Mullitization of black coal fly ashes

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In this paper are presented the results of experiments focused on the study of thermal treatment influence of selected black coal fly ashes from the heating plant in Kosice and the power plant in Vojany. The study was realized with original not pretreated samples. The obtained results confirmed that after the thermal treatment of both samples the phase's change of material occurred. At 1050 °C, the decrease of amorphous phase was remarked, being transformed to the mullite and spinel. This information allow of the use examined fly ashes samples as the matrix for the mullite composites preparation providing the stoichiometric change of thermally treated mixture.

***Key words**: black coal fly ash, mullite*

Introduction

Mullite ($3Al_2O_3.2SiO_2$) is the only one stabile chemical compound in Al_2O_3 - SiO_2 system (Hankýř et al., 2008). It was named by its occurrence in the Island of Mull on the west coast of Scotland. Its presence in the nature is very rare what bear ship to its genesis. Mullite in the nature originated by the contact of lava flows with the rocks of high Al content (Berry et al., 1987). Mullite is characterized by specific facilities as well as high heat proof to 1850 °C, relatively high hardness 7.5° of Mohs scale and high resistance to acids (Berry et al., 1987; Kušnierová et al., 1976). Just these properties determinate the areas of mullite or mullite and corundum substances industrial usage first and foremost in the heat proof materials and ceramic materials for metallurgy and glass industry (Treadwell et al., 1996; Valenta, 2007). Seeing that natural sources of mullite of industrial meaning weren't discovered until now and it is not probably that will be discovered, more technological processes of mullite and mullite substances production were developed. Prepared materials 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_4 $Si_4O_{10}(OH)_8$ and SiO_2 (Berry et al., 1987; Bűchner et al., 1991).

Thermal transformation process of natural and synthetic compounds on the mullite is often marked as mullitization. The process and definitive result of mullitization is influenced by several factors. One of the basics is the composition of the mixture and the rate of the basic components Al_2O_3 - SiO_2 as well as the form of the primary bounds. The many published results (Dana et al., 2004; Treadwell et al., 1996; Hankýř et al., 2008; Kušnierová et al., 1976; Karklit et al., 1974; Gončarov et al., 1961) 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 mullite including waste materials as well as energetic wastes (Dong et al., 2010; Suriyanarayanan et al., 2009; Jung, et al., 2001; Kušnierová et al., 2010). For the verification these assumptions, the orienting experiments were focused on the black coal fly ash.

Materials and methods

In the experiments there were used two point samples that have different chemical, physical and phas characteristics. One sample is from the heating plant in Kosice (TEKO) and the other one is from the power plant in Vojany (EVO). The difference between these two samples is that in the sample from EVO was in the transport process to the dump naturally separated the light fraction, the so called microspheres. The chemical composition of the examined samples is in table 1. Information about the main components distribution in the respective grain classes is documented in table 2.

Tab. 1. The contents of main components and amorphous phases in the examined samples.

Sample	SiO_2 [%]	Al_2O_3 [%]	Amorphous phases [%]
TEKO	40.96	17.50	79-83
EVO	64.00	23.70	96-99
Mullite	40.00	60.00	0

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Tab. 2. Distribution of main components in to the grain classes.

Sample	Grain class [mm]	Mass yield [%]	SiO_2 [%]	Al_2O_3 [%]
TEKO	0.1-0.5	16.21	41.50	-
	0.071-0.1	17.51	34.15	11.00
	0.04-0.071	18.12	45.30	16.20
	-0.04	48.12	52.91	20.90
EVO	0.1-0.5	84.27	68.00	24.60
	0.071-0.1	6.22	68.06	26.70
	0.04-0.071	1.87	61.90	24.40
	-0.04	2.64	50.16	20.70

The results of phases composition of examined samples is documented in fig. 1 and 2. From their comparison as well as information about the amorphous phase content follows also the different morphology of both samples, as it is shown in Fig. 3.

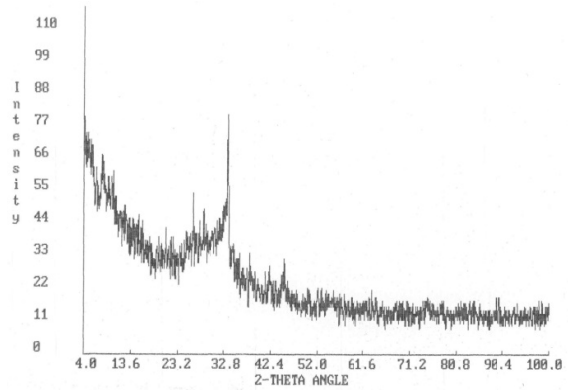

Fig. 1. X-Ray diffraction analysis of the TEKO sample.

