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# Investigation of Microfiber as Component of Cementitious Complex Binder

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The interaction of plasma sprayed zeolite microfiber with cementitious complex binder and with each of its components such as sodium liquid glass, metallurgical slag and calcium aluminate cement was investigated. The influence of aging and thermal treatment at 1000 °C temperature on the morphology of microfiber was analysed. Microscopic, EDS and XRD spectra analysis indicated that during the interaction of the components the surface of fibre encrusts with hydration products forming calcium aluminate, calcium aluminium silicate and sodium calcium aluminium silicates derivatives. According to the results of the experiments no erosion or destruction of the fibre aged in complex cementitious binder and calcinated at 1000 °C temperature was observed.

*Keywords*: zeolite microfibre, calcium aluminate cement, slag, sodium silicate, calcinating.

## 1. INTRODUCTION

The application of refractories is very wide. They are used in many industries as lining or insulating material for fabrication of steel, cement glass, etc. One group of the most important high temperature materials for these uses is cementitious materials. Durability, reliability and workability of those materials have been developed for years with notable improvements of their chemical, thermo-mechanical and functional properties.

Factors that influence strength of cementitious material under high temperatures can be divided into two groups: material properties and environmental factors. Heating rate, duration of exposure to maximum temperature, cooling rate, loading conditions and moisture regimes affect the heat resistance of cementitious materials [1, 2]. Properties of aggregates [3, 4], cement paste [5, 6], binders [7, 8], reinforcement agents [9] and their thermal compatibility between each other greatly influence the mechanical properties of refractories.

The main role of fibre as reinforcement material in cementitious matrix is to control the crack opening and propagation [9]. Thanks to fibres, large single cracks are replaced with dense systems of micro cracks, which may be acceptable from both safety and durability viewpoints. Fine fibres (up to 0.2 μm in diameter and 100 μm in length) control opening and propagation of micro cracks as they are densely dispersed in cement matrix. This allows retaining some significant mechanical resistance of a specimen even after multiple cracking events [10]. On the contrary, poor dispersion or agglomeration of fibres acts as potential failure initiators [9, 10].

Longer fibres up to several millimetres control larger cracks and contribute to increasing the final strength of fibre reinforced cementitious material (FRCM) [9, 11]. Undoubtedly there is an optimum fibre length and volume fraction determining effective bonding between fibre and matrix [11, 12], and it differs from composition to composition. At first, with the increase of fibre volume flexural strength of the material increases progressively and then starts to decrease, usually due to non homogeneous mix. At the same time rigidity of FRCM decreases significantly [10 – 13]. According to [9, 12], fibre volume up to 5 % is considered because higher volumes require special mixing technique to avoid fibre agglomeration and curliness.

With the increase of fibre diameter the crack width reduces after passing the maximum load, and it contributes to decreasing the workability of FRCM [13, 14]. Despite the same aspect ratio (length/diameter), larger fibre diameter can reduce diametrical tensile strength up to two times at the optimum volume fraction of fibre in cementitiuous material.

One of the most impressive strengthening methods for refractory concrete is the use of carbon fibres due to their high mechanical properties and high alkali-resistance. The limiting parameters in cementitious carbon fibre composites are relatively low working temperature (700 °C), weak bond between fibre and matrix [10] and plus it is expensive. Promising way to achieve tough and damage-tolerant cementitious material is to use ceramic fibre, which can withstand high temperatures and chemically aggressive environment [12, 15].

The reinforcement of cementitious material with zeolite microfiber would allow to improve performance parameters of refractory material and herewith to solve utilization problems of oil refinery industry waste.

The object of this paper is to investigate the interaction of plasma sprayed zeolite microfiber with refractory cementitious complex binder and with each component of the binder separately. The influence of aging and thermal treatment on the morphology of microfiber was analysed.

## 2. EXPERIMENTAL

The cementitious complex binder used in this study consists of calcium aluminate cement (CAC) (Gorka Enteprise, Tzrebinia, Poland), metallurgical slag (MS) waste (Cheliabinsk Electrometallurgic Plant, Russia) and 3.3 module ($SiO_2$/ $Na_2O$) sodium liquid glass (LG) with density 1250 kgm$^{-3}$. Chemical composition and properties of CAC and slag are detailed in Table 1.

