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Effect of Zeolite Addition on the Production of a Cast Porous Composite Based on AC-AlSi11 Silumin

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Abstract

The paper presents the application of the casting method for the production of porous composites, called syntactic foams, of the casting alloy - solid particles type. This method was used to produce composites based on Al alloys reinforced with particles of clinoptilolite, a natural mineral from the zeolite group. Before the casting process, tests were carried out on the morphology, physicochemical properties and chemical composition of the zeolite, which was obtained from a rock called zeolite tuff, mined in a quarry in Kucin, (VSK PRO-ZEO s.r.o., Slovakia). Observations of the microstructure of the produced composites were also carried out using a scanning electron microscope. Diffractometric tests of zeolite rock as delivered for research and of the produced samples reinforced with zeolite particles were also carried out. Initial studies of the density and porosity of the produced composites were performed. The usefulness of the presented method of composite production was assessed on the basis of the conducted structural tests, with particular emphasis on the particle distribution in the alloy matrix.

Keywords: Metal matrix composites, Casting, Zeolite, Syntactic foam, Aluminium alloy

1. Introduction

Porous metal materials are materials with a high degree of structural discontinuity. Their structure can be described as a geometrically disordered arrangement of pores in the metal matrix. They are mainly made of light metals or their alloys. One of the technologies for producing metal foams is adding a foaming agent directly to the molten metal in a liquid-solid state. As a gas-forming agent, titanium hydride is used, which decomposes into titanium and hydrogen gas [1-3]. An interesting method of generating the cellular structure are foams reinforced with particles by mixing liquid systems of aluminum alloy - ceramics.

The presented work proposes an innovative method of producing metal composite materials using the method in which aluminum alloy was used as a matrix, and as foaming granules - clinoptilolite, a natural mineral from the zeolite group [4]. Clinoptilolites are microporous crystalline aluminosilicates, used as industrial adsorbents and catalysts containing a large amount of silicon, calcium, sodium, potassium and admixtures of various metals, such as: barium, strontium, potassium, magnesium, and manganese.

Zeolites were formed by volcanic eruptions over millions of years under the influence of high temperature and pressure, when lava flowing out of the volcano came into contact with salty seawater. The reaction of volcanic ash with the salts present in the lakes transformed the ash into various groups of aluminosilicates with unique physicochemical properties. A characteristic feature of clinoptilolites is the presence in their structure of internal voids forming the system of channels, of various sizes 0.3 - 1 nm, filled

with water in molecular form (zeolite water). During drying, this water is removed without affecting the structure of the crystals, only some of their physical properties change. However, water can be reabsorbed or replaced by other liquids or gases [5,6].

The technology of producing metal foam by casting with an aluminum alloy matrix allows for the creation of porous structures of any shape and can be particularly useful for creating elements with high surface development. The solution allows for obtaining a structure with precisely set parameters, and also allows for an easy way to control the course of the structure manufacturing process. It is possible to obtain pores and syntactic pores with a very wide size range depending on the size of the zeolite additive granules used. Composites based on aluminum alloys reinforced with zeolite particles give a material with good properties, with lower density, greater strength, resistance to compressive stress and a lower thermal expansion coefficient compared to the solid material obtained by casting.

The innovative technology of casting metal foam with an aluminum alloy matrix, developed in the presented work, using clinoptilolite as foaming granules, can provide the ability to suppress sounds and vibrations. The zeolite used in the research was obtained from a rock mined in a quarry in Kucin by VSK PRO-ZEO s.r.o, Slovakia. The richness and purity of this deposit make it one of the world's best. The method of extraction in the quarry fully complies with modern requirements and regulations. The aim of the research was to make a composite, to assess the quality of the zeolite connection with the matrix, to examine the influence of zeolite particles on the casting properties and, based on these tests, to assess its application possibilities.

