Effect of Modifying Additives on Mechanical Properties of Refractory Concrete

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This experimental study presents the results of the combined effect of micro fibre and micro silica content on physical and mechanical properties of refractory concrete after exposure to high temperatures. A complex binder together with firestone aggregates was used for production of refractory concrete, which was reinforced simultaneously with micro fibre (1 wt % and 3 wt %) and micro silica (1.5 wt %, 3.5 wt % and 5 wt %). Unmodified concrete was produced as well. The results show that simultaneous modification with micro silica and micro fibre improves the flexural strength of the refractory concrete at all the temperatures investigated: 100 °C, 600 °C, 800 °C and 1000 °C. Contrary, the advantage of reinforcing agents on cold crushing strength of concrete was observed above 800 °C. It was determined that the mechanical strength of the refractory concrete increases with the increasing content of micro silica and reduces with the increasing content of micro fibre.

Keywords: fibre, silica, refractory, concrete, cement, compressive strength, flexural strength, high temperature.

1. INTRODUCTION

Calcium aluminate cements continue to be the most important hydraulic binder in the refractory concrete which is widely applied as linings of the furnaces used in cement, ceramics, glass or petrochemical industries as well as for restoring and protecting slag pits, drossing areas, etc. [1, 2]. Refractory concrete with complex binder is useful due to its fast operation after installation, its relative durability, short repair time and resistance to corrosive acidic atmosphere [2, 3]. Formation of cracks after thermal cycling or dynamic loads is the main disadvantage [3].

Better crack resistance, ductility as well as toughness of concrete is improved by adding different kind of fibres which change the behaviour of the matrix [4 – 8]. Incorporation of steel fibre up to ~2 % of concrete volume improves thermal conductivity and flexural strength; provides higher tensile capacity and blocks growth of micro cracks [7 – 10]. Dispersed fibres hinder lateral expansion which in turn increases the confining pressure and thereby enhances strength and ductility of concrete [9, 11] On the other hand addition of metallic fibres aggravates mixing, workability and results in poor fibres distribution and orientation in the matrix [4, 11]. One of the solutions is to use of a mix of short and long fibres as well as microfibers [7] or even a mix of fibres of various types such as carbon-steel, polymeric fibres with steel and etc. [5]. Another way is to incorporate silica into fibrous samples and thus improve fibre dispersion in the mixture as well as the strength of the material [4, 12]. Moreover, micro silica determines the growth of density and compressive strength of the concrete after firing at high temperature [3, 12], but simultaneously reduces operating temperature of the material [3]. As the material properties are greatly affected by the high temperature [12, 13] the presence of fibres can delay or even eliminate cracking of the concrete under firing [5, 6, 8]. At the same time application of fibres is restricted by their maximal working temperature or due to their degradation or corrosion in the matrix [14, 15]. Due to their chemical resistance and thermal stability at relatively high temperature the ceramic fibres are very attractive as reinforcing agents [16].

Our previous work [17] showed that fibrous material with mullite phase can be produced by applying plasma spray technique and additional thermal treatment. A complex binder, which consists of high alumina cement, liquid glass and metallurgical slag, can be reinforced with up to 3 % of plasma sprayed micro fibre without a significant reduction of the mechanical strength [18]. It was also determined that the incorporation of 5 % of micro silica increased the density of the complex binder and reduced the thermal shrinkage in the temperature range from 800 °C up to 1000 °C [18]. On the basis of those results the micro fibre and the complex binder was mixed with firestone aggregate for production of the fibre reinforced refractory concrete. The impact of thermal treatment as well as combined effect of micro silica and micro fibres addition on mechanical properties of refractory concrete was the main objectives of this study.