Waste catalyst of oil refinery and petrochemical industries (zeolite) was used as raw material for microfiber fabrication employing non-equilibrium plasma spraying

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technology at atmospheric pressure. Experimental setup had been depicted in detail elsewhere [16].

Results of our previous work [17] showed that as-produced fibre is amorphous material which crystallization starts at temperatures above 950 ºC. Main crystalline phase after annealing at 1000 ºC is mullite and cristobalite [17].

Fibre was immersed into four sealed test-tube filled with water extraction of each component of complex binder and in complex binder itself (Table 2). All samples were aged for 14 days and then they were calcinated at 1000 ºC for 3 hours.

Scanning electron microscopes (JEOL and ZEISS) equipped with energy dispersive X-ray spectrometer (EDS) were used to observe the morphology and the microstructure of the surface of aged and sintered fibre. X-ray diffraction (XRD) patterns were obtained using Cu-$K_\alpha$ radiation (DRON-UM1) source to identify the existing phases by the commercial search match program.

**Table 1.** Chemical composition and physical properties of cement and slag

| Chemical composition [wt. %] | CAC | MS |
|---|---|---|
| $Al_2O_3$ | 70.5 | 4.33 |
| CaO | 28.70 | 54.30 |
| $SiO_2$ | 0.35 | 29.60 |
| $Fe_2O_3$ | 0.10 | 1.34 |
| $TiO_2$ | 0.05 | – |
| MgO | – | 6.70 |
| $Cr_2O_3$ | – | 1.40 |
| Physical properties | | |
| Surface area, $m^2kg^{-1}$ | 420 | 250 |
| Bulk density, $kgm^{-3}$ | 1100 | 990 |

**Table 2.** The composition of medium for fibre aging

| Sample code | Composition | Additional water |
|---|---|---|
| F1 | Sodium liquid glass, metallurgical slag and calcium aluminate cement | 1 : 1 |
| F2 | Calcium aluminate cement | 1 : 1 |
| F3 | Sodium liquid glass | – |
| F4 | Sodium liquid glass and metallurgical slag | 1 : 6 |

## 3. RESULTS AND DISCUSSION

All samples were examined by SEM after aging for 14 days. It was observed that all fibres more or less were covered with some products of interaction. X-ray analysis of microfiber aged in all solutions showed only amorphous material (not depicted). Comparative EDS spectra of fibre with smooth surface and sediments deposited on fibre was performed. Smooth surface of fibre is marked as zone 1 and surface of fibre with observable sediments is marked as zone 2. The summary of EDS spectra results of all samples is presented in Table 3.

