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CERAMIC POROUS PREFORMS MANUFACTURED FROM WASTE MATERIALS

The goal of this study is to develop a method of manufacturing porous ceramic skeletons used as semi-finished products for reinforcement of composite materials or as filters. For manufacturing skeletons, only waste materials from coal combustion (fly ashes and bottom slags) as well as rubber granules from used tires and car parts were used. These granules were a pore-forming agent that underwent thermal degradation during sintering process. The influence of sintering temperature, portion, and type of rubber granules on the porosity of developed ceramic skeletons was determined. The study of structure of base materials and the developed ceramic skeletons in a scanning electron microscope as well as their X-ray phase analysis were made. Results will allow to predict phases that can be formed on the metal-reinforcement interface during pressure infiltration.

Keywords: composite materials; ceramic preforms; waste materials; fly ashes

1. Introduction

Every year the portion of coal in production of electricity in the world decreases, but in Poland, it is still the highest in the entire European Union and exceeds 70%. In addition, it should be mentioned that in 2020 the amount of electricity produced from coal in our country was at the same level as in the other 26 EU Member in total. During coal combustion, fly ashes and bottom slags are formed as by-products, which constitute 5-25% of its mass. According Agencja Rynku Energii Spółka Akcyjna (ARE SA), Polish power plants and heat and power plants produced 12.8 million tonnes of fly ashes and slags in 2019, not including by-products of biomass combustion. Currently, combustion by-products are used in cement production, soil stabilization, road reconstruction and filling mining excavation. Although there are many methods of ash management, the supply is still much greater than the demand, and about 40% of them are stored in heaps from where their smallest fractions are blown out, contributing to the formation of smog. In view of the above, it is justified to look for new ways of managing and using coal combustion by-products [1-2].

The portion of fly ashes in the mass of coal combustion by-products is about 75-85% because this is the percentage of unburned parts of fuel that leaves the combustion chamber together with waste gases. Fly ashes can be classified due to many criteria, which include type of furnace; chemical composition and type of fuel used – hard coal, lignite, biomass; type of flue gas desulphurization installation; unburned carbon content; or resulting from the previous ones – the chemical composition of the ash itself. The most common division of fly ashes in the literature is based on the American standard ASTM C 618, where two classes of ashes are introduced – "F" and "C" (F – from the combustion of hard coal – mainly silica ash, C – from coal brown, rich in calcium oxide) [3-6].

Fly ashes and bottom slags should be classified as ceramic materials, because apart from a small percentage of organic components in the form of unburned carbon, which for economic reasons may not exceed 10%, they contain oxides typical for ceramics, such as SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO, SO_3, Na_2O, K_2O. The chemical composition of ash mainly specifies chemical composition of fuel, but it is also influenced by such factors as temperature and burning time, boiler type or particle size distribution of combusted material. Phases occurring in ashes can be divided into primary – minerals occurring in coal that have not been transformed during its combustion, and secondary – formed during the combustion process. Although ashes derived from coal from the same source, produced in the same furnace, generally have comparable chemical composition, they are very heterogeneous on a microscopic scale, which is evidenced by the fact that, with the multitude of phases occurring in them, often single grains are composed of one or only a few [6-12].

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For years, many research centres in the world carried out investigations on developing advanced technology of modern engineering materials using waste or by-products of different processes. These works are often aimed to replace substrates used so far with waste or recycled materials. As the results of research shows, these materials are very often characterized by similar or even better properties than their prototypes made from primary raw materials. However, the main problem is the lack of repeatability of waste deliveries in terms of chemical composition and basic properties [13-22].

The aim of this study is to develop and optimize the technology of manufacturing porous ceramic skeletons based on coal combustion by-products – fly ashes and bottom slags as well as rubber granules from used tires and car parts.

2. Material and experimental procedure

Porous ceramic skeletons were manufactured by sintering fly ashes and/or bottom slags with a pore-forming additive in the form of recycled rubber granules. EPDM and SBR rubber granules were supplied by Unirubber Sp. z o.o. with headquarters in Zielonka, (Dolnośląskie Voivodeship). The manufacturer's specification shows that the EPDM type comes from rubber waste with the highest quality parameters (e.g., car gaskets, flanges from automatic washing machines), while the SBR type comes from post-production waste from the automotive industry and rubber screeds. The particle size of both granules was in the range 0.1-1 mm. Fly ashes and bottom slags come from TAURON Wytwarzanie S.A., Branch Łaziska Power Plant in Łaziska Górne. Bottom slags are characterized by high humidity; therefore, they were dried at 40°C for 24 hours. TABLE 1 shows the composition of powder mixtures used for production of porous sintered skeletons and their marks.