2. EXPERIMENTAL

Seven refractory concrete mixes were produced by mixing high alumina cement, metallurgical slag and liquid glass solution with chamotte aggregate (particle size up to 1 mm) and deflocculant Castament FS-20 (BASF, Germany) (Table 1). RW-Fuller micro silica (RW Silicium GnbH, Germany) was added as the percentage of 1.5 %, 3.5 % and 5 % by weight of binder but not replaced the cement. The chemical composition and properties of the components had been listed in [19]. Production and micro structural analysis of the micro fibre were depicted elsewhere in detail [17]. Before incorporated into concrete the micro fibre of 5 mm in length was heat treated at 900 °C for 2 h to get crystalline mullite phase. Only 1 %

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and 3 % of the micro fibre was used in this study because higher contents showed reduction of the strength of the binder at elevated temperatures [18]. A concrete mix without addition of micro silica and fibre was moulded as a reference material. Water to cement ratio was kept constant (w/c = 0.5) for all the mixes prepared.

Samples of dimensions of $(20 \times 20 \times 100)$ mm for the flexural strength were formed and cured in moulds for 3 days above the water and 4 days at the ambient temperature of (20 ± 2) °C. After curing all samples were dried at (100 ± 2) °C until they reached their constant weight. Each group of the samples were exposed to 600 °C, 800 °C and 1000 °C at heating rate of 5 °C/min. Samples were heat treated for 3 h [20] and cooled in the oven to room temperature before testing. Ten mixes were prepared for each series of the test. Flexural strength tests were performed according to LST EN 993-6:2001. Compressive strength tests were done on the specimens, which had been broken after the flexural strength tests, according to EN ISO 8895:2006. The mechanical tests were done by the Zwick Roell universal test machine of the capacity up to 50 kN. Bulk density and relative shrinkage were estimated according to standard LST EN 993-1:2001 and LST EN 1094-6:2001 respectively.

Relative values were expressed as a ratio of data obtained at different temperatures to data of dry samples.

Expanded uncertainty of the measurement corresponding to a coverage probability of less than 95 % is ±1.7 % for cold crushing strength; ±1.85 % for flexural strength tests; ±2.4 % for thermal expansion (shrinkage); ±0.06 % for density and for porosity.

X-ray diffraction (XRD) patterns were obtained using Cu-K_α radiation (DRON-UM1) source to identify the existing phases by the commercial Search Match program.

Scanning electron microscopy (JEOL, JSM 5600) was used to characterize the morphology and the microstructure of the material.

Table 1. The composition of the mixes (wt%)

Concrete mix	High alumina cement	Metalurgical slag	Sodium silicate	Chamotte	Deflocculant*	Water	Micro fibre*	Micro silica*
0FRC-0	28	9	7	38	0.25	18	–	–
1FRC-1.5	28	9	7	38	0.25	18	1	1.5
3FRC-1.5	28	9	7	38	0.25	18	3	1.5
1FRC-3.5	28	9	7	38	0.25	18	1	3.5
3FRC-3.5	28	9	7	38	0.25	18	3	3.5
1FRC-5	28	9	7	38	0.25	18	1	5
3FRC-5	28	9	7	38	0.25	18	3	5

* above 100 %.

3. RESULTS AND DISCUSSION

3.1. Apparent porosity and density

Relative changes observed in porosity and density of refractory concrete with and without additives as function of applied temperature are given in Figure 1 and Figure 2 respectively. Test results of apparent porosity and density of the samples are listed in Table 2. Relative porosity of

the unreinforced sample increased more than 30 % when temperature reached 800 °C and remained unchanged after heat treatment at 1000 °C (Fig. 1). Meanwhile sharpest decrease of density of all samples tested was detected at 600 °C (Fig. 2). Moreover, porosity of the mixes with less content of fibre showed the highest values at that temperature (Fig. 1). This could be attributed to dehydration reactions stimulating micro cracking formation and increase in porosity [21, 22]. However, the samples reinforced with micro silica and fibre showed up to 3 % higher porosity but lower density than the unreinforced samples in temperature range from 600 °C up to 800 °C. The effect of reinforcing agent was more evidence at 1000 °C when the higher content of fibre reduced density of the material instead of increment (Fig. 2) indicated by others [6]. Reduction of the porosity could be attributed to formation of ceramic bonds and sintering of material [22, 23] (Fig. 1).
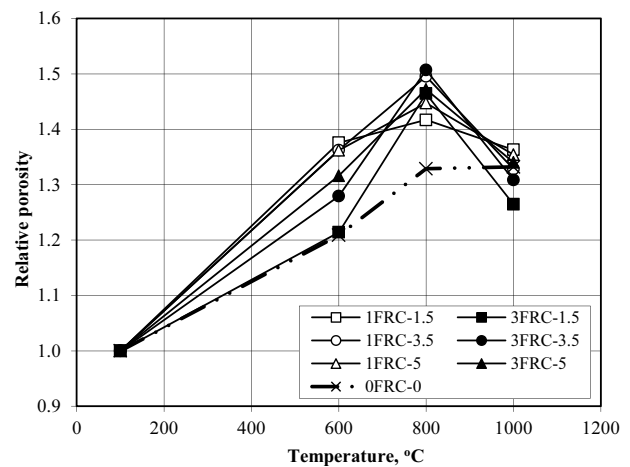