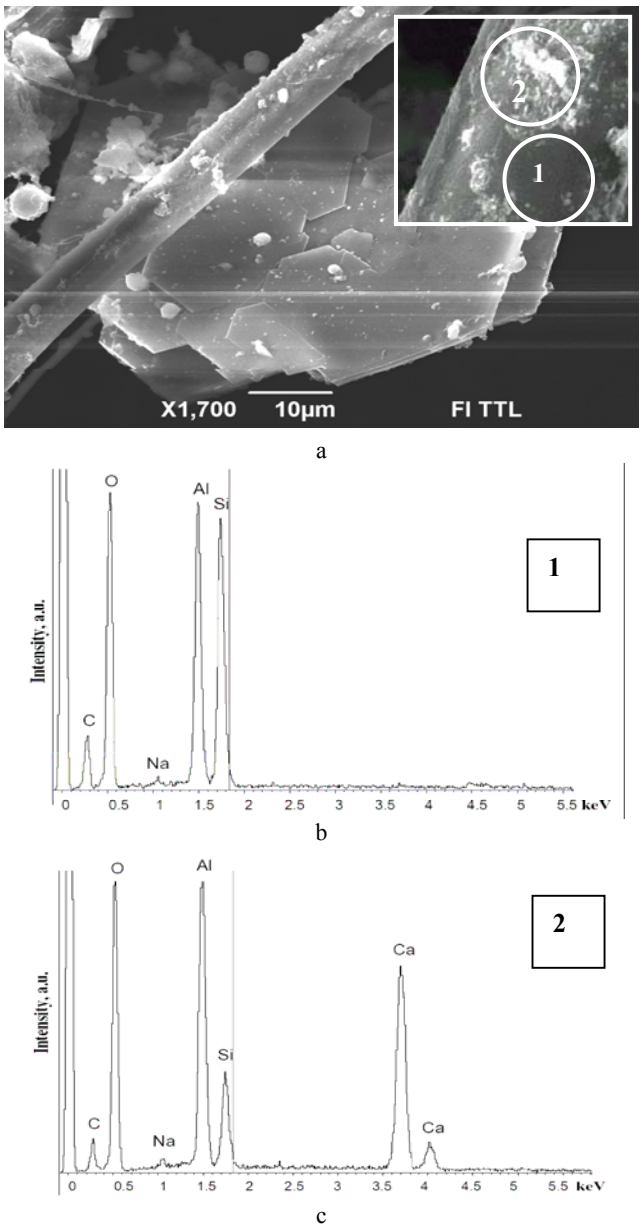



**Fig. 1.** SEM micrograph (a) of microfiber aged in extract of calcium aluminate cement and EDS spectra of material: on the smooth fibre surface in zone 1 (b) and on the surface with sediments in zone 2 (c)

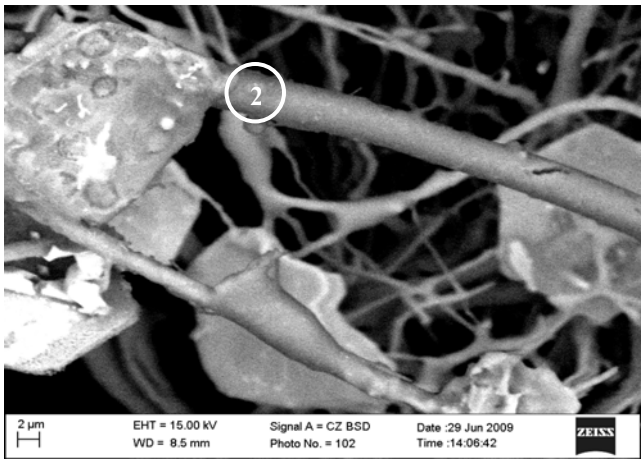
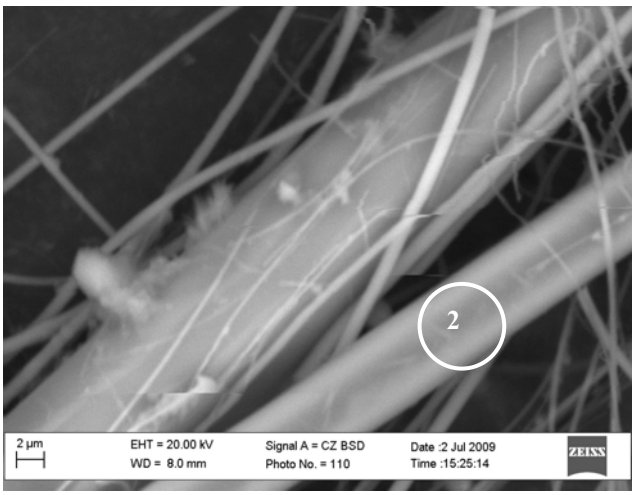
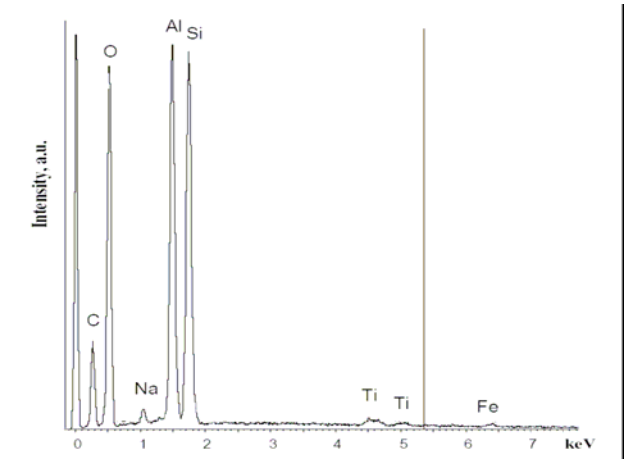


