

Microstructure study of lime-slag cement stone after thermal treatment at various temperatures

R R Akhtayamov^{1,2}, B Ya Trofimov¹, R A Zhivtsova¹

¹Institute of Architecture and Construction, Building materials and products, South Ural State University, 76, Lenin Avenue, Chelyabinsk 454080, Russia

²UralNIIstrom, 5/2, Stalevarov street, Chelyabinsk 454047, Russia

E-mail: 351@7359808.ru

Abstract. For the time being the problem of metallurgic waste utilization has obtained urgent importance. The slags of aluminothermic manufacturing of metallic chromium and ferrotitanium are considered to be the most promising component of thermally resistant lime-slag concretes. Fine dispersion particles of aggregates made of such slags participate in a hydration reaction in presence of alkali. This phenomenon allows for the prediction of hydration occurrence on the surface of coarse aggregate of the aluminothermic manufacturing process of metallic chromium and ferrotitanium to enhance cohesion between the aggregate and the cement stone. The paper reports on a study of the phase composition and the microstructure of lime-slag cement stone with the addition of the slags of metallic chromium and ferrotitanium after a thermal treatment at various temperatures. It has been observed that metallic chromium and ferrotitanium slag additives increase the highest admissible operation temperature of thermally resistant lime-slag concretes. Such effect is obtained due to refractory compounds formation on the aggregate surface.

1. Introduction

Metallurgic wastes may be utilized as aggregates for thermally resistant concretes [1-5]. High-aluminous slags of aluminothermic processes are of minor popularity [6-10]. The basic obstacle for wide use of such slags [11-15] in thermally resistant concretes based on Portland cement or aluminous cement is the low strength on the aggregate-cement stone border area [16-20].

For better understanding of processes occurring during the interaction of the lime-slag binding material and the superficial aggregate layer, it deemed advisable to carry out comparative studies of the phase composition and the microstructure of the lime-slag cement stone composed by a binding material (ferrochromium decomposing slag (FCS) tempered with technical caustic soda solution) or floured metallic chromium slag (MCS), or floured ferrotitanium slag (FTS), after thermal treatment at various temperatures.

2. Experimental

2.1. Materials

For lime-slag cement stone generation, the following materials were used:



- FCS from the process of OJSC «Chelyabinsky Electrometallurgical Integrated Iron and Steel Works»;
- MCS and FTS from the process of JSC «UK «RosSpetsSplyav-Group MidUral» Klutchevsky Ferrous-Based Alloy Works»;
- technical caustic soda, flake-grained, made by JSC «Bashkirian Soda Company»;
- utility water.

2.2. Sample preparations

The MCS and FTS were floured till complete passage through sieve No. 008.

For experiments with lime-slag cement stone, sample cubicles 2 cm x 2 cm x 2 cm were prepared, dried out at 120°C with subsequent thermal treatment at 350 °C, 800 °C, and 1200 °C.

2.3. Statement of Method

The microstructure of microsections of the lime-slag cement stone was studied by means of a JSM–700, 1F scanning electron microscope with a microanalytic system by Jeol Interactive Corporation, Japan.

3. Results

3.1. Microstructure

Figures 1-3 demonstrate photos of lime-slag cement stone samples of FCS-based and MCS- or FTS-based cement stone, respectively, at x3000 magnifying power which have been thermally treated at various temperatures.