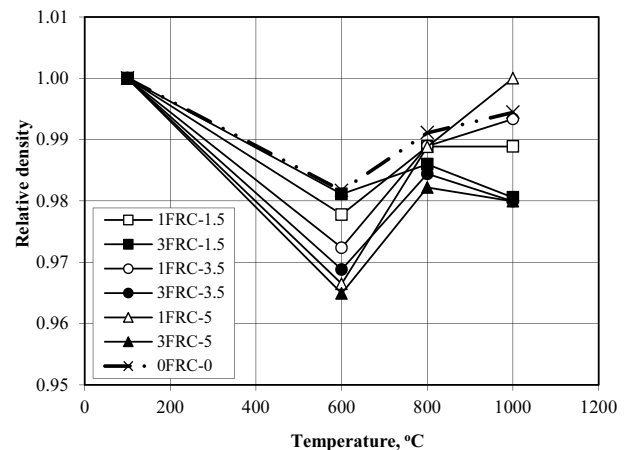**Fig. 1.** Relative porosity of the refractory concrete as a function of temperature

Fig. 2. Relative density of the refractory concrete as a function of temperature

3.2. Compressive strength

For all the refractory concretes tested cold crushing strength (CCS) increased together with the heat treatment temperature, except at 600 °C, where it slightly reduced only for unreinforced samples (Fig. 3). Relative cold crushing (compressive) strength results (Fig. 4) show very sharp growth of the reinforced samples strength. The higher content of micro silica and fibre is the bigger the strengthening effect. Relative strength of concrete with

3 % of fibre and 5 % of micro silica increased up to 3 times in the temperature range from 100 °C up to 1000 °C (Fig. 4). Meanwhile, relative strength of samples with the lowest content of additives as well as unreinforced material increased less than 1.5 times (Fig. 4). However, CCS results of concrete without additives were the highest at 100 °C (Fig. 3).
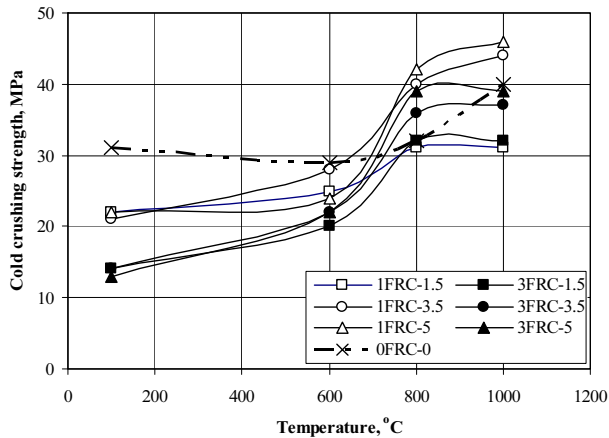

Fig. 3. Cold crushing strength of the refractory concrete as a function of temperature

