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Black coal fly ash as the Si-Al matrix for the heat proof materials preparation

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Abstract

Presented are the results of experiments focused on the study of thermal treatment influence of selected black coal fly ash from the heating plant in Košice. Study was realized with the original not pre-treated fly ash sample and sample with Al additive in different mixing rates. The obtained results confirmed that after the thermal treatment occurred the phase´s change of the material. By the 1 050 °C degree there was the decrease of amorphous phase remarked that was transformed on the mullite and corundum. This information allowed the possibility to use the examined fly ash sample as a matrix for the mullite composites preparation providing the stoichiometric change of thermally treated mixture.

Key words: black coal fly ash, refractory materials, mullite

Introduction

The black coal fly ash is the accessory waste product of the black coal combustion in the power plants and heating plants. All unburnable components contained in burned coal are concentrated in the fly ashes. Some of the accessory minerals occur in the original form without any qualitative changes, e.g. quartz and magnetite. Alumosilicates and the part of quartz is under the heating influence transformed on the new Si, Si-Al crystalline structures, e.g. cristobalite, feldspars, mullite, montmorillonite, etc. (Fečko et al., 2005; Kušnierová et al., 2005).The bulk of the unburnable components (over 80 %) is transformed on the amorphous vitric Si-Al phases in the combustion process.

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is the only one stabile chemical compound in Al_2O_3 – SiO_2 system (Hankýř et al., 2008). Mullite in the nature originated by the contact of lava flows with the rocks of the high Al content (Berry et al., 1987). Mullite is characterized by specific facilities as well as the high heat proof to 1 850 °C, relatively high hardness 7.5° of the Mohs scale and the high resistance to acids (Berry et al., 1987; Kušnierová et al., 1976). Just these properties have determined the areas of the mullite, mullite and corundum substances industrial usage preferably in the heat proof and ceramic materials for metallurgy and glass industry (Treadwell et al., 1996; Valenta, 2007). Technological processes of mullite and mullite substances production are based on natural minerals from the aluminosilicates group. It is concerned on the group of three polymorphous minerals Al_2SiO_5 (andalusite, sillimanite and kyanite) as well as topaz $Al_2SiO_5(FOH)_2$ and in a large extent also the mixture of kaolinite $Al_4Si_4O_{10}(OH)_8$ and SiO_2 (Berry et al., 1987; Bűchner et al., 1991).

Many authors, e.g. Dana et al. (2004), Treadwell et al. (1996), Hankýř et al. (2008), Kušnierová et al. (1976), Karklit et al. (1974) and Gončarov et al. (1961) achieved results that have confirmed that the mullitization pass on the different materials basics containing the basic components Al_2O_3 – SiO_2 in its matrix, providing treatment of its stoichiometric ratio content in the mullite including waste materials as well as the energetic wastes (Dong et al., 2010; Suriyanarayanan et al., 2009; Jung et al., 2001; Kušnierová et al., 2010).

The high content of Si and Al in the fly ashes is a good precondition for its use as a secondary raw material for the heat proof materials and the mullite heat proof materials production. This is resulting from the consideration that the natural sources of mullite of industrial meaning were not discovered until now and it is not probable that will be discovered. The next factor for the fly ashes usage is the resemblance of its genesis in the nature to the processes running by the coal combustion and fly ashes generation. The melted not burned part of the fly ash is in touch with the isothermal components containing Al and mullite is produced in the process consequently what was confirmed by XRD analysis (Fečko et al., 2005).

Fečko et al. (2005) and Michalíková et al. (2005) write that the mullite content in the fly ashes depends on the composition and content of the accessory unburnable parts of coal as well as on the process and temperature

of combustion. The fact is that from the point of Si and Al content are the brown coal fly ashes more perspective. These are nowadays in the high amounts used in the building industry for their qualitative parameters and they are free for the use in this industrial area in the whole produced capacity. On the other hand the black coal fly ashes are for their qualitative parameters hold to be waste in the whole scale in Slovakia and are dumped. That is why there was realized a research of the black coal fly ash from the heating plant Teko Košice for its usage as a matrix for the heat proof Si-Al materials of mullite type preparation.

Experimental procedures

Fly ash sample properties

The experiments were realized with the black coal fly ash sample from the heating plant Teko Košice of properties that are summarized in the Tab. 1. The ratio of the main building components Al : Si in the fly ash matrix is 0.44.