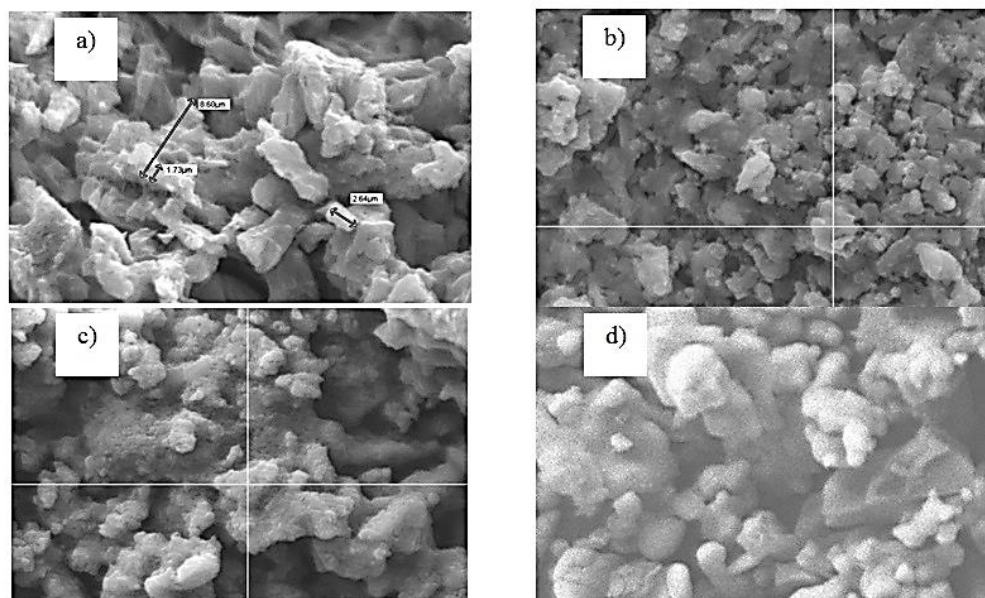


Figure 1. Microstructure of lime-slag cement stone based on FCS, after thermal treatment at: a) 120 °C; b) 350 °C; c) 800 °C; d) 1200 °C

The structure of additive-free lime-slag cement stone is visibly uniform. Figure 1 shows that increasing temperature leads to smaller size of particles composing the cement stone.

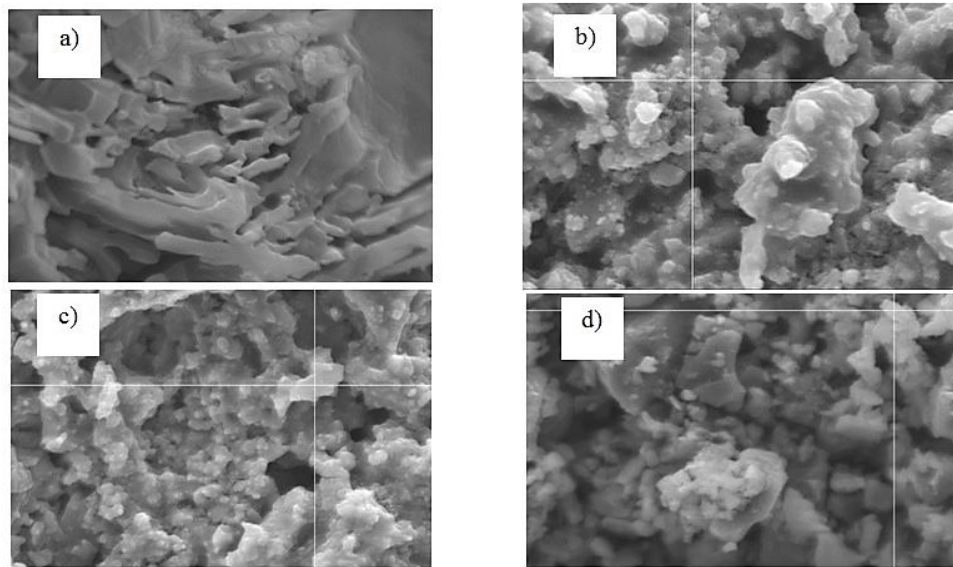


Figure 2. Microstructure of lime-slag cement stone based on MCS, after thermal treatment at: a) 120 °C; b) 350 °C; c) 800 °C; d) 1200 °C

As evident from Figure 2, the structure of the lime-slag cement stone based on MCS is not visibly uniform. At increasing temperature of the thermal treatment of lime-slag cement stone, the sizes of the cement stone particles of sodium and magnesium Al-Cr-silicates of calcium get smaller, the acicular and plate crystal hydration products get loose, spheroid.

As evident from Figure 3, the structure of the lime-slag cement stone based on FTS is not visibly uniform. At increasing temperature, the particle size of the cement stone get smaller, acicular particles get loose, spheroid.

