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The Influence of the Degree of Blastfurnace Slag Crystallization on the Properties of Artificial Slag Brick

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Abstract: The study gives consideration to the influence of characteristic properties of chemical and mineralogical composition and structure of blastfurnace slag on artificial brick physical and mechanical properties formation of during hard firing. The researchers have examined blastfurnace slags with variety of compositions and structures and have found out the peculiarities of heating structure formation depending on the type of additive. The results of experimental work analysis show that the temperature and range of sintering of the materials under consideration having high concentration of alkaline-earth oxides (CaO, MgO) depend both on the total content of such oxides in a raw mixture and on the phase state of their compounds as well as on the type of structure of a slag component.

Key words: Blastfurnace slag, structure, glass phase, melilite, akermanite, dendrite structure, strength, sintering characteristics, hard firing

INTRODUCTION

Non-equilibrium in the phase composition of blast furnace slags causes difficulties in determining interrelation between the mineralogical composition, the properties and the conditions of structure formation. For example, lack of data on optimal parameters of cooling process behavior of melts results in inconsistent conclusions of different authors regarding the phase composition and the structure of blast furnace slags. With well-studied general mechanisms of slag crystallization (Lee *et al*., 2004; Ozturk and Fruehan, 1986; Seok *et al*., 2007) the detailed data related to metallurgical industry enterprises in the Russian Federation have been not yet currently analyzed.

The mechanisms of slag crystallization involve incomplete correspondence between the course of crystallization, the mineralogical composition of slag and the ternary diagram (Muller and Erwee, 2011; Smolchik, 1980) which could be explained by complex chemical composition and frequently occurring non-equilibrium crystallization conditions: fast cooling of melts, lack of interaction between the liquid phase and the already evolved crystals, variations in the degree of crystallization (Goncharov *et al*., 2003; Budnikov and Ginstling, 1971). Deviations of the slag crystallization processes from the ternary diagram are externalized through so called one-step crystallization when the process does not flow according to eutectic pattern but every phase crystallizes continuously in a single step (Budnikov and Ginstling, 1971). Even in the case of slow cooling of melted slag under the conditions proximal to equilibrium the courses of crystallization deviate from the ternary diagram and crystallization temperatures of individual phases are always lower than the prescribed (Dovgopol, 1978; Antonov *et al*., 1996). This research is aimed at study of the influence of chemical and mineralogical composition as well as of structure of blast furnace slags and additives for them such as sodium silicate and aluminum silicate on formation of artificial brick performance characteristics.

MATERIALS AND METHODS

In the course of the experimental work the researchers studied the structures of blastfurnace slag with various chemical compositions (acid, basic and neutral ones) produced by several enterprises of the Russian Federation (Table 1) as well as the peculiarities of formation of heating structure of slag material without additives and with such additives as sodium silicate and aluminum silicate. Phase composition of the raw materials, the products of hydration and heat treatment were determined by the method of X-ray phase analysis and the crystal-optical method. The X-ray phase analysis was performed with the aid of "DRON-3" apparatus (Cu anode, Ni-filter). Identification of diffractograms was made according to the JCPDS catalogue with use of PDF-2 electronic filing developed by ICDD Company (USA) and PDWIN Software suite (powder methods of X-ray analysis). Crystal-optical investigations were carried out

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Table 1: Chemical composition of blast furnace slag