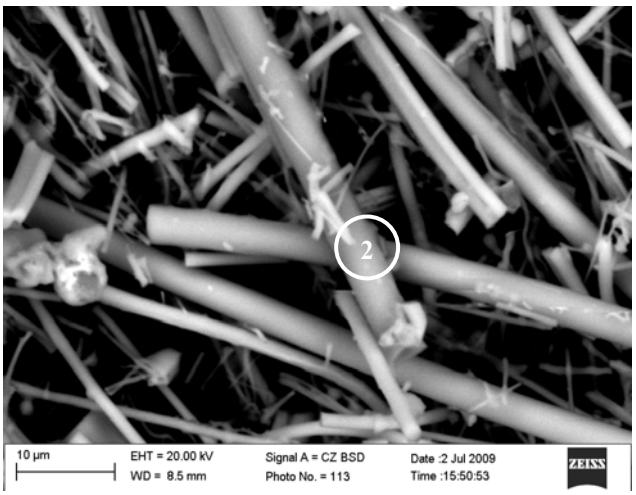

**Fig. 2.** SEM micrograph of microfiber aged in extract of calcium aluminate cement and calcinated at 1000 ºC 3h. 2 – zone of EDS spectra analysis




a




b




c

**Fig. 3.** SEM micrograph (a) and EDS spectra (b) of microfibre aged in sodium liquid glass and SEM micrograph (c) of microfibre annealed at 1000 °C for 3 hours (c). 2 – zone of EDS spectra analysis

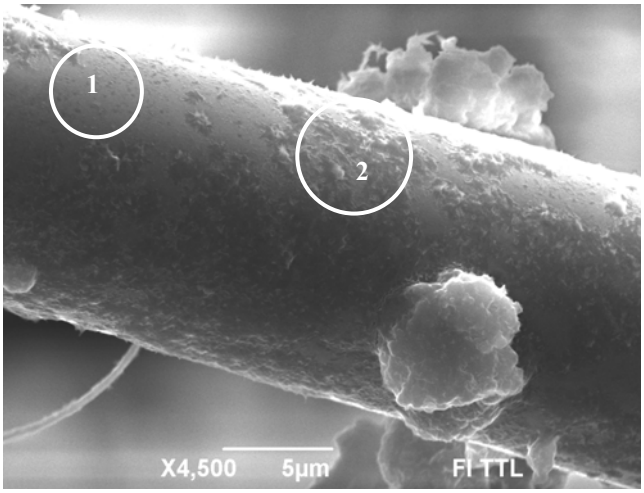
Figure 1 represents microstructure of fibre aged in calcium aluminate cement extraction (sample F2). The peaks of EDS spectrum show that sediments on the surface of the fibre are rich of calcium – 26 wt% (Fig. 1, c). In accordance with the literature [2, 4, 18] due to cement interaction with water $CAH_{10}$ conversion by two possible reactions take place with formation of $C_3AH_6$, $C_2AH_8$, $AH_3$ and H. The crystals of calcium aluminate hydrate of regular shape can be seen as well (Fig. 1). EDS analysis of the surface of the fibre after calcinations at 1000 °C for 3 hours (Fig. 2) is referred in Table 3. According to EDS data there are high amount of calcium (33.92 wt. %), aluminium (18.73 wt. %) and silicon (7.05 wt. %) that indicates crystallization of CA phase in 900 °C – 1000 °C temperature range [6].

Less amount sediments were found on the surface of the fibre aged in the sodium liquid glass medium (Fig. 3) compared to sample F2 (Fig. 1, a). EDS spectra (Fig. 3, b) showed relatively low intensity peak of sodium and high intensity peak of carbon. It seems likely a result of carbonization process of sodium liquid glass.

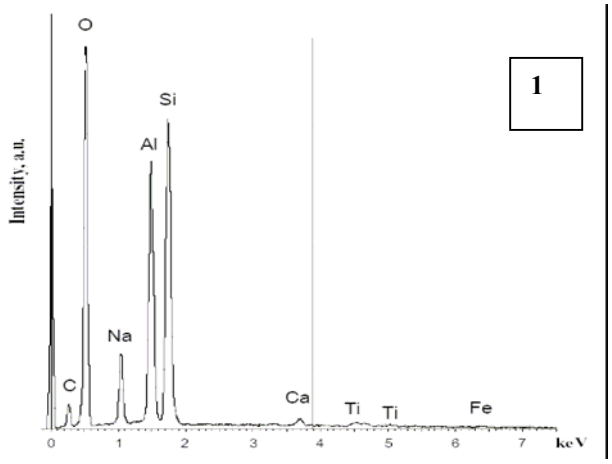
No changes in elemental composition (Table 3) and no erosion of the surface of the fibre were observed after heat treatment at 1000 °C temperature (Fig. 3, c). The ratio of aluminium to silicon of heat treated fibre remains approximately the same as for aged fibre (~0.78) (Table 3).