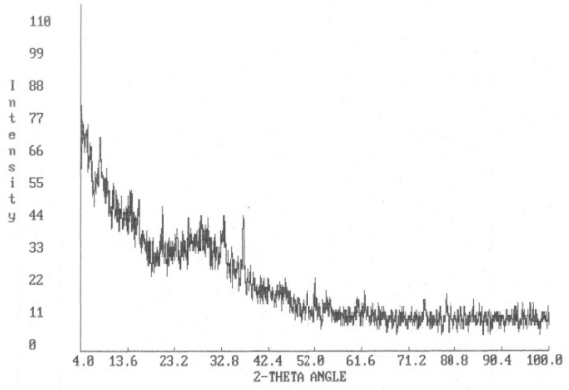

Fig. 2. X-Ray diffraction analysis of the EVO sample.

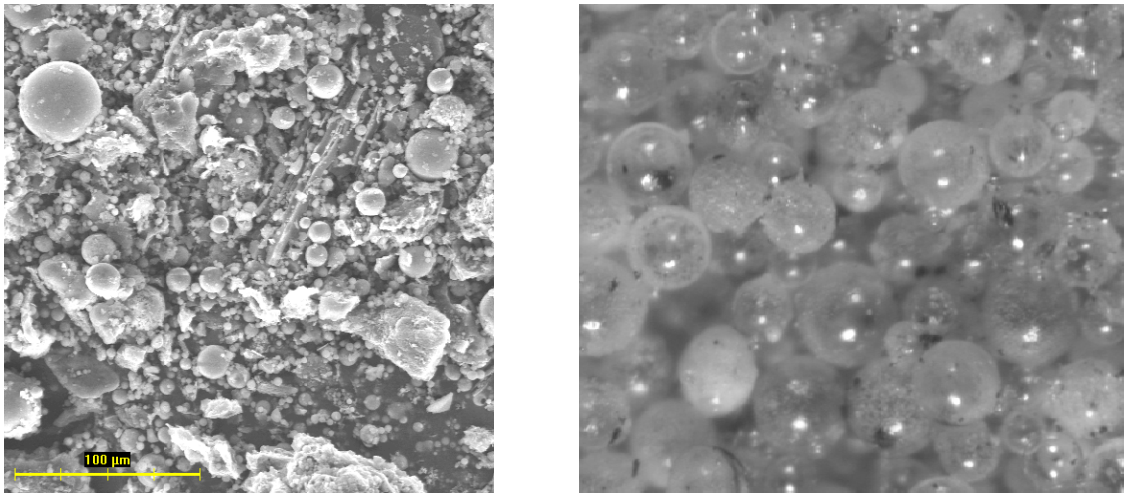

Fig. 3. The morphology of examined fly ash samples, A – TEKO sample, B – EVO sample (magnification 25x).

The mullitization process was realized in the electric furnace in the temperature range 0-1500 °C and the phases changes of the composite mixture were evaluated at 0, 850, 1050 and 1500 °C.

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

Results and discussion

From the comparison of the samples chemical analysis it is apparent that both the fly ash samples have not the optimal stoichiometric ratio of the Al_2O_3:SiO_2 content, as it is written in the literature 3:2 (Tošev, 1972). That's why the aim of the realized experiments was to find out if, under these conditions, will occurs the thermal transformation of part of an Al_2O_3 and SiO_2 on the mullite ($3Al_2O_3.2SiO_2$).

The results of mullitization of fly ash samples are documented by X-Ray diffraction (Fig. 4 and Fig. 5), where are, for comparison, shown the data for different stage of the thermal treatment (0, 850, 1050 and 1500 °C). Semiquantitative content of each phases at the particular temperature are shown in Tables 3 and 4.

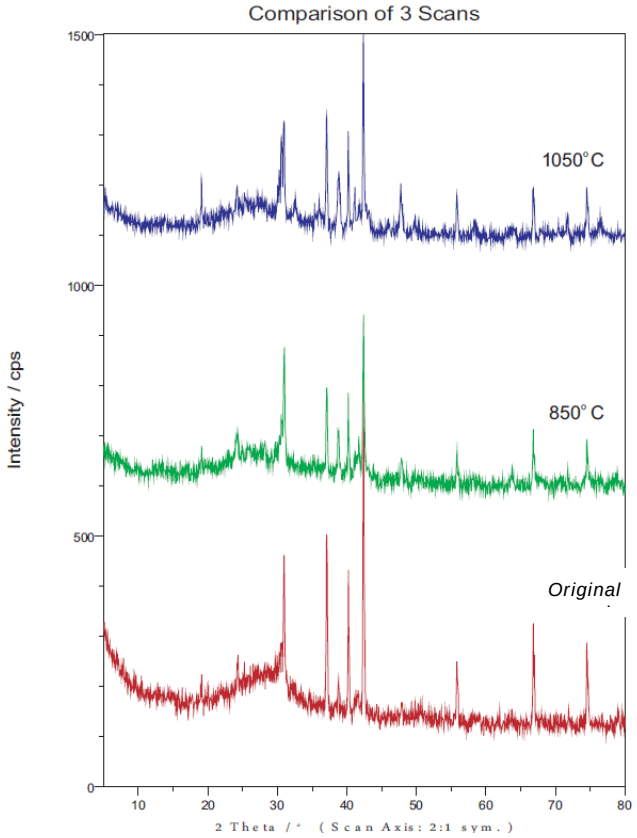

Fig. 4. Results of the X-ray diffractions of the original sample TEKO in particular stages of thermal treatment.

