Impact of metakaolin additive on residual mechanical properties of cement based composites loaded by high temperature

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Abstract

The aim of this paper is to describe the influence of the composition of refractory composites on their response to gradual thermal loading. Aluminous cement binder system was modified by metakaolin additive which is produced by calcination and grinding of natural clay. Studied aluminous additive is often used for production of high strength composites with increased mechanical and durability properties. The fundamental problem of these composites is their brittle rupture which is why studied composites were reinforced by very short ceramic fibers.

Studied aluminate binder system in combination with natural basalt fine aggregates ensures sufficient resistance to high temperature exposure. The influence of composition changes was evaluated by the results of physical and mechanical testing – compressive and flexural strength and bulk density were determined on the different levels of temperature loading. Application of ceramic fibers brought an expected linear increase of mechanical parameters of studied composites just up to dose of 4% by volume. Metakaolin replacement showed the optimal dose just about 20% of aluminous cement weight.

The extensive application of cement supplementary materials has an important motivation because of high energy consumption of aluminous cement based refractory composites. It was experimentally verified that the appropriate combination of aluminous cement with metakaolin additive and natural crushed basalt aggregates ensure sufficient properties for practical utilization of proposed composites.

Keywords: metakaolin additive, ceramic fiber reinforcement, temperature loading, strength.

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1 Introduction

A common problem of new types of structures made from high performance materials is their behavior in certain specific conditions and situations. A typical example of such specific situation is fire; lack of fire resistance can be expected especially in the case of very subtle concrete structures. This deficiency is necessary to be solved by other additional protection in the form of fire tiling or other kind of arrangement.

Development of new types of refractory composites requires a different approach. High-performance concrete (HPC) and ultra-high-performance concrete (UHPC) are generally based on the increasing of binding matrix quality and density of the material. Even very durable concretes are not able to resist the impact of high temperature during fire or in some industrial and nuclear applications. Concrete – all of its constituents – undergoes a sequences of structural changes by actual thermal load level. Significant phase is the evacuating of physically bonded water up to 200°C. Low permeability of HPC causes internal stresses incurred by accumulated steam. Sudden escaping of steam is often the reason of surface spalling of HPC described in several studies and practical experiences [1, 2]. The behavior of concrete surface layer of high-performance concrete with special consideration to spalling was described in [3].

Authors in [4] tried to replace silica fume by metakaolin in heat-resistance concrete and established that ultimate compressive strength after temperature loading at 800°C and 1200°C is higher by 5% and 10% (compared to silica fume). It has been shown in [5] that appropriate addition of metakaolin improves final resistance against sudden thermal shock. Application of pozzolanic additives to increase fire resistance is a suitable solution because of the reduction of $Ca(OH)_2$ content in hardened concrete. Previous research [6] was focused on the aluminous cement replacement by ceramic powder, positive impact to residual mechanical and fracture properties was confirmed. Replacement of cement brings positive environmental impact.

Asbestos fibers applied in anti-fire tiling had a significant role.The excellent properties of these fibers are unfortunately limited by their undesirable health aspects, which was powered after numbers of performed reconstructions. However, the result of the extensive use of asbestos-containing products was also exposure of numerous workers in diverse occupations to asbestos, and the consequent development of asbestos-related disease after a certain period of latency [7]. The evident relation between asbestos exposure and risk of cancer has been presented in several research works [8, 9].

It is necessary to find new, alternative, reinforcing materials with satisfactory properties [10, 11] and the required resistance to fire or aggressive environments. With regard to economic aspects, applied basalt and ceramic fibers have suitable primary resistance. Ceramic fibers have been chosen for this research work together with the natural crushed basalt aggregates, aluminous cement and metakaolin additive.