SEM view of microfiber aged in the extraction of sodium liquid glass with metallurgical slag (sample F4) is shown in the Figure 4. It was observed quite sizeable nodules on the surface of the fibre distinct form the sample F2 or F3 moreover rich in sodium (24.88 wt. %) as well as calcium (7.52 wt. %) (Table 3; Fig. 4, c). According to [18] this indicates formation of various sodium-calcium hydrates as result of reactions of glass with slag. Observation of SEM micrographs showed that all fibres in the sample F4 were more or less covered with products of hydration but no deterioration of the fibre was noticed (Fig. 4). SEM micrograph of the calcinated fibre (Fig. 5, a) shows fairly large agglomerates of additives adhered to the microfiber meanwhile the surface of the fibre is nearly smooth without destruction. Comparing EDS spectra of zone 1 of calcinated and aged fibre (Fig. 4, b, and Fig. 5, b) no differences were observed whereas in zone 2 significant decrease of sodium and increase of calcium was indicated (Fig. 4, c, and Fig. 5, c). According to [18] gehlenite as well as albite could be formed after calcination. But due to high amount of additional water in the sample F4 (Table 2) supposedly only calcium silicates was formed.

Figure 6 represents SEM micrograph of microfiber aged in complex binder (sample F1). SEM observation showed small-scale sediments densely distributed on the surface of the fibre (Fig. 6, a). In the free regions of the fibre (Fig. 6, b) small peak of sodium (2.64 wt. %) was detected whereas sediments (Fig. 6, c) are rich in Na (19.83 wt. %), Ca (6.77 wt. %) and Al (4.25 wt. %) (Table 3). These and XRD results indicate formation of various amorphous sodium-calcium-aluminum silicate hydrates (Fig. 8, a). The shape of sediments changed and the surface of the microfiber remained relatively smooth after heat treatment (Fig. 7, a). EDS spectra of calcinated fibre (Fig. 7, b) showed only Al, Si, Na and O – 20.08 %, 26.27 %, 2.89 %, 49.53 % respectively. Consequently X-ray diffraction analysis of sample F1 was performed. As produced microfiber is amorphous material [17] therefore XRD data of fibre aged in complex binder (Fig. 8, a) shows only few peaks corresponding to calcium aluminium oxide which formation takes place at room temperature [6].




a

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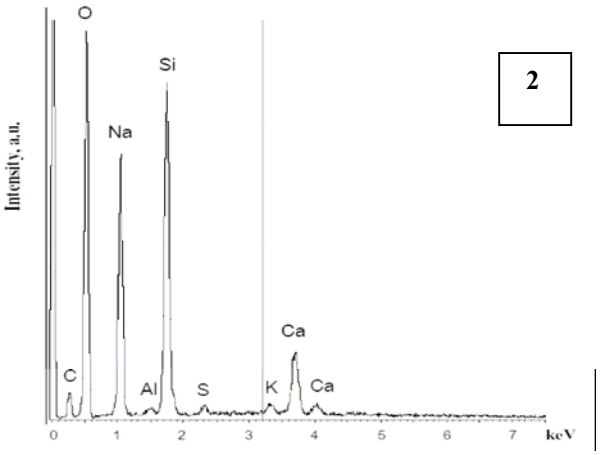
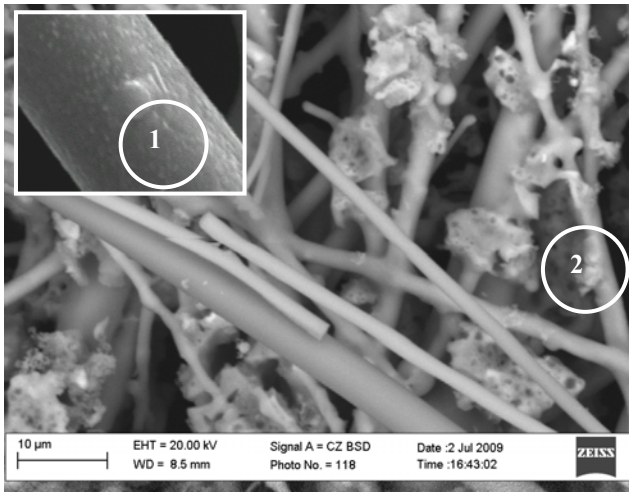



c

**Fig. 4.** SEM micrograph of microfiber aged in metallurgical slag with sodium liquid glass (a) and EDS spectra of material: on the smooth fibre surface in zone 1 (b) and on the surface with sediments in zone 2 (c)