From the XRD analysis of fly ash sample it was find out that the dominant phase in the fly ash is an amorphous vitric phase. Identified were also following minerals: quartz, cristobalite, anhydrite, feldspar, corundum, magnetite, hematite and graphite.

From the morphological point of view there can be in the fly ash differentiated the spherical (Fig. 1A), idiomorphic and allotriomorphic vitric particles as well as the porous particles (Fig. 1B) of unburned coal (Fig. 1C) and particles of originally not transformed minerals. Physical properties of the fly ash as well as the specific surface, softening range, taw fusion point are summarized in Tab. 2.

The fly ash sample can be characterized as a very fine-grained ploy-component dispersion of 0 – 1 mm grain size. We can see from the results showed in the Tab. 3 that the content of particles under 40 μm is of 50 %. That is advantage for composite mixture from the point of its contact surface. Results in Tab. 3 offer also information about the main building elements as well as Al and Si distribution. The content of these elements is different in the different grain sizes and the most profitable it is in the finest grain size under 40 μm.

Tab. 1
Chemical properties of fly ash sample

Annealing lost (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	TiO_2 (%)	MgO (%)	Na_2O_3 (%)	K_2O (%)	P_2O_5 (%)	S_{total} (%)	pH
15.5	47.10	20.86	8.83	23.80	0.76	1.21	0.78	2.14	0.35	0.15	12.4

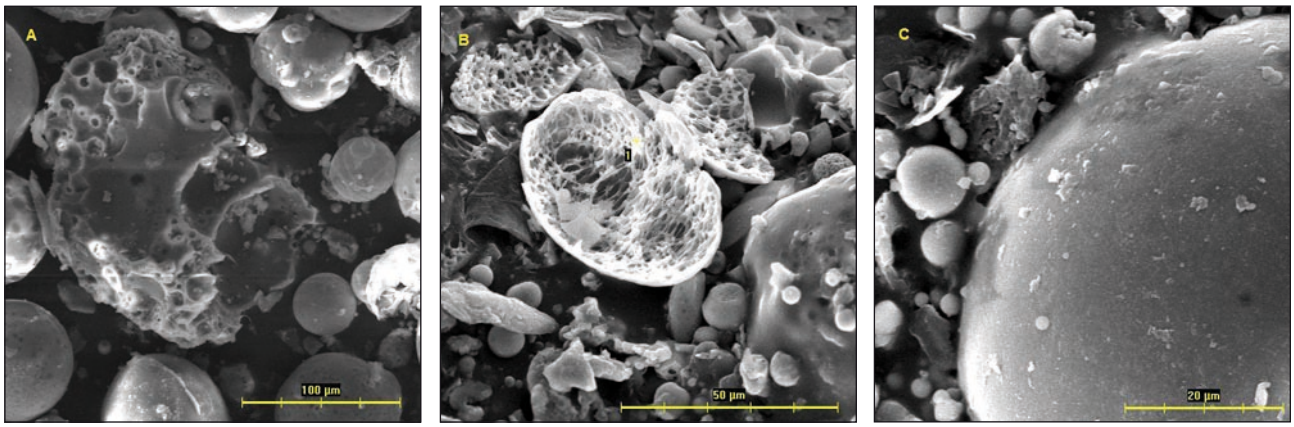

Fig. 1. Morphology of fly ash. A – spherical particles, B – porous particles, C – unburned coal particles.

Tab. 2
Physical properties of fly ash

Specific weight (kg/cm^3)	Softening range (°C)	Taw point (°C)	Fusion point (°C)
2.49	1 140 – 1 240	1 210 – 1 310	1 300 – 1 380

Tab. 3
Fly ash grain class composition and its main elements distribution

Grain class (mm)	Mass yield (%)	SiO_2 (%)	Al_2O_3 (%)
0.1 – 0.5	16.22	41.50	–
0.071 – 0.1	17.52	34.15	11.00
0.04 – 0.071	18.13	45.30	16.20
– 0.04	48.13	52.91	20.90

Composite mixtures

The composite mixtures were prepared using the Al additive ($Al(OH)_3$) form in three mixing rates. Prepared were mixtures with the stoichiometric ratio Al : Si similar to ratio of mullite that is 1.5. Each component was weighted in considered ratio of the fly ash and the additive as is shown in Tab. 4.