TABLE 1

Composition and marks of powder mixtures

Mark	Component mass fraction, wt.%			
	Fly ash	Bottom slag	EPDM	SBR
F40E	60	—	40	—
F40S	60	—	—	40
S40E	—	60	40	—
S40S	—	60	—	40
FS40E	30	30	40	—
FS40S	30	30	—	40
F50E	50	—	50	—
F50S	50	—	—	50
S50E	—	50	50	—
S50S	—	50	—	50
FS50E	25	25	50	—
FS50S	25	25	—	50

The base assumption in developing compositions of powder mixtures was to create skeletons based on fly ashes, bottom slags, and their combinations. Moreover, the use of different types and proportions of rubber granules will enable to estimate their influence on porosity of fabricated sinters.

Prepared powder mixtures were wet milled for 10 h in a Fritsh Pulverisette 4 planetary ball mill using ZrO_2 vessels and grinders. The ratio of 20 mm spherical grinders to ground material was 7:1. There was no need to grind the rubber granulate at a reduced temperature (in a cryogenic mill) because sharp and hard particles of ashes and slags act as an abrasive cutting rubber granulate. The suspension prepared in this way was frozen and freeze-dried under reduced pressure for 48 hours (freeze-dried) and then sieved through a sieve number 250. Powder mixtures were uniaxially pressed in a matrix with the diameter of 30 mm in a hydraulic manual press. The pressing pressure was 100 MPa.

The compacts were sintered freely in a chamber furnace in an air atmosphere with a flow of 1 l/min. Two sintering temperatures, 850 and 900°C were used to determine its influence on the structure of fabricated skeletons. Temperature course of sintering process shown in Fig. 1 consists of slow heating 50°C/h to temperature 800°C (temperature of complete thermal degradation of organic additives – rubber granules and carbon residues), withstanding for 2 hours, rapid heating at 300°C/h to 850°C or 900°C, sintering for 2 hours and cooling with the furnace.

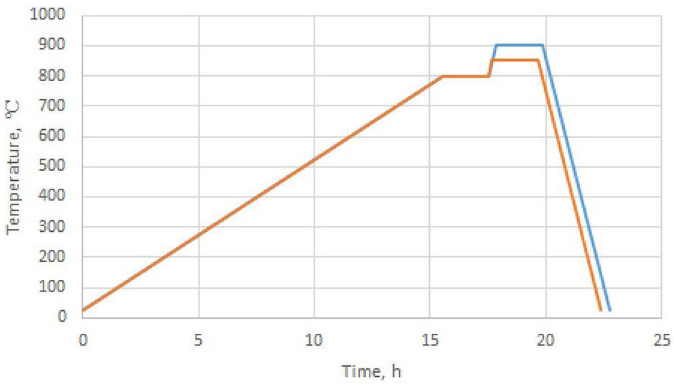

Fig. 1. Temperature course of sintering process

To determine the portion of coal in fly ashes, bottom slags, and organic compounds in rubber granules, they were heated in a furnace to temperature 800°C and heated for 1 hour. Then weight loss of materials was estimated. Porosity of skeletons was determined on the base of measuring their dimensions, mass, and density of solid material from which they were made. To assess it, heat treatment was made in accordance with the temperature sintering process (Fig. 1) of loose powder mixtures and then their density was determined using an automatic gas pycnometer Micrometritics AccuPyc II 1340. Observations of ashes, slags and fractures of porous skeletons manufactured on their base were made in scanning electron microscope (SEM) of the Zeiss Supra 35, and their chemical composition was also examined using the EDS scattered X-ray analysis. The phase composition tests were carried out in X'Pert PRO MPD X-ray diffractometer by Panalytical, equipped with an X-ray tube with a cobalt anode ($\lambda K\alpha = 0.179$ nm) and a PIXcel 3D detector. Diffractograms were recorded in Bragg-Brentano geometry in a range of angles 5-100°

2Theta with a step of 0.026° and a count time per step of 80 s. X-ray qualitative phase analysis was made using HighScore Plus software (v. 3.0e) and a dedicated database of inorganic crystal structures PAN-ICSD.