Structure type	Chemical composition, weight ratio (%) SiO_2	Al_2O_3	CaO	MgO	FeO	TiO_2	MnO	K_2O	Na_2O	Alkali-lime index
Aphanitic	36.3	12.39	37.45	10.79	0.50	1.45	0.52	0.39	0.26	0.89
Aphanitic	40.27	5.67	45.63	5.32	0.41	0.20	0.03	0.87	0.49	1.11
Vitrophyric	39.00	6.61	43.64	6.70	0.2	0.12	0.03	0.3	0.2	1.10
Vitrophyric	34.93	8.46	38.46	9.60	1.88	1.21	0.21	0.4	0.35	1.10
Vitrophyric	43.9	11.4	38.7	3.59	0.2	0.35	0.31	0.88	0.21	0.76
Vitrophyric	40.08	7.50	41.66	9.35	0.51	0.45	0.63	0.1	0.2	1.07
Vitrophyric	38.74	6.87	47.47	3.73	0.92	0.15	0.39	0.1	0.26	1.13
Non-holocrystalline	34.29	13.9	37.7	8.97	0.71	2.11	0.59	0.76	0.24	0.98
Non-holocrystalline	38.54	6.87	47.27	3.93	0.92	0.15	0.39	0.2	0.36	1.13
Holocrystalline	40.08	7.50	41.66	9.35	0.51	0.45	0.63	0.1	0.2	1.07
Holocrystalline	40.27	5.67	45.63	5.32	0.41	0.20	0.03	0.87	0.49	1.11

with the help of MIN-8 polarization microscope. Diagnostics of mineral phases in the source materials and products was made with parallel and crossed Nicols with use of transparent microscopic slides-polished specimens.

In the course of study of the heating structure formation peculiarities blast furnace slag was preliminary ground with ball crusher (fineness of grinding 350 m^2 kg^{-1}). The samples were formed by semidry molding in metal moulds with use of a hydraulic press (molding sand humidity 10%, compression molding pressure 50 MPa). The samples were sintered in the temperature range of 800-1200°C.

RESULTS AND DISCUSSION

The analysis of slag X-ray patterns showed that slags No. 1 and 2 had the highest glass phase concentration, crystalline phase (no >5…10%) was represented by such crystalloids as melilite $Ca_2(Al, Mg)[(Si, Al)_2O_7]$ with (d/n, Å-3.105; 2.876; 2.738; 2.522) and wollastonite (d/n, Å-4.162; 2.921). The structure of these slags refers to Aphanitic type. The structures of blastfurnace slags No. 3…7 characterized by 10…25% crystalline component content refer to Vitrophyric type. The composition of devitrified part of the named slags is represented by melilite $Ca_2(Al, Mg)[(Si, Al)_2O_7]$ (akermanite) with (d/n, Å-5.039; 4.230; 3.079; 2.867). It is difficult to make accurate identification of this phase since the X-ray analysis data for akermanite and melilite containing up to 10% of gehlenite component are almost similar and the refraction index for this phase is very close to akermanite (Muller and Erwee, 2011; Budnikov and Ginstling, 1971). The second place in a quantitative sense is occupied by merwinite $3CaO{\cdot}MgO{\cdot}2SiO_2$ with (d/n, Å-2.71; 2.683; 2.652; 2.468; 2.287). Among other auxiliary minerals rankinite (d/n, Å-3.500; 3.069; 2,867; 2.687; 1.916; 1.821) and larnite (d/n, Å-4.004; 3.290; 3.038; 2.921; 2.738; 2.571,) prevail in slag No. 6; anorthite $Ca[Al_2Si_2O_6]$ (d/n, Å-3.27; 3.15; 3.36), monticellite $CaMg[SiO_4]$ (d/n, Å-2.66; 1.84; 2.58; 2.38; 2.28) larnite (d/n, Å-5.522; 3.35; 3.290; 3.038; 2.921; 2.738; 2.571) slag No. 7.

Blast furnace slags No. 8 and 9 have non-hollocrystalline type of structure with 30…40% content of crystalline component. Principal minerals in slag No. 8 are represented by melilite, perovskite $CaTiO_3$ (d/n, Å-3.40; 2.16; 2.33), dicalcium silicate (d/n, Å-2.75; 2.71; 2.61; 2.49; 3.01), anorthite $Ca[Al_2Si_2O_6]$ (d/n, Å-3.27; 3.17; 3.90) was also detected. The X-ray patterns of No. 8 slag screenings (particle size <0.63 mm) represented mainly by light-colored grains show reflections typical for aluminum diopside CaAl $[Si_2O_6]$ and monticellite CaMg $[SiO_4]$ (d/n, Å-2.68; 2.57; 5.53; 5.09; 4.62). The X-ray patterns of the screenings represented by dark-colored inclusions show presence of wollastonite $CaSiO_3$ (d/n, Å-2.98; 3.49; 3.40; 3.30; 2.57) and perovskite in small amounts.