According to [22–24] we assume that addition of fibre and micro silica retard CA rapid reaction with water and determine the lower compressive strength at 100ºC. After firing at 600 °C (Fig. 3) the reduction of compressive strength of concrete without additives was caused by destruction of all hydrates formed at the lower temperatures. Loss of mechanical strength was observed by others [21, 22] as well as mentioned that no hydrates exist with the crystalline phase above 600 °C. Despite of porosity growth at 800 °C of reinforced concrete (Fig. 1), CCS increased sharply (Fig. 3). Compressive strength of samples with the lowest content of additives was approximately the same as of the unreinforced concrete, meanwhile others showed up to 30 % higher values of CCS (Fig. 3). Heat treatment at 1000 °C temperature determined growth of CCS of reference material, meanwhile strength of reinforced samples remained unchanged or increased up to 10 % (Fig. 3). However, only two groups of samples (1FRC-5 and 1FRC-3.5) showed better CCS results in comparison with the unreinforced concrete at 1000 °C (Fig. 3).
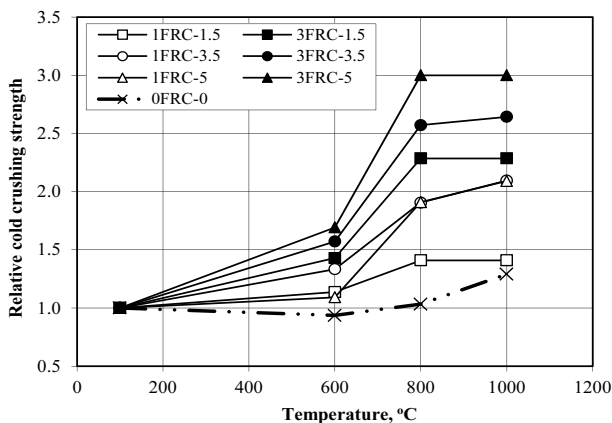

Fig. 4. Relative cold crushing strength of the refractory concrete as a function of temperature

Table 2. Density and apparent porosity of the refractory concrete

Sample	Density, g/cm³			
	100 °C	600 °C	800 °C	1000 °C
0FRC-0	1.80	1.77	1.78	1.79
1FRC-1.5	1.80	1.76	1.78	1.78
3FRC-1.5	1.80	1.77	1.75	1.77
1FRC-3.5	1.81	1.76	1.79	1.80
3FRC-3.5	1.80	1.74	1.77	1.76
1FRC-5	1.79	1.73	1.77	1.79
3FRC-5	1.80	1.73	1.76	1.76
	Apparent porosity, %			
0FRC-0	29.75	35.96	39.53	39.63
1FRC-1.5	25.68	35.33	36.39	35.00
3FRC-1.5	28.02	34.02	41.03	35.44
1FRC-3.5	27.10	36.93	40.54	36.00
3FRC-3.5	26.67	34.12	40.19	34.90
1FRC-5	27.99	38.12	40.51	37.90
3FRC-5	25.89	34.07	38.11	34.70

3.3. Flexural strength

Flexural strength of refractory concrete with and without reinforcing agents increases with increasing firing temperature (Fig. 5). Results of the relative flexural strength (Fig. 6) showed that combination of the highest content of fibre and micro silica (3FRC-5) gives the biggest strengthening effect, as well as in the case with the compressive strength (Fig. 4). Contrary, less but still positive reinforcement was achieved with lower content of fibre after heat treatment above 600 °C (Fig. 6). However, the reinforced samples showed approximately from 20 % up to 50 % higher flexural strength in comparison with the unreinforced one in all the temperature range tested (Fig. 5). After heat treatment at 1000 °C the best results of the flexural strength were determined for samples with the lower content of fibre, moreover the strength increased with increasing content of micro silica addition (Fig. 5).
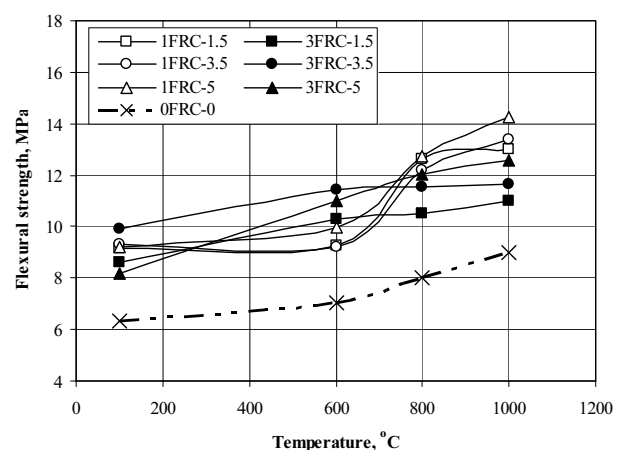