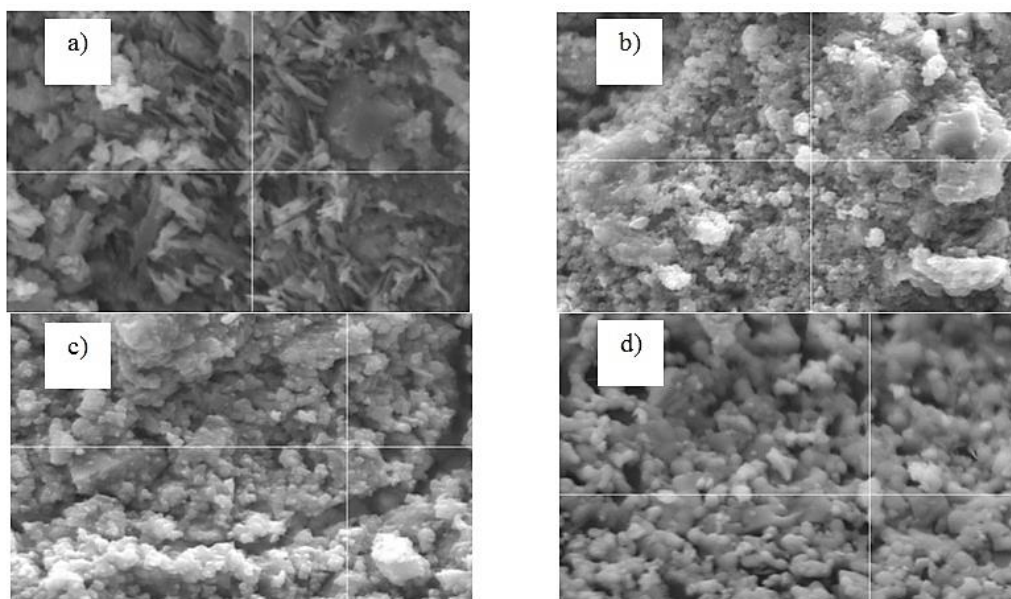


Figure 3. Microstructure of lime-slag cement stone based on FTS, after thermal treatment at: a) 120 °C; b) 350 °C; c) 800 °C; d) 1200 °C

3.2. Qualitative and Quantitative Analysis

Qualitative and quantitative analysis over sample surface and in points of the lime-slag cement stone based on FCS (LS CS on FCS), MCS (LS CS on MCS) and FTS (LS CS on FTS) after drying out at 120 °C and subsequent thermal treatment (TT) at 350, 800, 1200 °C, see Table 1.

Table 1. Qualitative and quantitative analysis over specimen surface and points.

Sample	TT, °C	Weight ratio of the element, % wt															
		Over surface								In point							
		O	Na	Mg	Al	Si	Ca	Cr	Fe	O	Na	Mg	Al	Si	Ca	Cr	Fe
LS CS on FCS	120	47,6	4,4	4,1	2,1	8,6	22,3	1,9	0,5	51,5	3,4	2,1	0,3	13,7	28,2	0,4	0,3
										46,2	3,2	1,5	0,6	17,4	30,3	0,9	0,0
	350	47,3	2,7	4,6	2,3	10,7	26,5	2,4	0,0	42,0	1,9	0,7	52,0	0,6	1,6	1,2	0,0
										46,4	1,6	2,6	1,0	13,1	35,3	0,0	0,0
	800	45,1	1,3	4,8	2,5	12,3	30,7	2,8	0,8	50,1	7,4	2,4	1,6	11,7	22,5	4,3	0,0
LS CS on MCS										27,0	0,0	16,9	18,2	0,0	1,1	36,8	0,0
	1200	42,9	0,6	5,9	2,6	12,6	31,8	2,9	0,9	49,8	0,9	2,7	1,9	14,2	29,4	1,2	0,0
										37,2	0,0	20,5	21,6	1,6	2,5	15,9	1,0
	120	46,5	32,9	0,4	11,8	0,6	2,0	3,3	1,7	51,9	5,7	0,20	10,8	30,4	0,4	0,0	0,0
										44,5	24,4	0,4	5,7	2,3	18,9	2,4	1,5
LS CS on FTS	350	46,2	6,9	0,9	27,3	0,9	4,6	4,8	1,8	50,3	3,7	0,9	30,3	1,2	7,7	4,9	0,9
										42,8	0,3	0,0	55,7	0,0	0,3	0,9	0,0
	800	45,8	6,8	0,9	34,9	1,7	3,6	6,4	1,9	55,8	5,7	0,8	28,9	1,9	1,2	4,1	1,3
										39,9	5,2	0,0	53,2	0,0	0,0	1,6	0,0
	1200	44,2	4,2	1,1	39,8	2,6	4,5	6,7	2,4	48,6	2,9	0,3	37,9	0,0	2,5	6,5	1,1
LS CS on FTS										49,9	4,5	0,7	30,7	3,3	4,7	4,7	1,2
	120	48,2	17,1	4,6	11,3	3,7	10,9	3,5	0,6	52,8	35,1	0,7	2,5	1,3	6,6	0,7	0,3
										41,5	1,4	16,7	32,9	0,7	0,5	6,2	0,0
	350	46,7	4,5	6,6	17,8	4,3	11,7	5,2	0,7	48,4	4,4	7,7	20,2	5,4	9,7	3,5	0,6
										31,6	0,0	19,1	42,4	0,0	0,7	6,1	0,0
LS CS on FTS	800	43,2	4,4	6,9	19,6	5,0	13,2	9,2	0,9	47,6	3,3	7,7	23,1	3,8	7,1	7,6	0,0
										32,9	0,0	18,5	39,5	0,0	0,5	8,6	0,0
	1200	37,6	2,5	7,8	20,3	5,1	14,2	11,1	1,4	42,9	2,7	4,9	24,4	4,6	13,2	6,7	0,7
										34,9	0,0	18,7	42,2	0,0	0,6	3,7	0,0