Afterwards the homogenization (10 minutes) and mechanical activation (10 minutes) in the planetary mill of prepared composite mixtures have followed.

Tab. 4
Mixing rates of prepared composites samples

Sample	Fly ash and Al additive mixture ratio	Al to Si mixture rate
P	1 : 0	0.44
T1	1 : 1	1.80
T2	2 : 1.5	1.48
T3	2 : 1	1.10
mullite standard	–	1.50

Mullitization

Prepared mixtures were thermally treated in the temperature range of 0 – 1 500 °C. The process of thermal transformation by 0, 850, 1 050 and 1 500 °C was evaluated by the XRD analysis.

There was added to the process of mullitization the inert standard-pure ZnO (ca 5 weight %) with the aim to quantify amorphous components and new-produced phases in the composite mixtures. The samples were homogenized with this standard by the micro-milling and consequently and boxed up to the glass cuvette.

Measurement was provided by the full automatic diffraction meter URD-6 (Rich Seifert-FPM, Germany) under the following conditions: emission of CoKα/Ni rejecter, potential of 40kV, electric current 35 mA, step mode 0.05° 2Θ with the step time of 3 s with the digital processing of measured data. For the measuring and results evaluation there was used the software RayfleX (RayfleX ScanX and RayfleX Analyze, 2.289 version).

Results and discussion

The process of the thermal treatment of the original fly ash without occurring phases changes is documented in the Tab. 5 and Fig. 2.

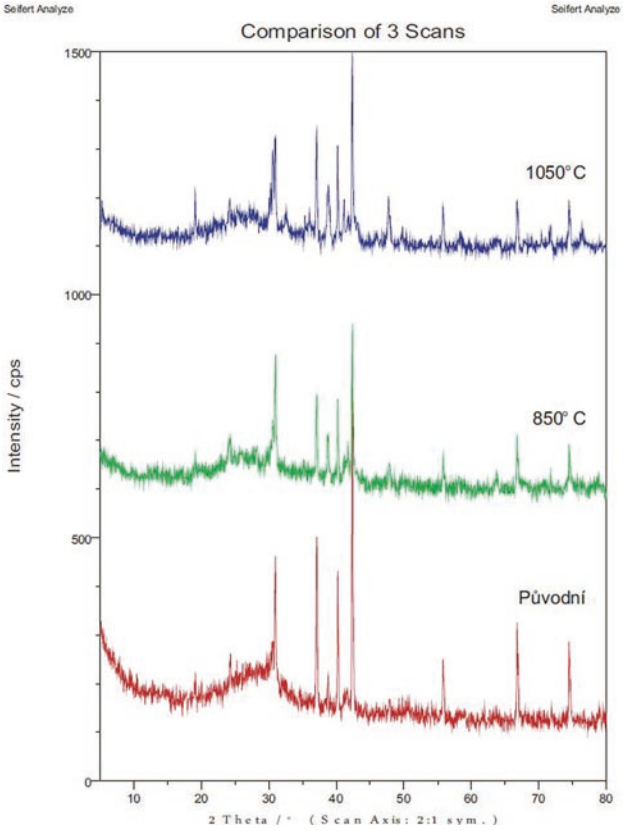

Fig. 2. The comparison of XRD analysis of original fly ash sample (P) and sample thermally treated by 850 and 1 050 °C.

Presented results inform that the increasing of temperature of the thermal transformation of original fly ash caused the decrease of the amorphous phase from 83.05 % to 64.30 %. There was detected also an increase of mullite composition from 10.55 to 22.70 % and by 850 °C the corundum production, that was by

Tab. 5
The thermal treatment of fly ash and its composite mixtures influence on its phases composition

Sample	Burning temperature (°C)	Amorphous phases (%)	Mullite (%)	Corundum (%)	Amount of mullite and corundum (%)
P	0	83.05	10.66	–	10.66
	850	72.30	9.29	2.96	12.25
	1 050	64.30	22.70	–	22.70
	1 500	melting	melting	melting	–

Tab. 6
The influence of thermal treatment on the composition of fly ash composites