Main crystalline phase of slag No. 9 is represented by dicalcium silicate, there were also found out reflections typical for melilite, rankinite and wollastonite. Slowly cooled blastfurnace slags having holocrystalline type of structure (No. 10, 11) were completely devitrified. Main mineral phase is represented by melilite. In the course of experimental work the researchers carried out the investigation of the particularities of heating structure formation in slag material without additives and with such additives as sodium silicate, high-melting and low-melting aluminum silicates. Slags were primarily ground in crusher (particle size 350 m^2 kg^{-1}). The samples were formed by semidry molding (molding sand humidity 10%). The samples were sintered in the temperature range of 800…1200 °C.

The analysis of the obtained experimental data referring to study of high-temperature structures of artificial brick showed that at time of heat treatment of low-basic crystalline slags consisting mainly of melilite (akermanite) and accessory minerals merwinite and larnite there were observed the processes of recrystallization. Like in granulated slags the crystalline slags (No. 10, 11) demonstrate the reaction of merwinite decomposition at the temperature of 1000°C. Study of the structure of the heat treated slag samples having vitrophyric structure (No. 4, 6) by the optical microscopy method showed evolving four patterns of melilite, namely dendrite (Fig. 1a), platy (Fig. 1b), tabular (Fig. 1c) and x-shaped (Fig. 1b) crystals. The dendrite patterns of crystals are generated at time of the granulated slags (No. 1-8) decrystallization, formation of the platy, tabular and x-shaped patterns involves recrystallization of crystalline slags (No. 9, 10).

Skeleton (dendrite) crystal growth patterns are conditioned by various reasons, i.e. uneven thermal conductivity of crystals and liquid, presence of an additive (Goncharov*et al*., 2003), unequal conditions of supply of a growing crystal, etc. Different mechanisms of growth play significant role in generation of various crystal patterns. Formation of crystals with equilibrium pattern under the conditions of moderate supercooling is effected through growth and development of two-dimensional nuclei across the whole area of side planes. Thus for example crystals with tabular pattern are formed from envelope-like crystals (Fig. 1c).

Maturing of the samples with dendrite pattern (Fig. 1a) under the temperature in the range from 800-1000°C results in gradual growth of dendrites, thickening of their branches and decrease of inter-crystalline glass quantity. However, the higher temperatures (over 1000°C) result in the tendency to transition from the skeleton growth patterns to the well-structured crystalline patterns, i.e., platy, tabular and x-shaped. The dendrite structures have better mechanical properties as compared to the porphyritic ones (Budnikov and Ginstling, 1971) which is obviously conditioned by stronger interlocking of dendrite crystals and more intimate intergrowth through inter-crystalline glass. Within the bounds of dendrite structure type the less crystals size the higher mechanical strength.

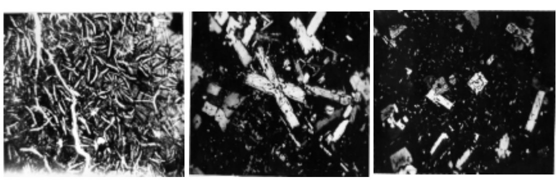

Fig. 1: High-temperature structures of slags

Formation of the structure of slag brick with such additives as sodium silicate and aluminum silicate is characterized by a range of peculiarities. The analysis of the experimental studies results (Fig. 2) showed that the samples based on acid or basic slags with vitrophyric structure without additives demonstrate insignificant change of physical and mechanical properties in the range of temperatures from 800-1100°C. Further increase of temperature up to 1200°C results in more rapid ascent of the breaking strength curve for the acid slag (up to 65 MPa) while the basic slag showed twofold lower compression strength under this temperature. Temperature increase up to 1250°C resulted in melting of the acid slag samples while the basic slag samples demonstrated the compression strength of 65 MPa.