The quantitative analysis over specimen surface has lead to detection of varying sodium contents. The smallest quantity of sodium was found out in the lime-slag cement stone on FCS, the biggest quantity of sodium was found out in the lime-slag cement stone on MCS. The activity of the slags as to caustic soda is decreasing within the sequence FCS-FTS-MCS.

Figure 1 and Table 1 demonstrate that in the specimen of lime-slag cement stone based on FCS, after thermal treatment at 120°C, only hydration products are visible, like sodium and magnesium calcium silicates; after thermal treatment at 350°C, there are alumina particles, original slag and hydration products; after thermal treatment at 800°C, there are particles of Cr-Al-magnesite; after thermal treatment at 1200°C, there are particles of well-crystallized magnesite and Al-Mg-silicate, and de-hydrated particles of hydration products.

Figure 2 and Table 1 demonstrate that in the specimen of lime-slag cement stone based on MCS, after thermal treatment at 120°C, only hydration products are visible, and free caustic soda with contaminants; after thermal treatment at 350°C, there are alumina particles and hydration products; after thermal treatment at 800°C, there are particles of crystallized alumina and hydration products;

after thermal treatment at 1200°C, there are numerous particles of well-crystallised alumina, corundum, and de-hydrated particles of hydration products.

Figure 3 and Table 1 demonstrate that in the specimen of lime-slag cement stone based on MCS, after thermal treatment at 120°C, only hydration products are visible, like sodium and magnesium calcium Al-Cr-silicates, and free caustic soda with contaminants; after thermal treatment at 350°C, there are small particles of Al-Mg-chromite, and hydration products; after thermal treatment at 800°C, there are particles of crystallized Al-Mg-chromite and hydration products; after thermal treatment at 1200°C, there are numerous particles of well-crystallised Al-Mg-chromite, and de-hydrated particles of hydration products.

4. Conclusion

The initial MCS and FTS slags are polymineral products, the most active compounds containing calcium, magnesium, silicon and iron ions participate in the hydration reaction with the alkali (caustic soda). Based on the results of microstructure, qualitative and quantitative analyses, it was established, that at heating up to 1200°C, the most active minerals almost completely interreact with the caustic soda combining compounds which ensure the adhesion of the aggregate.

After heating up to 1200 °C, there are grains of refractory compounds distinctly visible in the cement stones which do not participate in the hydration reaction and are inert to the alkali at a high temperature.

Basic conclusions of the paper:

- based on the number of the refractory grains in the cement stone after heating up to 1200 °C, one can forecast that the slags could be assigned to the respective highest admissible operating temperatures of concrete as follows: FCS, FTS, MCS, respectively, in the ascending order of temperature;
- based on the number and particle size of the hydration products after thermal treatment at a temperature of 120 °C, one can forecast that the slags could be assigned to the compression strength scale as follows: FCS, FTS, MCS, respectively, in the descending order of the compression strength value.

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