3. Experimental results and their discussion

Based on the weight loss caused by thermal degradation of carbon remaining in ashes and slags, its portion was determined 4.1 and 15.9 wt.%, respectively. Moreover, the same method was used to estimate the portion of ashes in rubber granules, which is 30.8 wt.% for EPDM and 38 wt.% for SBR. This information was helpful in predicting the influence of rubber granules portion on the porosity of developed skeletons, as carbon remaining in by-products of combustion additionally acts as a pore-forming agent, while the ash from rubber degradation will be a part of the skeleton's building material.

TABLE 2 summarizes the porosity of developed ceramic skeletons and the density of materials they are made of (fly ashes and/or bottom slags and ashes from thermal degradation of rubber granules). The highest porosity, exceeding 50%, is characteristic for skeletons made of bottom slags with 50% EPDM granulate, while the lowest – semi-finished products made of fly ashes with 40% addition of SBR granules. The porosity of skeletons based on bottom slags is higher than when fly ashes were used for their production. It was also observed that EPDM granules are a better pore-forming agent, probably due to lower ashes content, while the sintering temperature in range 850-900°C has a slight effect on porosity.

TABLE 2

Comparison of ceramic skeletons porosity and density of materials they are composed

Mark	Density, g/cm^3	Porosity, %	
		Sintering 850°C	Sintering 900°C
F40E	2.29	18.89	17.06
F40S	2.26	15.89	13.61
S40E	2.40	41.76	41.45
S40S	2.35	37.14	36.70
FS40E	2.35	33.05	31.60
FS40S	2.30	28.46	25.29
F50E	2.35	35.84	35.12
F50S	2.29	32.24	31.47
S50E	2.45	51.94	51.27
S50S	2.38	46.53	46.70
FS50E	2.40	43.01	42.11
FS50S	2.34	39.98	36.95

Observations of coal combustion by-products in the SEM scanning electron microscope show that among fly ash grains, spherical forms with a smooth glassy surface dominate, and their diameter is most often in range of 0.5-10 μm (Fig. 2a). Bottom slags, on the other hand, have a much more diverse morphology. They contain both spherical and very irregular grains, with a rough surface, which are most likely residues of mineral parts present in coal, which did not melt during its combustion. The slag particles are larger than fly ash one and are in a range from several dozen to over 200 μm (Fig. 2b).