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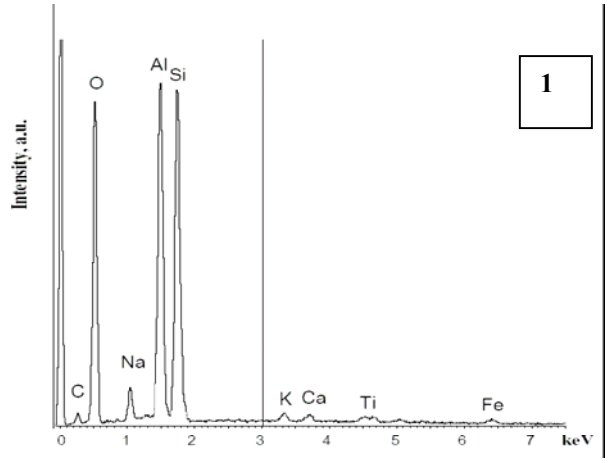


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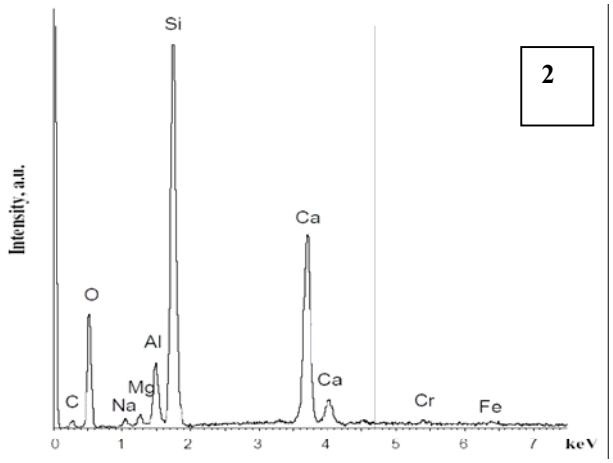
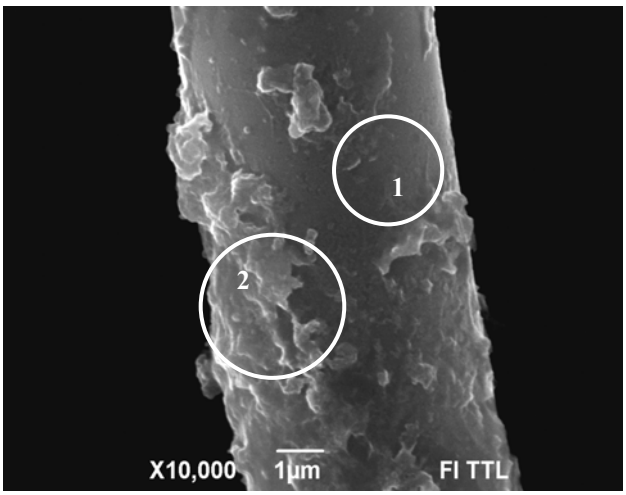



c

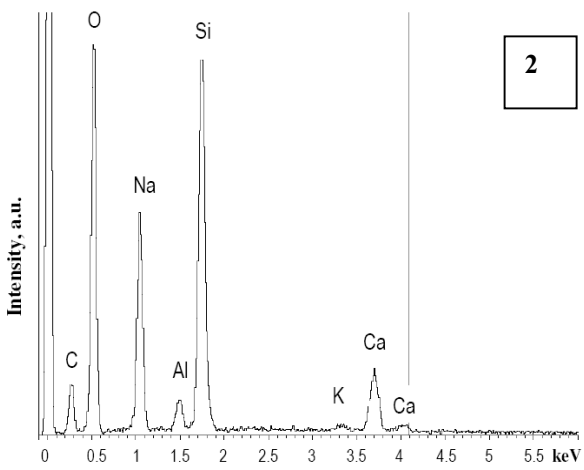
**Fig. 5.** SEM micrograph of fibre aged in metallurgical slag with sodium liquid glass and annealed at 1000 °C at 3 h (a) and EDS spectra of material: on the smooth fibre surface in zone 1 (b) and on the surface with sediments in zone 2 (c)

After annealing at 1000 ºC formation of mullite, calcium and sodium silicates was identified (Fig. 8, b). The ratio of elements (Al/Si) before and after heat treatment remained approximately the same (Table 3).