Sample	Burning temperature (°C)	Amorphous phases (%)	Mullite (%)	Corundum (%)	Amount of mullite and corundum (%)
T1	0	30.00	5.40	–	5.40
	850	86.58	3.96	1.44	5.40
	1 050	54.00	12.70	23.90	36.60
	1 500	2.10	59.00	38.90	97.90
T2	0	37.40	4.61	–	4.61
	850	88.50	3.84	0.54	4.38
	1 050	63.00	14.30	13.30	27.6
	1 500	21.50	63.80	13.30	77.1
T3	0	50.50	6.79	–	6.79
	850	86.20	4.82	0.85	5.67
	1 050	69.20	14.54	7.45	21.99
	1 500	39.80	56.80	2.35	59.15

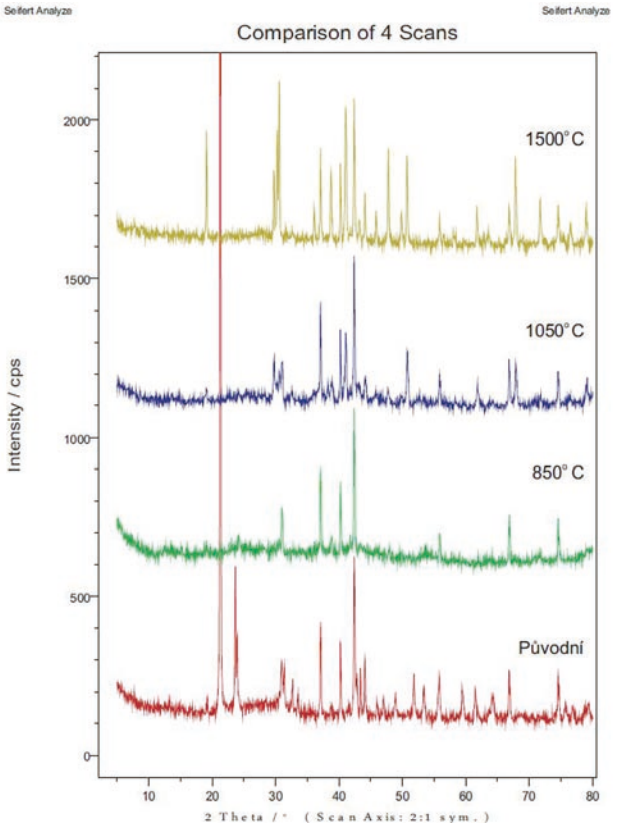

Fig. 3. The comparison of XRD analysis of fly ash mixture sample (T1) of 1 : 1 mixing rate thermally treated at 850, 1 050 and 1 500 °C.

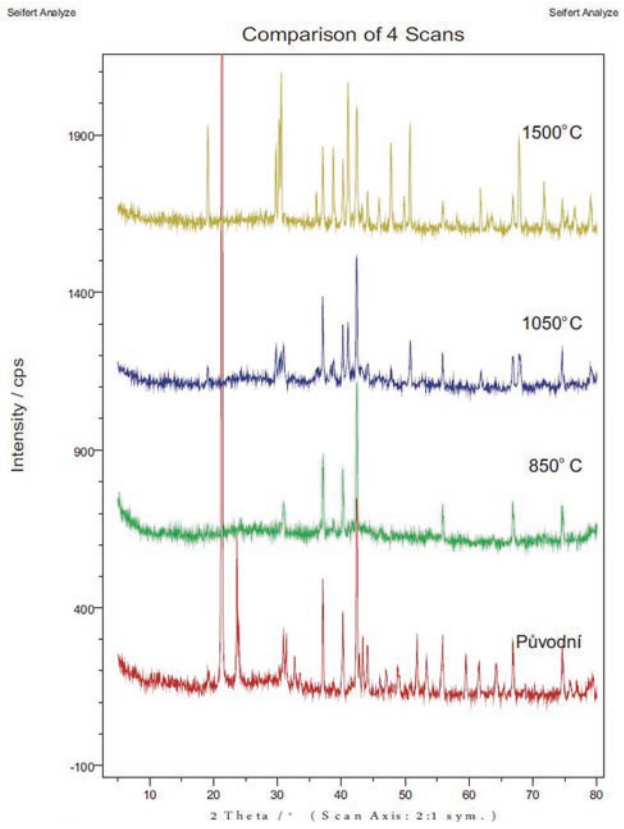

Fig. 4. The comparison of XRD analysis of fly ash mixture sample (T2) of 2 : 1.5 mixing rate thermally treated at 850, 1 050 and 1 500 °C.