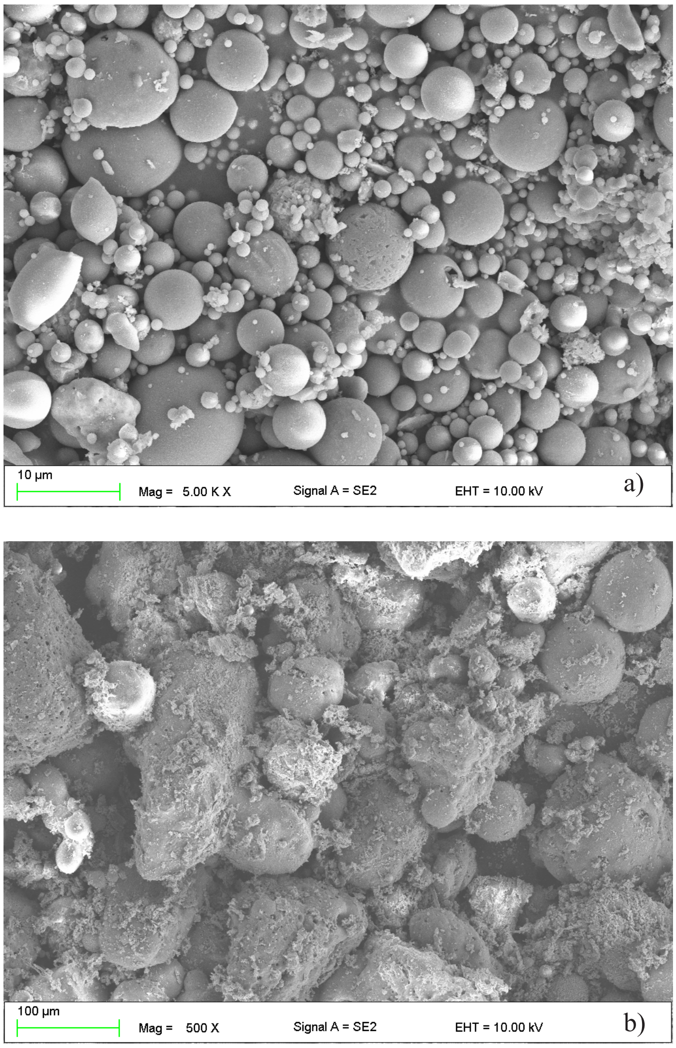

Fig. 2. Structure of coal combustion by-products: a) fly ashes, b) bottom slags

Figure 3 shows structure of fracture new developed porous ceramic skeletons sintered at 850°C. They consist of sintered groups of particles of irregular shape, without a clear boundary of their separation. Around the ceramic phase, there are channels and interconnected pores formed due to thermal degradation of EPDM and SBR rubber granules. Sintered bottom slags include much larger groups of particles than fly ashes, and thus the pores and channels around them also have larger sizes. Their diameter often exceeds 1 μm, which is not observed in the case of fly ash skeletons. Larger pore sizes of slag skeletons affect their porosity more than twice in comparison with skeletons of the "F" series (TABLE 2). Preforms made on the base of mixtures of ashes, slags and rubber granules are characterized by intermediate values of size and portion pores in the volume. Due to above, it is possible to model size and proportion of pores, not only by changing size and ratio of pore-forming additives, but also a type

