% SiC was used for this purpose [19, 20]. The tests have shown that molten metal recovered smaller-sized
silicon carbide with lower contents of the crystalline phase $\alpha$-SiC. The above-mentioned sizes and SiC contents have been accepted and approved as the optimum requirements to be met by manufacturers.

**Figure 3.** (Scanning) electron microscopic images of a fragment of sample No.3; marked with rectangle is an area subjected to a local electron microprobe analysis.
Figure 4. Integral intensities of three discovered phases expressed in relative units.

References
[1] Greenwood N 2008 Chemistry of the elements (Moscow: BINOM) p 607
[2] Gasik M I 2006 Smelting steel in arc furnaces of a machine-building complex with replacement of cast iron with carbon-carbide-silicon briquettes Electrometallurgy 6 2–13
[3] Gasik M I, Ovcharuk A N, Semenov I A and Derevianko I V 2004 Progressive technologies of electric steel smelting with replacement of cast iron by CSiC briquettes Steel 4 26–30
[4] Zubov V A and Gasik M I 2002 Electrometallurgy ferrosilicon (Dnepropetrovsk: State Scientific and Production Enterprise “System Technologies”) p 704
[5] Ryabchikov I V 1966 Thermodynamic studies of the Si-O-C system at high temperatures Izvestia of the USSR Academy of Sciences. Metals 2 14–19
[6] Derevianko I V 2005 Development of technology for extracting silicon carbide and graphite from secondary materials of electrothermal production Metallurgical and mining industry 3 22–27
[7] Urazlina O Yu, Gasik M M and Gasik M I 2004 Investigation of the physical properties of thermoanthracite during high-temperature calcination Metallurgical and mining industry 4 17–20
[8] Tolstoguzov N V 1992 Theoretical foundations and technology of smelting silicon and manganese ferroalloys (Moscow: Metallurgy) p 238
[9] Porada A N and Gasik M I 1990 Electrothermia of inorganic materials (Moscow: Metallurgy) p 232
[10] Volynkina B P, Strakhov V M and Litvin E M 1998 Anthracite-based briquettes for steelmaking Coke and Chemistry 9 36–39
[11] Chalykh E F 1972 Technology and equipment for electrode and electric coal enterprises (Moscow: Metallurgy) p 432
[12] Bestuzhev N I, Mikhailovsky V M, Bestuzhev A N, Chepyzhov B A, Grudnitsky I P and Pashkevich V F 2003 Complex inoculating treatment of liquid cast iron Foundry 10 6–8
[13] Lekakh S N 223 Resource-saving technologies for obtaining high-quality cast iron for machine-building castings (Minsk: Science and Technology) p 223
[14] Lekakh S N and Bestuzhev N I 1992 Out-of-furnace treatment of high-quality cast iron in mechanical engineering (Minsk: Science and Technology) p 269
[15] Bestuzhev N I, Mikhailovsky V M, Bestuzhev A N, Chepyzhov B A, Grudnitsky I P and Pashkevich V F 2003 Complex inoculating treatment of liquid cast iron *Foundry* 10 6–8
[16] Peregudov L V, Malashin M M and Druzhbina T V 1982 Interaction of melt and siliceous additives when modifying cast iron *Foundry production* 4 6–7
[17] Cirilli V and Appendino P 1980 The mechanism of action of inoculants for gray iron *Accord. Nas Lincein. Mem elsei fis Mate Natir.* 2 16–20
[18] Decrop M and Masere C 1969 Etude de la formation graphite dans le fotes Mecanisme de l’inoculation *Fonderie* 276 105–120
[19] Brandtzag S R, Linda H and Oze H A 1983 Structural changes in graphite by heat treatment *Light Metals* 711–725
[20] Ollesinki R W and Abbashian G J 1984 The C-Si (cfrbonsilicon) system *Vull Alloy Phase Diagr.* 5 486–489