1 050 °C transformed on mullite. With the next increase of temperature the pure fly ash sample without any additive was melted that disable analysis. Melting of the sample is related with its thermal properties as well as the taw and fusion points (1 300 – 1 380 °C).

The process of the thermal changes of fly ash and Al additive samples is documented in Tab. 6 and Figs. 3, 4 and 5. In all cases there was registered a high increase of the amorphous phase content by the 850 °C. By this temperature the majority of the sample fractions were

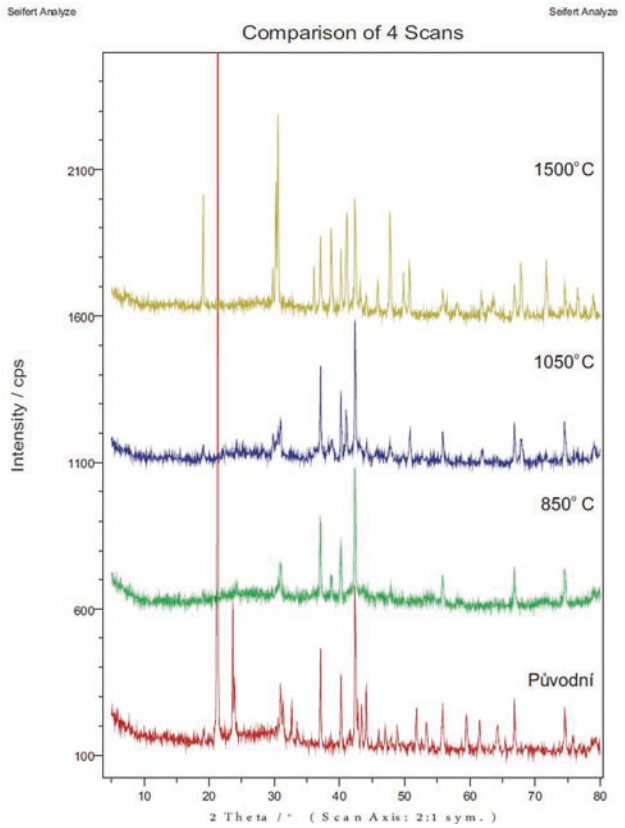

Fig. 5. The comparison of XRD analysis of fly ash mixture sample (T3) of 2 : 1 mixing rate thermally treated at 850, 1 050 and 1 500 °C.

changed and the sample changed to vitric. By the next temperature increasing the sample vas devitrified and the heat proof components as mullite and corundum were crystallized.

The comparison of achieved results of the thermal mullitization from the point of Al : Si ratio in prepared samples showed the important influence of this factor on the process of samples phases transformation. The highest content of mullite (63 %) was reached by the thermal transformation of the sample T2 (mixing rate 1.48) by the temperature 1 500 °C.

The highest content of the heat proof phases together (mullite and corundum) was in the sample T1 (mixing rate 1.8) by the temperature 1 500 °C. In this sample was the content of mullite 59 % and corundum 38.9 %.

In terms of qualitative changes of the composite mixtures and its dependence on temperature is apparent that by the 850 °C were original crystalline phases destroyed and the content of vitric amorphous phase increased. This case is related with the Al additive content, that´s taw point is at 300 °C. Near the temperatures over 1 050 °C was the melt devitrified and mullite and corundum originated. In this range over the 1 050 °C there can be anticipated as optimal conditions focused on the thermal transformation of the thermally treated composite dispersion on the mullite material.

Conclusion

Presented informative results showed that the Si-Al matrix of the black coal fly ashes can be used for the heat proof and abrasive industrially useful materials production by the optimal thermal conditions and mixing rates with the suitable Al additive. The fly ashes mullitization process belongs among the sophistic technologies of the waste black coal fly ashes usage as the secondary raw material. Fly ashes wastes economical appreciation will depend on the further study of this process and optimization of the conditions of thermal transformation. The wide field offers the modelling of the mullite composite mixtures from the fly ashes and additives as well as natural or waste products of high Al content.

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