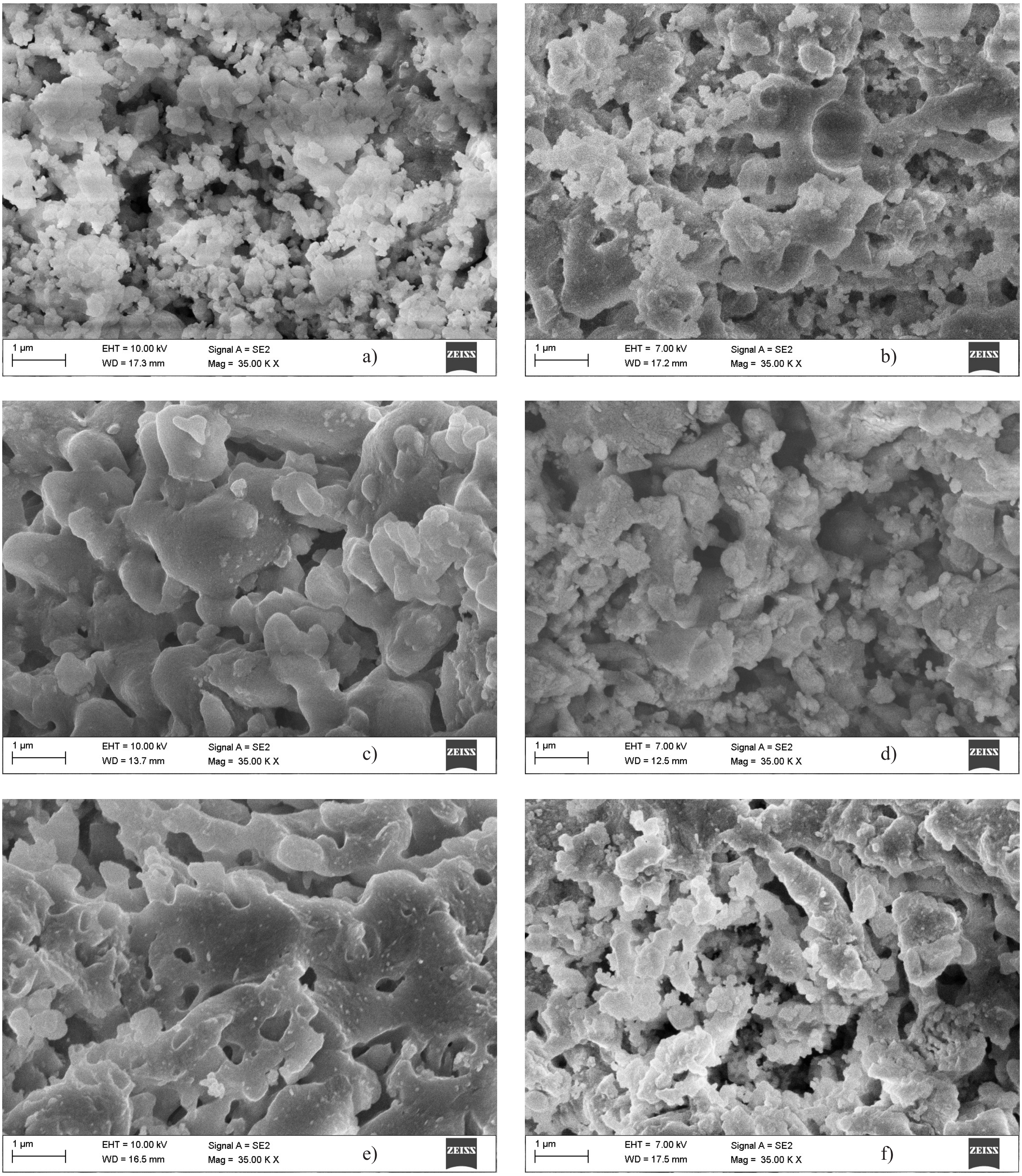

Fig. 3. Structure of fractures of porous ceramic preforms a) F40E, b) F40S, c) S40E, d) S40S, e) FS40E, f) FS40S

of waste materials that constitute them. Low porosity and small size of voids around sintered fly ash particles may exclude the sinters obtained from them from being used as reinforcement for composite materials manufactured by low-pressure infiltration method, as it will prevent their penetration with liquid metal. However, these materials can be used as liquid and gas filters.

The chemical composition of manufactured skeletons was investigated in X-ray quantitative microanalysis made with the use of an EDS X-ray scattered radiation spectrometer. Results of these microanalysis presented in Fig. 4 and TABLE 3. were limited to sinters manufactured with the pore-forming additive in the form of EPDM rubber granules because its type does not significantly affect the difference in the chemical composition of final sinter. Zirconium identified in skeletons does not come from fly ashes or bottom slags. Its presence is a result of grinders and vessels made of zirconium oxide that wear out during grinding. The knowledge of the chemical composition of fabricated skeletons will facilitate the interpretation of X-ray diffraction patterns.

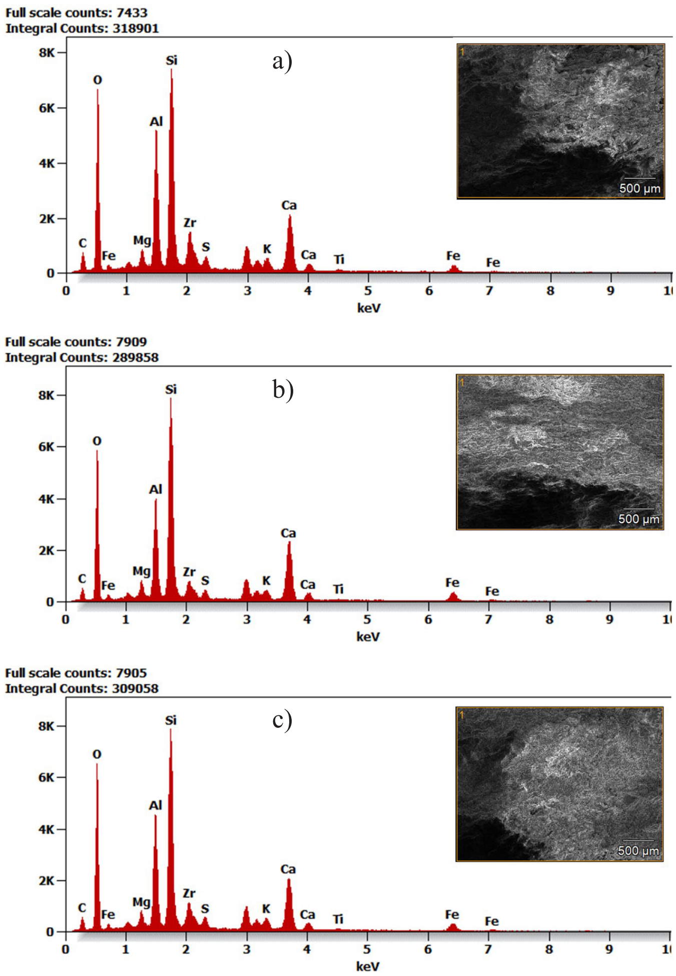

Fig. 4. Diagram of intensity as a function of energy of scattered X-ray radiation in a material sample: a) F40E, b) S40E, c) FS40E

