

The Analysis of Fire-Resistant Composites’ Properties Based on Metallurgical Slags and Clays

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Abstract

At heat-resistant materials’ production the main attention is paid to achievement of necessary heat fastness. The article presents theoretical justification of high heat fastness of materials that is based on slags and clays with excipients’ addition.

Keywords: heat-resistant composites, heat fastness.

1 Introduction

Composites based on milled metallurgical slags and clays have rather high operational characteristics and can be used in various industries, for example, in manufacture of heat-resistant products [1-3], etc.

The factors that influence on material’s heat fastness can be divided into two groups: caused by properties of the tested material and depending on conditions and a method of carrying out tests.

The first group includes the chemical and mineral composition of material, particles' size, the relative arrangement and a ratio of crystal and glassy phases causing intensity of their interaction in the time of heating. The form of exemplar and, partly, its installation on a fire-resistant support (with an inclination or directly), test heating speed, distribution of temperatures and an arrangement of exemplar in the working camera, etc. belong to the second group.

Heat fastness of materials that based on clays in big degree depends on the contents in their composition of various oxides. The increase in quantity of Al_2O_3 raises a heat fastness. Alkaline metals' oxides are strong fluxes, that reduce clays' heat fastness [4, 5].

Heat fastness of the clays that are used for clay-slag material's production is low (1060 - 1100°C). Therefore, heat fastness of material can be increased due to using clays and slags with elevated temperature of melting, or due to introduction the finely milled heat-resistant additives possessing high rates of heat fastness (chamotte, technical alumina, corundum etc.).

2 Experimental study

The exemplars based on Issinsk clay ($S_{sp} = 498 \text{ m}^2/\text{kg}$) and milled granulose Lipetsk domain slag ($S_{sp} = 335 \text{ m}^2/\text{kg}$) at their optimum ratio were made for carrying out the experiment. A type and an amount of fillers and excipients were varied in different limits (the amount of filler was considered from weight of a binder). As an activator of hardening was used NaOH (2% of mix's mass). Formation was carried out by method of vibrocompaction and pressing. Six structures were made:

- 1 - Clay:Slag = 40:60 (humidity of the forming mix $W=33 \%$)
- 2 - Clay:Slag = 40:60 + 100% of chamotte sand (humidity of the forming mix $W=34 \%$)
- 3 - Clay:Slag = 40:60 + 20% of finely milled chamotte (humidity of the forming mix $W=12 \%$)
- 4 - Clay:Slag = 40:60 + 50% of finely milled chamotte (humidity of the forming mix $W=12 \%$)
- 5 - Clay:Slag = 40:60 + 100% of finely milled chamotte (humidity of the forming mix $W=12 \%$)
- 6 - Clay:Slag = 40:60 + 100% of technical alumina (humidity of the forming mix $W=12 \%$)

3 Results and discussion

According to the obtained data, the melting temperature of the clear clay-slag binder is 1150-1170°C, its melting temperature with addition of chamotte sand - 1180-1200°C. The second indicator is slightly higher that is explained by rather high melting temperature of a heat-resistant component - chamotte ($t_{ml}=1670-1680^\circ\text{C}$).

Input of finely milled excipient has a greater influence on heat fastness, than compact-grained, and increases it at addition of finely milled chamotte in clay-slag system: at 20% of an excipient addition – to 1200-1220°C, at 50% of an excipient addition – to 1230-1250°C and at 100% of an excipient addition – to 1270-1290°C. Heat fastness of a clay-slag binder especially strongly increases at input of technical alumina ($t_{ml}=2015-2043^\circ\text{C}$). At the 100% contents it increases to 1300-1320°C.

It is considered that with increase of ratio of material crushing with other equal things the indicator of heat fastness decreases [6]. It is bound to that with aggregate size's decrease their surface increases and, respectively, quantity of the liquid phase which is formed, first of all, in places of particles' contact and the promoting to deformation of a trihedral truncated pyramid increases too.

However in case of addition of finely milled chamotte in a binder heat fastness increases that probably is possible to explain by formation of new high-melting connections as a result of the reactions between clay, slag and chamotte considerably raising an indicator of melting temperature.