Fig. 5. Flexural strength of the refractory concrete as a function of temperature

3.4. Linear shrinkage

Figure 7 shows the variation of the linear shrinkage of the refractory concrete as a function of temperature. Reinforcement with less content of fibre leads to expansion of

material with the increasing temperature up to 600 °C, whereas higher content of fibre determines shrinkage. The higher the content of micro silica the lower dimensional changes of samples are. Contrary, data obtained after heat treatment above 800 °C showed that shrinkage of concrete with 5 % of micro silica addition was more than 1 %. Meanwhile, samples with lower content of micro silica shrank or expanded less than 1 % (Fig. 7). According to [25] the presence of micro silica induces reduction of the expansion values. By contrast, (Fig. 7) the highest shrinkage was estimated for refractory concrete without fibre and micro silica addition after heat treatment at 1000 °C.

Fig. 6. Relative flexural strength of the refractory concrete as a function of temperature

Fig. 7. Linear shrinkage of the refractory concrete as a function of temperature

3.5. Microstructure and phase composition

Microstructure changes of the refractory concrete heat treated at various temperatures are presented in Figure 9. SEM micrograph of dry samples (Fig. 9, a, A) shows that microstructure consists of interlinked particles of matrix and aggregates, as well as fibre are covered with the hydration products in the fibre reinforced samples. According to [26] nanoclusters and nanolayers of only amorphous hydrates of aluminate cement are formed in the hardened structure of complex binder. However, main crystalline phases such as $CaO·Al_2O_3$ (CA), $CaO·2Al_2O_3$ (CA_2), $3Al_2O_3·2SiO_2$ (A_3S_2), $γ-2CaO·SiO_2$ ($γ-C_2S$) and SiO_2 and no hydrates were indicated by X-ray analysis of the dry samples (Fig. 8). (Fibre and micro silica content variations did not affect the composition of the refractory

concrete, therefore XRD patterns of sample with the highest amount of additives were presented). Due to CA_2 slow reaction with water at early age of hydration, the mechanical strength of the dry samples are relatively low [21 – 23].

No phase changes were obtained after heat treatment at 600 °C (Fig. 8), but higher porosity was visible in SEM micrographs of unreinforced samples (Fig. 9, B). According to DTA results of the complex binder [3] endothermic peak was estimated approximately at 600 °C. The beginning of aggregates reaction with liquid glass at 600 °C was mentioned in [2] as well as formation of amorphous products of reaction as a result of decomposition of hydrates [21, 22]. Growth of porosity and simultaneous reduction of density (Table 2) reduces the compressive strength of the refractory concrete without reinforcement (Fig. 3) meanwhile, presence of fibre and micro silica acts as reinforcing agents and increases the compressive and the flexural strength (Fig. 3, Fig. 5).
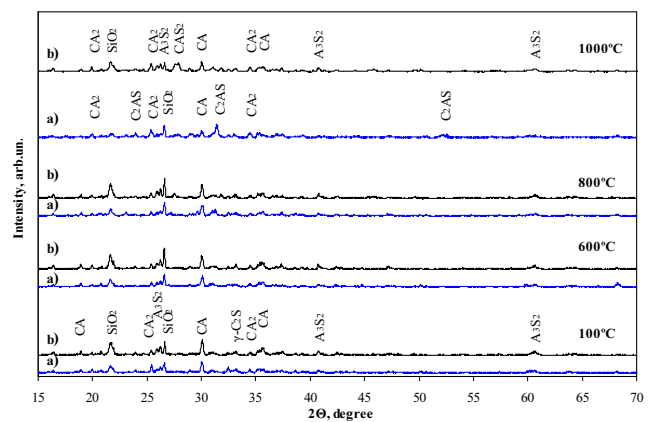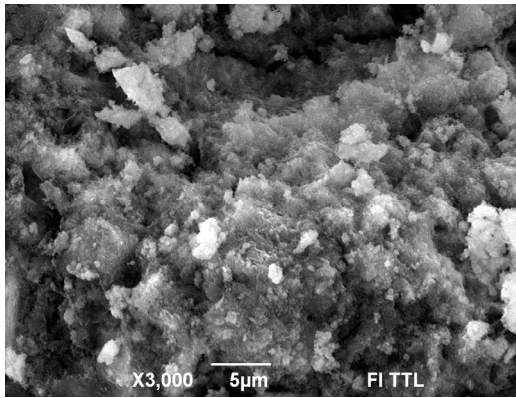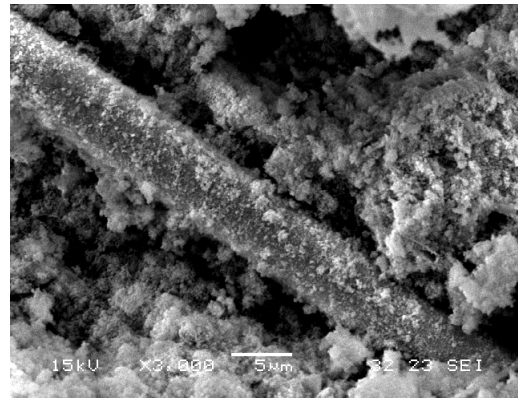