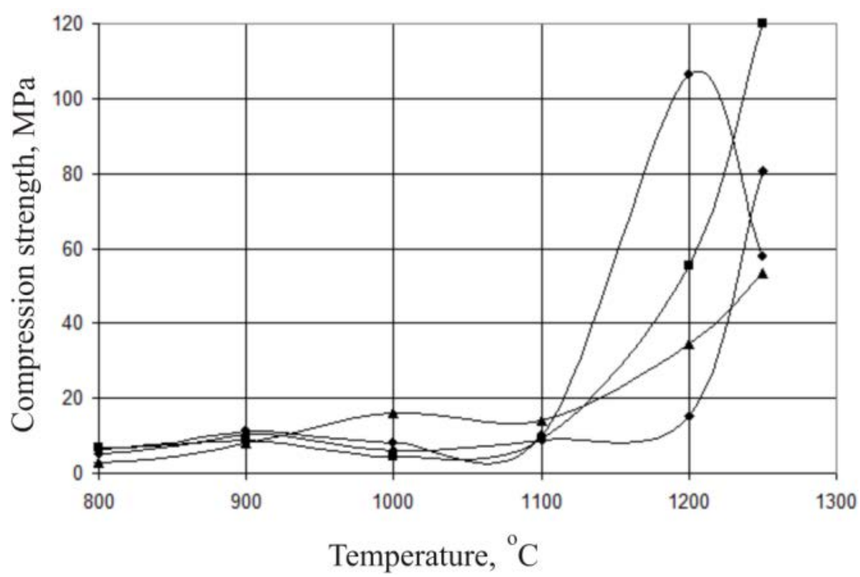

Fig. 2: Physical and mechanical properties of additives-free artificial slag brick. Legend: ▲; basic slag with vitrophyric structure, ♦; neutral slag with aphanitic structure, ■; non-holocrystalline-granular acid slag, •; acid slag with vitrophyric structure (Temperatuer over 1000°C)

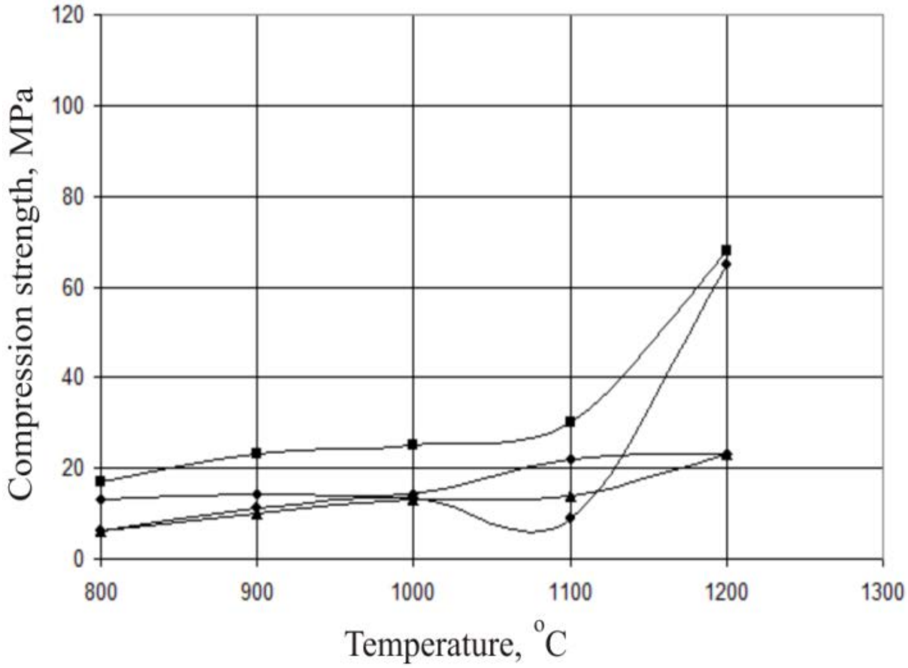

Fig. 3: Physical and mechanical properties of artificial slag brick with sodium silicate additive. Legend: ▲; basic slag with vitrophyric structure, ♦; neutral slag with aphanitic structure, ■; non-holocrystalline-granular acid slag, •; acid slag with vitrophyric structure (Temperature 900-1100°C)