In all cases the indicator of heat fastness of clay-slag material is higher than temperature of melting of clear clays ($t_{ml}=1060-1100^\circ\text{C}$). It can be explained by higher heat fastness of domain slag in comparison with clay. According to [7], heat fastness of finely milled domain slag is 1390°C. Some authors point to effectiveness of input of granulose domain slag in sand form in a binder that based on slags. According to Fomichev N. A. researches [8], at input in the binder that based on martin slag (the binder was prepared on the basis of finely milled martin slag with 50% of granulose slag addition and at 60% of chamotte addition) domain slag in number of 50% material's heat fastness is 1340°C while at input in the same binder 60% of chamotte the heat fastness is 1280°C. Thus, it is possible to make a conclusion [8] that granulose domain slag is more effective than chamotte and allows to increase melting material's temperature considerably. On other sources [9] heat fastness of slags fluctuates from 1170°C to 1200°C. Contradiction of data can be explained, in our opinion, by the fact that slags can be highly basic, neutral and acid with various maintenance of CaO and Al₂O₃ and therefore with increase of the one and a half-basic and dibasic calcium silicates it decreases, and with increase of aluminates of calcium and aluminosilicates of calcium it raises. On heat fastness slag minerals are distributed as follows: melilita, solid solutions of gelenit $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ($t_{ml}=1590^\circ\text{C}$) and an akermanit $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ($t_{ml}=1461^\circ\text{C}$), rankinit $3\text{CaO} \cdot 2\text{SiO}_2$ ($t_{ml}=1150-1200^\circ\text{C}$), larnit $2\text{CaO} \cdot \text{SiO}_2$ ($t_{ml}=2130^\circ\text{C}$), pseudo-wollastonite $\text{CaO} \cdot \text{SiO}_2$, anortit $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($t_{ml}=1550^\circ\text{C}$), montichellit $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ (melting with decomposition at $t_{ml}=1610^\circ\text{C}$), montichellit $\text{CaO} \cdot \text{MgO}_2 \cdot 2\text{SiO}_2$ ($t_{ml}=1391^\circ\text{C}$).

In clay-slag material the chemical and mineralogical structure is generally presented by compounds of hydrosilicates, hydroaluminates and alkaline sodium hydroaluminosilicates which are formed in clay-slag structure as a result of reactions of slag hydration in the presence of alkaline activator NaOH.

The special attention should be paid to the new growths which are formed between minerals of slag and clay at high temperatures.

Since 900-1000°C, hydrated calcium silicates are dehydrated with formation of calcium silicates with basicity 1,5-1,8 (from gel CSH (A) and C_2SH_2); larnit, usually available as a part of basic slags and not hydrated in usual conditions of hardening; at the sufficient maintenance of MgO (in Lipetsk slag it is 9,4%) akermanit and diopside are contained. All this limits the temperature of using concrete based on a slag binder to 1350-1500°C (depending on the maintenance of Al_2O_3 in filler and an excipient) [10].

Also it should be especially noted a formation of crystal connection $3Al_2O_3 \cdot 2SiO_2$ in Al_2O_3 - SiO_2 system that is called mullite. The structure of mullite can be changed from $3Al_2O_3 \cdot 2SiO_2$ to $2Al_2O_3 \cdot 2SiO_2$ and forms the continuous number of solid solutions with Al_2O_3 . Melting temperature of mullite is 1910°C. Formation in slag system of this connection can increase considerably a heat fastness of a binder that based on slag.

4 Conclusion

Thus, as a result of the analysis it was established that a burned clay-slag binder contains in the structure gelenit, rankinit, akermanit and melilit which have a melting temperature in limits 1150-1590°C, and in a burned binder with chamotte addition the main phases are presented by melilits and anortit which have melting temperature 1461-1590°C and 1550°C respectively. Emergence of these phases can serve as justification of increase of clay-slag binder's heat resistance for the account of increase of adamant content that presented in the binder by chamotte fillers and excipients.

The obtained data allow to make a conclusion that the combination of clays with milled domain slag (in the presence of a concreting activator) with formation of clay-slag binder and in the presence of fire-resistant filler gives the chance to receive a composite heat-resistant material which based on a clay-slag binder with melting temperature to 1300°C. The clay-slag excipient (technical alumina, finely milled chamotte) in number of 50-100% the mass of clay-slag binder can be considered as the most efficient for increase of heat fastness.

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Received: March 6, 2015; Published: June 24, 2015