2 Experimental methods

All investigated parameters were determined on prismatic specimens 40 x 40 x 160 mm^3 first dried at 105°C and after thermal loading. Flexural strength f_{tm} measurement was organized as a three point test with support distance of 100 mm, [12], and was calculated with help from the maximum reached force. For this testing universal loading machine MTS 100 was used allowing control of the experiment by the deformation speed which was set up to 0.2 mm/min. The compressive strength test f_{cm} was performed on two fragments left after flexural test. The area under compressive load (40 x 40 mm^2) has been demarcated by the loading device.

The action of high temperature and its influence on mechanical properties (flexural strength f_{tm} and compressive strength f_{cm}) was the main goal of this experimental program. Further to the mechanical properties, changes of bulk density were studied since they are related to structural transformation during heating. All these parameters were investigated after loading to two levels of temperature 600°C and 1000°C compared to reference specimens dried at 105°C for 24 hours (to evaporate free water from inner pore structure). Gradual temperature loading was performed in the automatic electric furnace at the 10°C/min heating rate. After reaching the required level (600 or 1000°C) the samples were, after three hours, spontaneously cooled down.

3 Studied materials

The binder and its hydration product significantly control final properties, behavior and thermal resistance of composite [13]. A common problem of aluminous cement lies in the risk of subsequent conversion of hydration products and decrease of composite mechanical parameters when temperature of hardening mixture exceed just about 35°C. It should be noted that structural aluminous cement concretes have been banned because of the risk of conversion and weakening that can take place under certain temperature/humidity conditions [14]. Total amount of Al_2O_3 in aluminous cement determines the temperature resistance of hydrated cement, thus for high-temperature applications up 1000°C aluminous cement with its content higher than 70% has to be used.

Metakaolin is produced by controlled kaolin calcination when the temperature of calcination is dependent on the actual raw material composition but generally it is just about 800°C [15]. The utilisation of calcined clay, in the form of metakaolin (MK), as a pozzolanic material for mortar and concrete has received considerable attention in recent years [16]. The chemical composition and specific surface area ($m^2 \cdot kg^{-1}$) measured by Blaine apparatus of used aluminous cement Secar®71 and metakaolin Mefisto K 05 is shown in Table 1. The positive effect of metakaolin dose in high strength concrete and high performance concrete has been verified in several research works [17, 18] when the long-term characteristics due to the pozzolanic reaction were gradually increased; high specific surface area measured by Blaine apparatus is a prerequisite of its high reactivity.

Table 1: Composition of used aluminous cement and metakaolin.

Chemical properties	Secar ®71	Mefisto K 05
Al_2O_3	70.80%	38.50%
CaO	27.50%	0.20%
SiO_2	0.58%	58.70%
Fe_2O_3	0.42%	0.72%
Na_2O	0.27%	0.05%
MgO	0.21%	0.38%
K_2O	0.06%	0.85%
TiO_2	-	0.50%
Specific surface area	381 $m^2 \cdot kg^{-1}$	306 $m^2 \cdot kg^{-1}$

Ceramic micro fibers were used to strengthen resistance of developed composites to cracking. Choice of reinforcing material is the fundamental problem especially for composites for special application. For the development of new types of refractory composites, very short ceramic fibers (length 0.2 mm, diameter 0.01 mm) were used. Positive impact of ceramic fibers to final mechanical properties was confirmed in work [19]. Chemical composition of used ceramic fibers is shown in Table 2.

Table 2: Chemical composition of used ceramic fibers.

Al_2O_3	CaO	SiO_2	K_2O	TiO_2	Fe_2O_3	SrO	ZrO_2
44.0	0.22	53.7	0.20	0.60	0.66	0.01	0.57

For the development of a new type of refractory material materials with primary resistance to high temperature were used – basalt aggregates of two different grading, aluminous cement and ceramic fibers, except for plasticizer based on the polycarboxylates to ensure suitable rheology of fresh mixture [20]. Influence of application of flammable admixture was studied by Jogl *et al.* [21]. Experimental research did not confirm negative affecting of final properties of aluminous cement based composites by application of mentioned admixture. The composition of all studied mixtures is clearly shown in Table 3.

Table 3: Composition of studied composites.