Fig. 8. XRD patterns of refractory concrete without modifying additives (a) and with 3 % of fibre and 5 % of micro silica (b) heat treated at various temperatures
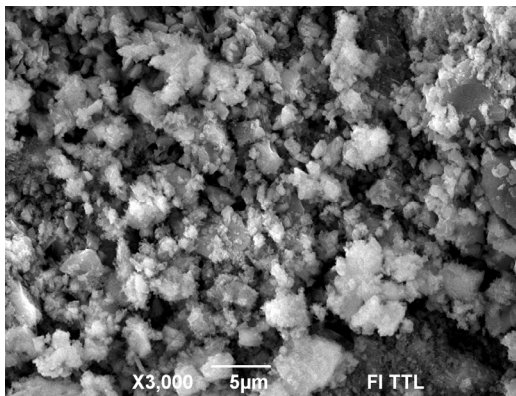
The distinct microstructure of reinforced and unreinforced samples was observed after heat treatment at 800 °C (Fig. 9). The refractory concrete without additions has more homogeneous structure with fine grained particles (less than 1 μm) and small pores in size (Fig. 9, C). Meanwhile, the microstructure of the reinforced concrete shows coalescence of the grains into large conglomerates (~5 μm) and their cohesion with fibre (Fig. 9, c). Due to presence of large pores it is the sharp increase of the relative porosity of reinforced samples at 800 °C (Fig. 2) is obvious. It was pointed out [1, 21, 25] that addition of micro silica determines the formation of the low melting point phases, such as anorthite and gehlenite. Anorthite $CaO·Al_2O_3·2SiO_2$ (CAS_2) was identified at $2Θ = 27.5$ for reinforced samples (Fig. 8, b) after firing at 800 °C, while samples without reinforcement had small peak of gehlenite $2CaO·Al_2O_3·SiO_2$ (C_2AS) at $2Θ = 31.4$ (Fig. 8, a). Sintering process was obvious after heat treatment at 1000 °C (Fig. 8) when formation of CAS_2 and CA_2 or C_2AS and CA_2 on the expense of the CA took place. SEM micrographs of concrete with modifying additives (Fig. 9, d) show presence of some amount of glassy phase which partially fills pores and cavities in the material resulting in decrease of porosity (Fig. 1) accompanied with little shrinkage (Fig. 7).