2. Materials

For the production of the composite, AC-AlSi11 silumin was used as a matrix and crushed natural zeolite from the deposit located in the eastern Slovakia in Kucin as a filling. The natural zeolite fraction 2-4 mm was separated to the tests. On the other hand, for the physicochemical tests, ground zeolite with average particle size below 200 μm was used. The shape and arrangement of the zeolite grains are shown in Figures 1 and 2.

Fig. 1. Crushed zeolite particles

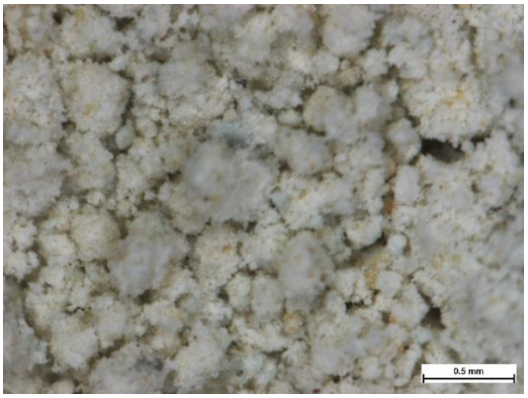


Fig. 2. Ground zeolite powder

Before the casting process, the physicochemical properties and chemical composition of the zeolite were tested using the JSM-7100F scanning electron microscope. The content of the elements was determined by X-ray microanalysis in the EDS X-Max AZtec series analyzer by OXFORD INSTRUMENTS. The spectrum of X-rays taken from the surface of the zeolite particles and the content of individual elements are shown in Figure 3 and Table 1.

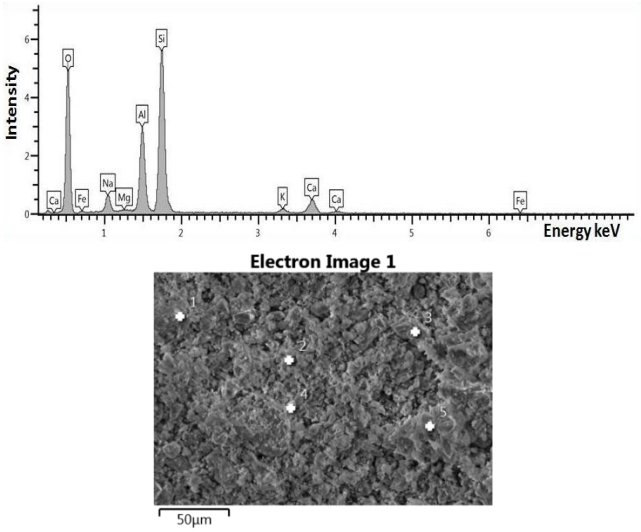


Fig. 3. The energy spectrum for emitted X-rays for zeolite particles

Table 1.
Major elements found in zeolite

Chemical compositions, at%			
Zeolite	**Al**	**Si**	**K**
	5-14	23-32	2-14
	Ca	**Fe**	**O**
	1-2,5	>1,5	40-50

Before the consolidation, the as-delivered zeolite material was tested by X-ray diffraction analysis. The phase composition of the zeolite was identified using the powder method, i.e. the Debye-Scherrer-Hull (DSH) method. The analysis was carried out by means of a Bruker D8 Discover diffractometer operating in Bragg-

Brentano mode equipped with a CuKα radiation source, a Ni filter, and a LYNXEYE_XE detector. The mineral composition was determined and calculated on the basis of the licensed databases by ICDD (International Centre for Diffraction Data), ICSD (Inorganic Crystal Structure Database), and NIST (National Institute of Standards and Technology). The data were registered and analysed using Bruker AXS DIFFRAC v.4.2 and TOPAS v.4.2 software. The phases of the as-delivered zeolite rock samples were identified using X-ray diffraction (XRD) analysis. Phase composition of the zeolite is presented in Table 2.