Within the range of temperatures from 900-1100°C (Fig. 2) the additives-free samples of any composition showed almost unchanged compression strength, volumetric fire shrinkage and apparent porosity which is indicative of rather broad range of solid-phase sintering. When the temperature is raised up to 1200°C the sintering process becomes more intensive because of liquid phase occurrence as evidenced by considerable strength increase in case of acid slags. Adding of sodium silicate (Fig. 3) flattens undular nature of curves of physical and mechanical properties of heat treated slag brick. Within the range of temperatures from 800-1100°C shrinking deformation does not exceed 1% for all compositions except for the acid slag samples which showed 3% volume increase.

With the temperature increase up to 1200°C the samples of acid slag with vitrophyric structure as well as of slag with non-holocrystalline structure demonstrate considerable shrinkage deformations amounting to 15…20%. Introduction of sodium silicate into the raw mixture composition based on slags with aphanitic structure type allows increasing the temperature of liquid phase formation as well as preventing uneven changes of properties of materials which are caused by the processes conditioned by the Hedvall effect (Tretyakov, 1999). Softening action of sodium silicates is also associated with ability of sodions to substitute calcium isomorphically in crystal lattice of melilite which is the final high-temperature phase of the materials based on blastfurnace slags.

Aluminum silicates do not have univocal influence on sintering of slag materials. Addition of high-melting aluminum silicate results in considerable extension of the sintering range (up to 300°C) (Fig. 4). Simultaneously the samples strength improvement up to 35…60 Mpa can be observed within the range of solid-phase sintering. Adding charge mixture of low-melting aluminum silicates (Fig. 5) does not have effect on the solid-phase sintering range but the quantity of liquid phase gets higher at the sintering temperature over 1100°C. The highest growth is observed when the slags with vitrophyric structure are used together with aluminum silicate. Blastfurnace slag with non-holocrystalline structure is characterized by poor interaction with various additives therefore it would be advisable to subject it to preliminary mechanochemical activation.

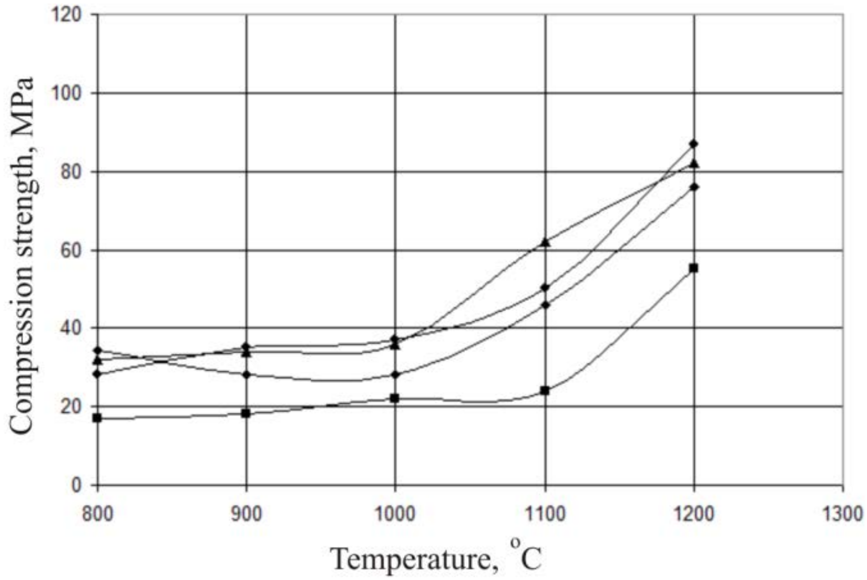

Fig. 4: Physical and mechanical properties of artificial slag brick with high-melting aluminum silicate additive. Legend: ▲; basic slag with vitrophyric structure, ♦; neutral slag with aphanitic structure, ■; non-holocrystalline-granular acid slag, •; acid slag with vitrophyric structure (Temperature 800-11000°C)