Ceramic fibers			Basalt aggregates ($kg \cdot m^{-3}$)		Fine components ($kg \cdot m^{-3}$)		Liquids ($kg \cdot m^{-3}$)	
0.0%	0.25%	4.0%	0/4 mm	2/5 mm	Cement	Metakaolin	Water	Sika 1035
0 kg	5 kg	80 kg						
R-0	A-0	B-0	880	220	900	0	224	22.75
R-10	A-10	B-10	880	220	810	90	224	22.75
R-20	A-20	B-20	880	220	720	180	224	22.75

4 Results and discussion

The following text presents results of measuring of compressive strength (f_{cm}), flexural strength (f_{tm}) and bulk density of all mixtures with differing amounts of ceramics fibers (0.25% and 4.0%) and metakaolin replacement. All these values are presented after drying at 105°C (reference set) and after exposure to 600°C and 1000°C. The values presented in Table 4 and Table 5 are the mean of three samples (with the exception of compressive strength f_{cm} which is an average from six performed tests).

Table 4: Results of bulk density.

	ρ (kg·m^{-3})		
	105°C	600°C	1000°C
R-0	2330	2260	2185
R-10	2270	2180	2160
R-20	2370	2260	2220
A-0	2300	2260	2190
A-10	2270	2180	2160
A-20	2360	2250	2220
B-0	2350	2220	2215
B-10	2270	2190	2130
B-20	2290	2150	2130

Table 5: Results of mechanical properties determination.

	f_{tm} (MPa)			f_{cm} (MPa)		
	105°C	600°C	1000°C	105°C	600°C	1000°C
R-0	5.2	2.1	1.5	47.7	31.1	18.8
R-10	4.8	2.2	1.9	41.5	29.5	24.4
R-20	9.1	3.2	2.8	85.1	49.2	29.2
A-0	8.2	4.4	2.0	57.8	55.2	19.9
A-10	7.3	3.0	2.0	61.8	31.4	17.8
A-20	10.1	4.8	2.7	57.0	37.5	27.7
B-0	8.2	3.1	2.0	78.1	57.3	20.9
B-10	8.6	4.4	2.5	59.8	40.9	22.6
B-20	13.2	5.3	3.4	72.2	56.3	32.7

We can observe the gradual decline of bulk density due to the effect of high temperature, when moisture and physically bounded water is evaporated first. Increase of temperature leads to further decrease of bulk density which is caused by partial chemical decomposition of hydration products. Reduction of the residual bulk density by metakaolin replacement can be observed. In the case of mixtures with application of ceramic fibers, values of bulk density after temperature loading are quite similar to reference mixtures just up to 20% of metakaolin replacement. Higher amounts of studied additive dramatically reduces final values of bulk density.

Flexural strength is predominantly affected by fibers dose. Reference set of mixtures (without fibers) exhibits lower values of flexural strength of the rate about 75%. Extensive increasing of fiber dose seems not very effective with respect to reached parameters. Set of mixtures "A" with dose of 0.25% of volume achieved flexural strength of about 90% of mixture set "B" with eightfold dose of ceramic fibers. Metakaolin affected values of flexural strength positively up to the dose of 20% of cement replacement. Following replacement of aluminous cement has an undesirable effect to residual strength. Detailed results are shown in Table 4.

Relative values of studied properties are shown in Figures 1, 2 and 3; as reference (100%) was considered the original value before temperature loading for each mixture.

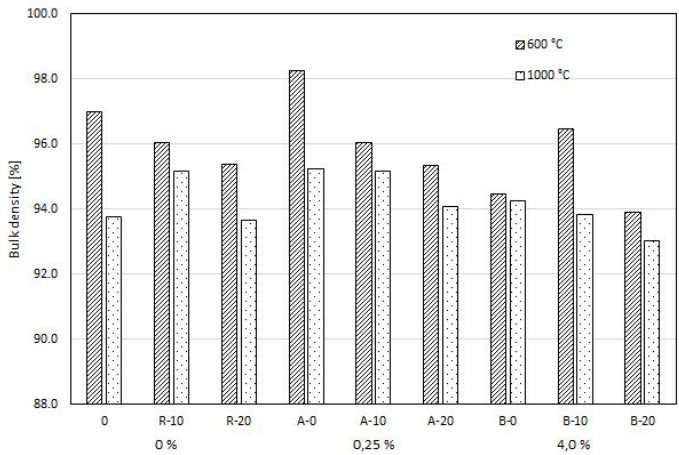

Figure 1: Relative values of residual bulk density.