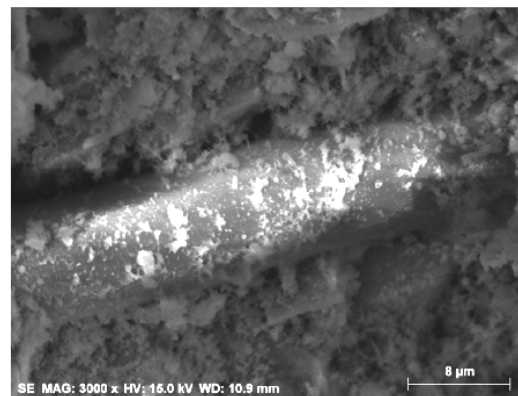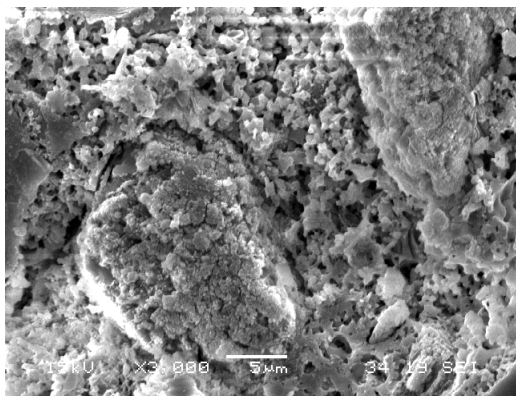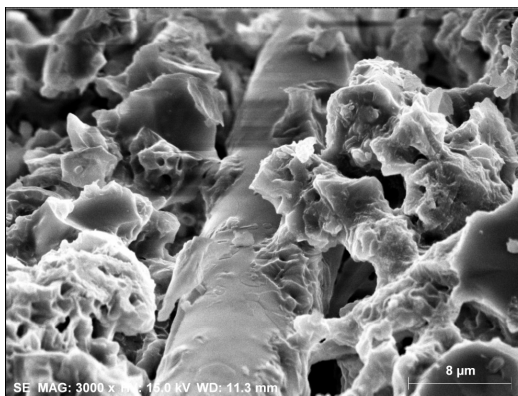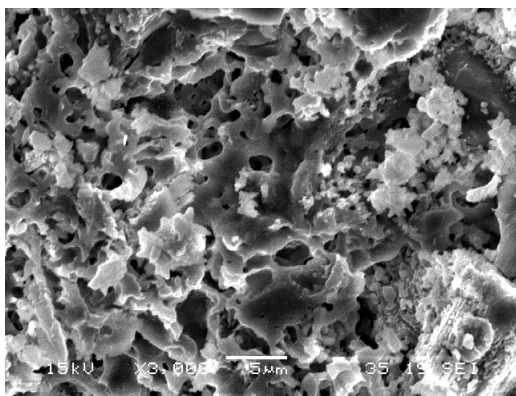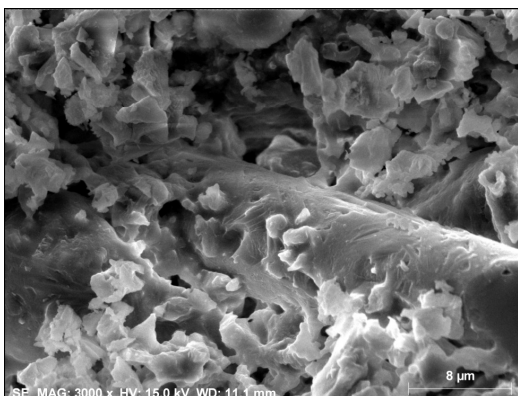
A

a

B

b

C

c

D

d

Fig. 9. Microstructure of the refractory concrete without modifying additives (capital letters) and with additives heat treated at temperature: A, a – 100 °C; B, b – 600 °C; C, c – 800 °C; D, d – 1000 °C

4. CONCLUSIONS

The effect of the modifying additives such as microfiber and micro silica as well as firing temperature on mechanical strength of refractory concrete with complex binder was investigated. The following conclusions may be drawn:

– enhancement of flexural and compressive strength of refractory concrete can be attained with simultaneous modification with microfiber and micro silica in temperature range from 100 °C up to 1000 °C;

– mechanical strength of the refractory concrete with modifying additives increases with increasing heat treatment temperature;

– addition of higher content of microfiber determines the lower compressive and flexural strength results, notwithstanding their increases with the increasing content of micro silica;

– modifying additives reduce dimensional changes of the refractory concrete, but the lower content of micro silica is preferable.

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