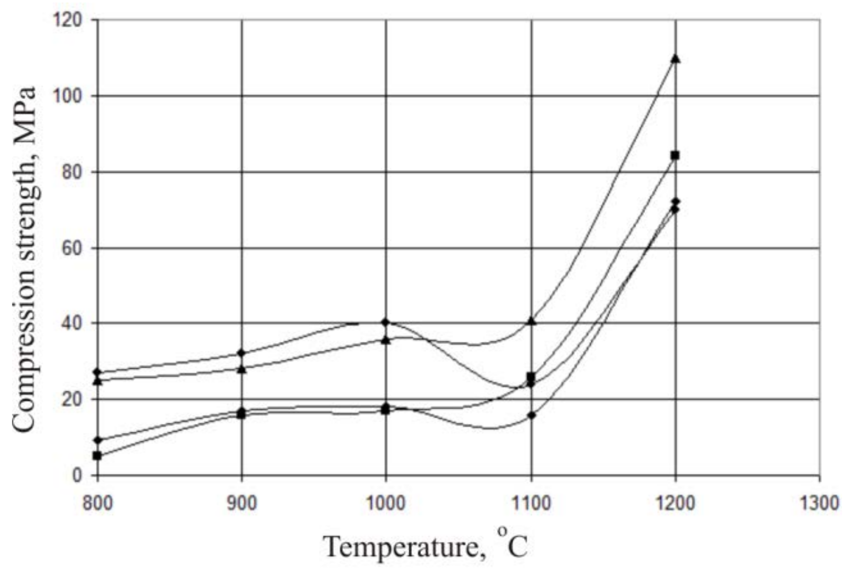

Fig. 5: Physical and mechanical properties of artificial slag brick with low-melting aluminum silicate additive. Legend: ▲; basic slag with vitrophyric structure, ♦; neutral slag with aphanitic structure, ■; non-holocrystalline-granular acid slag, •; acid slag with vitrophyric structure (Teperatuer upto 1200°C)

CONCLUSION

Summarizing the above mentioned data it is necessary to point out that the sintering temperature and range of the studied materials having high concentration of alkaline-earth oxides (CaO, MgO) depend not only on the total content of the same in a raw mixture but on the phase state of their compounds and the type of structure of a slag component. Thus for example if an alkaline-earth component in a raw mixture is represented by free calcium or magnesium oxides which originate from carbonates of these elements intensive sintering within the narrow temperature range may be observed which is conditioned by strong chemical interaction between these oxides and acid component of slag ingredient or other silicate phases. If calcium or magnesium oxides are a component of wollastonite, melilite, diopside or other stable crystalline compounds which do not have such intensive reaction with more acid components of a raw mixture then the range of solid-phase sintering will be significantly wider. The value of the mentioned range is also influenced by the type of structure of a slag component (aphanitic, vitrophyric, non-holocrystalline, holocrystalline). Phase transitions and changes of phase state of blastfurnace granulated slags with various crystallization degrees at time of hard firing have ambiguous effect on performance properties of a finished product. Addition of sodium silicate and aluminum silicate to a raw mixture composition based on slags allows preventing uneven changes of properties of materials. The obtained new data on interaction between chemical and mineralogical composition, structure of slag, type of additive and sintering temperature of artificial brick based on blastfurnace slag will give an opportunity to ensure scientific background for production of materials with multifunctional application as well as products and structures based on slags.

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