Tab. 3. The temperature influence on the phases change and qualitative content of particular phases of not treated black coal fly ash from the heating plant TEKO Kosice.

Sample	Firing temperature [°C]	Amorphous phases [%]	Mullite [%]	Corundum [%]	Quartz [%]	Hematite [%]	Spinel [%]
TEKO 0	0	83.05	10.66	-	6.29	-	-
TEKO 1	850	72.30	9.29	2.96	8.72	5.81	0.93
TEKO 2	1050	64.30	22.70	-	5.92	4.91	2.20
TEKO 3	1500	melting	melting	melting	melting	melting	melting

The results from the Tab. 3 and 4 shows that the original fly ash from the coal boiling contained 10.66 % of mullite. The fraction of the amorphous phase was temporarity transformed to corundum and quartz at 850 °C. After the thermal treatment at 1050 °C, occurred the 18.5 % decrease of amorphous phases and the 12.04 % increase of mullite phases and the spinel formation was detected. At the next enhancing of transformation temperature on 1500 °C the sample was melted and it wasn't possible to do qualitative and quantitative measurements. Achieved results confirmed that the mullitization process of the sample from heating plant occurred already at 1050 °C and obviously in consequence of the stoichiometric ratios of the main components was the process of mullitization stopped and the whole volume of the sample were melted.

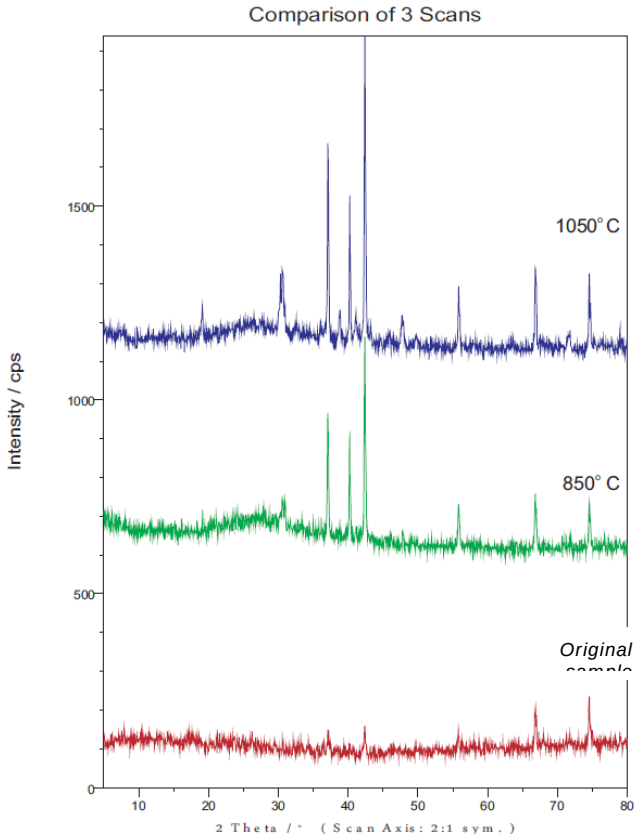

Fig. 5. Results of the X-ray diffractions of the original sample EVO in particular stages of thermal treatment.

Tab. 4. The temperature influence on the phases change and qualitative content of particular phases of microsphere black coal fly ash from the power plant EVO Vojany.

Sample	Firing temperature [°C]	Amorphous phases [%]	Mullite [%]	Corundum [%]	Quartz [%]	Spinel [%]
EVO 0	0	95.00	2.90	-	-	-
EVO 1	850	91.20	5.83	0.60	2.33	-
EVO 2	1050	61.80	33.80	1.44	0.87	2.11
EVO 3	1500	melting	melting	melting	melting	melting

The similar results were achieved also by the sample form the power plant EVO Vojany. The difference was that the mullite content was higher namely 30.9 % that is in a manner corresponding with the 30.9 % of amorphous phases decrees, that was partially transformed on spinel (2.11 %). At the temperature of 1500 °C occurred the similar situation as by the firs sample and the fly ash sample was melted.

Conclusion

The realized experiments confirmed that by the thermal treatment of the exterminated fly ashes samples and its fractions phase changes occurred. The part of amorphous phase transformation on the mullite and spinel passed at the 1050 °C. The amount of the new originated phases obviously connects to the stoichiometric ratio of the main elements in the samples as well as with the Al_2O_3 and SiO_2 contents. The cumulative content of Al_2O_3 and SiO_2 was for sample TEKO of 22.7 % and for sample EVO of 33.8 %. The achieved results show on the possibility of the examined samples of the black coal fly ashes utilization as the basic matrix for the mullite composites preparation providing the change of stoichiometric ratio of the Al_2O_3 a SiO_2 that are the basic elements.

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