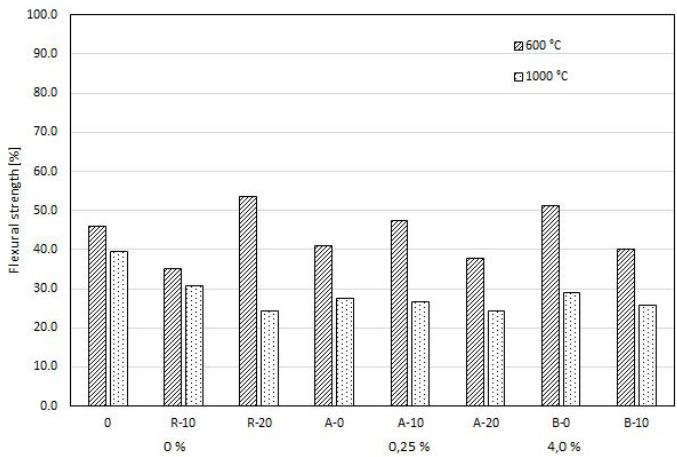

Figure 2: Relative values of residual flexural strength.

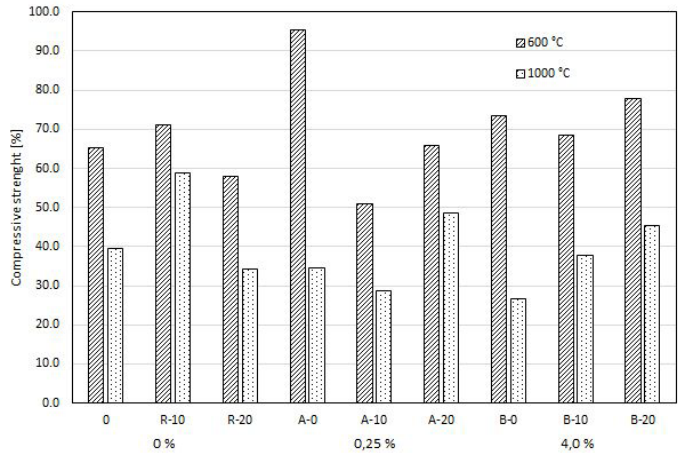

Figure 3: Relative values of residual compressive strength.

5 Conclusions

Refractory fiber-reinforced aluminous cement based composites with various amounts of fibers and metakaolin addition were developed in this study and exposed to action of two levels of high temperature. Basic physical and mechanical properties and their changes after three hours temperature loading were investigated by using conventional mortar specimens of size 40 x 40 x 160 mm^3.

It was experimentally verified that the appropriate combination of aluminous cement with metakaolin additive and natural crushed basalt aggregates ensure sufficient properties for practical utilization. Based on the provided experiments we can conclude that the most suitable is a combination of 180 $kg \cdot m^{-3}$ of metakaolin (20% of aluminous cement weight) and 4% (of volume) of ceramic fibers in terms of compressive strength and residual strength after exposure to 1000°C.

Based on the comparison of final decrease of compressive strength and flexural strength we can see that the reduction of flexural strength is higher. Graphical representation of reached results describe well the stability of developed fiber-reinforced composites. After 600°C the f_{cm} decreases to 77.9% of original value while the f_{tm} decreases to 40.2% of original value. The situation after 1000°C continues in the same trend (45.0% of original values in case of compressive strength and 25.8% for flexural strength.

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