Structural study of the performance of plasma formed fibre in the investigated environments and after aging at 1000 °C temperature showed that microfiber has not been attacked. No visible destruction, erosion or other degradation of microfiber was observed. Plasma sprayed microfiber remains unchanged after prolonged hydration as well as heat treatment and withstands good stability like glass or carbon fibres in the fibre-reinforced cement composites [10, 13, 14]. Addition of fibre (3 wt. % – 5 wt. %) in a refractory mixture permits to obtain a material with substantially better characteristics [15]. Although a wide variety of fibres has been used in cement-




a

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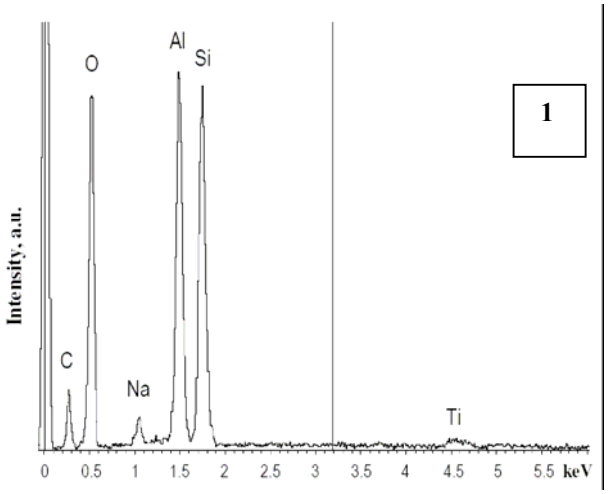
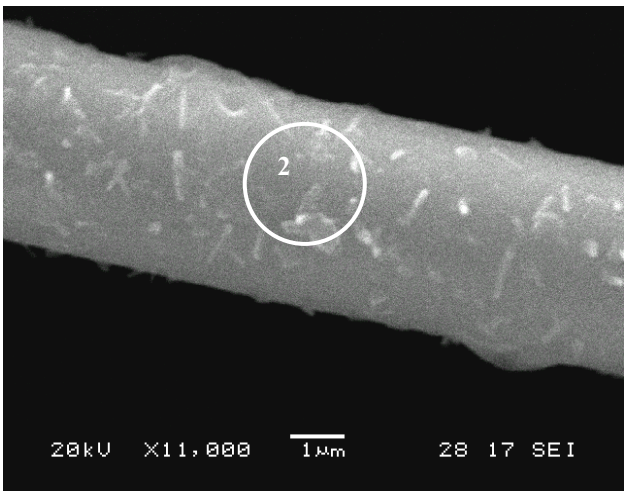


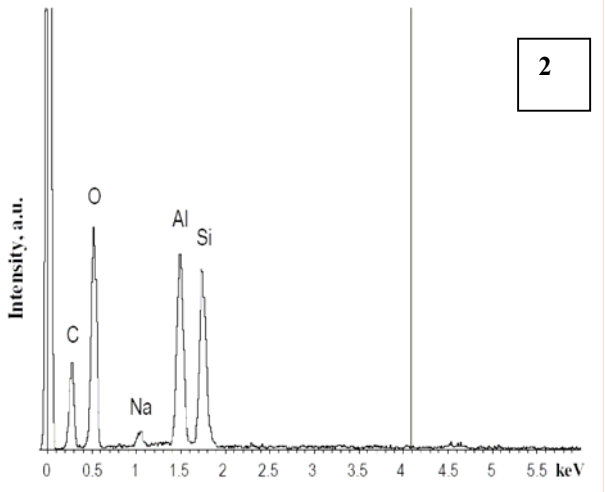

c

**Fig. 6.** SEM micrograph of microfiber aged in cementitious complex binder medium (F1) (a) and EDS spectra of material: on the smooth fibre surface in zone 1 (b) and on the surface with sediments in zone 2 (c)

based materials, plasma sprayed microfiber seems to be potentially suitable strengthening component for high temperature cement applications.




a




b

**Fig. 7.** SEM micrograph of microfiber aged in cementitious complex binder medium (F1) and annealed at 1000 °C at 3 h (a) and EDS spectra of fibre in zone 1 (b)