TABLE 3

Chemical composition of obtained ceramic skeletons

Sample	F40E		S40E		FS40E	
Element	Weight, %	Atom, %	Weight, %	Atom, %	Weight, %	Atom, %
C	6.0	10.6	4.7	8.4	4.9	8.7
O	44.8	59.5	44.8	59.8	45.5	60.5
Mg	1.2	1.1	1.4	1.2	1.3	1.1
Al	9.8	7.7	8.5	6.7	9.2	7.2
Si	16.0	12.1	18.5	14.1	17.4	13.2
S	1.1	0.7	1.0	0.6	1.2	0.8
K	1.3	0.7	1.2	0.7	1.3	0.7
Ca	8.2	4.3	10.3	5.5	8.7	4.6
Ti	0.6	0.2	0.6	0.2	0.5	0.2
Fe	2.6	1.0	4.3	1.6	3.5	1.3
Zr	8.3	1.9	4.8	1.1	6.5	1.5

Fig. 5. shows X-ray diffraction patterns of fabricated ceramic skeletons based on fly ashes and/or bottom slags sintered at 850 °C. Also, in this case, presented results were limited to sinters manufactured with the pore-forming additive in the form of EPDM rubber granules because its type did not affect phase composition. X-ray qualitative phase analysis methods revealed the presence of low-temperature β-quartz, cristobalite, mullite and hematite in all cases. Results obtained as part of the research are convergent with literature reports [7-10]. Zirconium phases identified in diffraction patterns do not come from batch materials used for production of porous skeletons. Their presence is a result of grinders and vessels made of zirconium oxide that wear out during grinding. Knowledge of the phase composition of developed ceramic skeletons will allow for a better understanding of the changes that will take place on metal-reinforcement interface during their pressure infiltration with aluminium alloy.

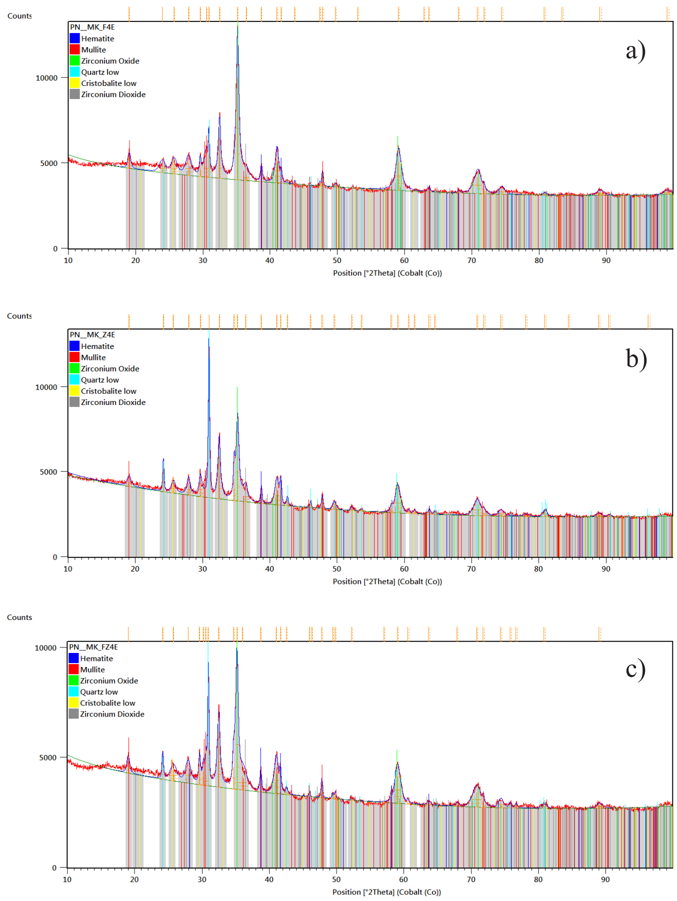

Fig. 5. XRD patterns of obtained ceramic preforms a) F40E, b) S40E, c) FS40E

4. Conclusion

The developed technology of manufacturing ceramic skeletons, consisting of pressing and sintering by-products of coal combustion with a pore-forming agent in the form of recycled rubber granules, makes it possible to achieve their porosity exceeding 50%. Values at this level are only achievable when for the skeletons production bottom slag are used. The use of fly ashes, due to their finer-grained structure and lower portion of unburned carbon (4.1% against 15.9% for slags), reduces size and number of pores and channels present in sinter, which may exclude them from applications as reinforcement of composite materials fabricated by pressure infiltration methods. Study of chemical and phase composition of skeletons was not aimed at determining changes taking place during their production, as it has already been the subject of many scientific works. Research results are to help in description of microstructure of interfacial boundaries of fly ashes and/or bottom slags – aluminium alloy in composite materials produced by infiltration of developed porous sinters, which is the subject of currently conducted scientific research.

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