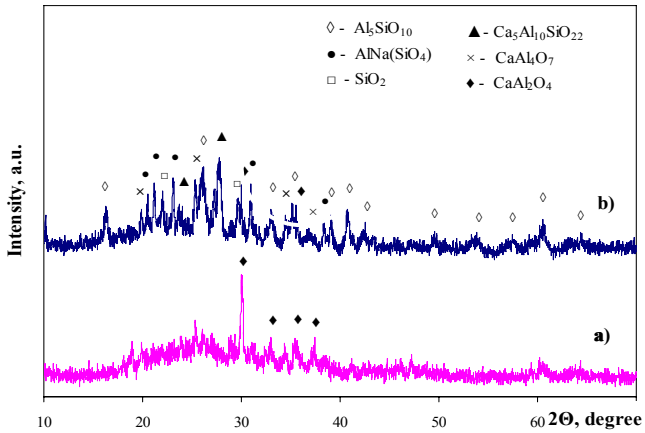



**Fig. 8.** XRD data of microfiber aged in cementitious complex binder medium (a) and annealed at 1000 °C 3 h (b)

## CONCLUSIONS

The interaction of plasma sprayed zeolite microfiber with cementitious complex binder and with each of its

**Table 3.** Summary of EDS spectra elemental analysis of aged and heat treated zeolite fiber

| Sample code | Calcined at 1000 °C 3 h | Elemental analysis, wt % | | | | | | | Zone of analysis in the Figure |
|---|---|---|---|---|---|---|---|---|---|
| | | Na | Al | Si | Ca | Ti | Fe | O | |
| F2 | | 0.72 | 20.81 | 26.78 | 20.28 | 0.45 | 0.57 | 50.18 | Fig. 1, zone 1 |
| F2 | | 1.00 | 22.39 | 8.96 | 26.51 | 0.00 | 0.00 | 41.14 | Fig. 1, zone 2 |
| F2 | + | 0.79 | 18.73 | 24.05 | 33.92 | 0.57 | 0.00 | 38.98 | Fig. 2, zone 2 |
| F3 | | 1.90 | 20.41 | 26.56 | 0.13 | 0.50 | 0.60 | 49.89 | Fig. 3, zone 2 |
| F3 | + | 1.42 | 20.64 | 26.94 | 0.00 | 0.36 | 0.67 | 49.97 | Fig. 3, zone 2 |
| F4 | | 4.21 | 18.66 | 26.73 | 0.54 | 0.68 | 0.00 | 49.18 | Fig. 4, zone 1 |
| F4 | | 24.88 | 1.12 | 24.73 | 7.52 | 0.26 | 0.00 | 41.48 | Fig. 4, zone 2 |
| F4 | + | 3.82 | 19.99 | 25.43 | 1.12 | 0.20 | 0.60 | 48.84 | Fig. 5, zone 1 |
| F4 | + | 0.68 | 3.42 | 32.15 | 16.28 | 0.32 | 0.41 | 46.74 | Fig. 5, zone 2 |
| F1 | | 2.64 | 20.21 | 26.06 | 0.44 | 0.63 | 0.51 | 49.51 | Fig. 6, zone 1 |
| F1 | | 19.83 | 4.25 | 27.83 | 6.77 | 0.00 | 0.00 | 43.31 | Fig. 6, zone 2 |
| F1 | + | 2.89 | 20.08 | 26.27 | 0.39 | 0.28 | 0.57 | 49.53 | Fig. 7, zone 2 |

components such as sodium liquid glass, metallurgical slag, calcium aluminate cement was investigated. SEM-EDS analysis of all samples aged for 14 days showed formation of hydration products on the surface of the fibre except the sample with sodium liquid glass where additives weren't clearly visible. EDS data of the smooth surface of the fibres showed peaks of Al, Si, O and Na, meanwhile additives had more or less intensive peak of Ca. It was not found any destruction, erosion or other degradation of fibre after annealing at 1000 ºC. It can be seen that the ratio of aliuminium to silicium in fibre composition almost kept constant after interaction in the environments investigated and is close to non treated fibre (Al/Si = 0.78). The amorphous interaction products formed on microfiber during aging in complex binder crystallize to mullite, calcium aliuminate, sodium calcium aluminum silicates after heat treatment at 1000 ºC for 3 h.

## *Acknowledgements*

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