Table 2.
Phase compositions of the as-delivered zeolite

Phases	Percentage, %
Clinoptilolite	34-36
Feldspars	28-30
Quartz	11-12
Illite+muscovite	1-3
Kaolinite	<2
Amorphous substance	20-21

The crystalline phases obtained by XRD are illustrated in Figure 4.

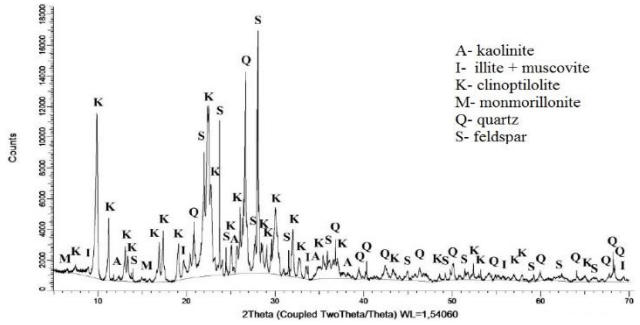


Fig. 4. X-ray diffractogram of the as-delivered zeolite

After diffraction tests, a BET study of zeolite particles in powder and crushed form was carried out. The adsorption capacity tests were carried out for both crushed and ground zeolite using the ASAP 2020M sorptomat from Micromeritics Norcross, GA, USA. The parameters characterizing the micro- and mesoporous structure of the studied zeolites were determined on the basis of the adsorption potential distribution function. The mentioned parameters were determined from the experimental nitrogen vapor adsorption / desorption isotherm at the temperature (-196 ºC) after prior degassing of the sample under strictly controlled temperature (200 ºC for 24h) and reduced pressure (10^{-3} hPa).

The following parameters were determined [7-9]:

- the specific surface area (SBET) was determined based on the theory of multilayer adsorption by the Brunauer-Emmett-Teller method, the so-called (BET) in the range of 0.05 ÷ 0.2 relative pressure, (p, p_0 - equilibrium pressure and nitrogen saturated vapor pressure), taking into account the area occupied by a single nitrogen molecule in the adsorption monolayer (the so-called settling surface) equal to 0.162 nm^2 [10].
- the total pore volume (V_t), being the sum of the micropore volumes (V_{mi}) and mesopores (V_{me}), was determined by the one-point method [11] from the nitrogen adsorption isotherm from the volume of adsorbed nitrogen for relative pressure $p/p_0 = 0,99$
- the mesopore volume (V_{me}) was determined by subtracting the micropore volume (V_{mi}) from the total pore volume (V_t).
- mesoporosity (%) was calculated as the ratio of the mesopore volume (V_{me}) to the total pore volume (V_t).
- the mean pore diameters D_p were calculated according to the formula $D_p = 4V_t/SBET$.

Figure 5 shows the surface structure of the zeolite particles subjected to the BET test.

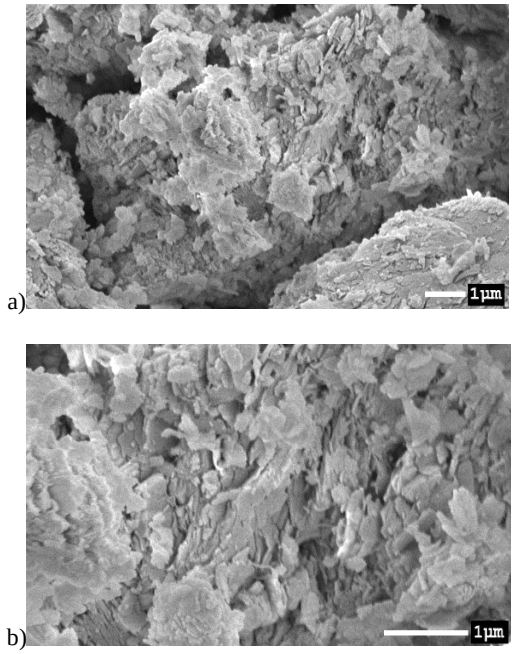


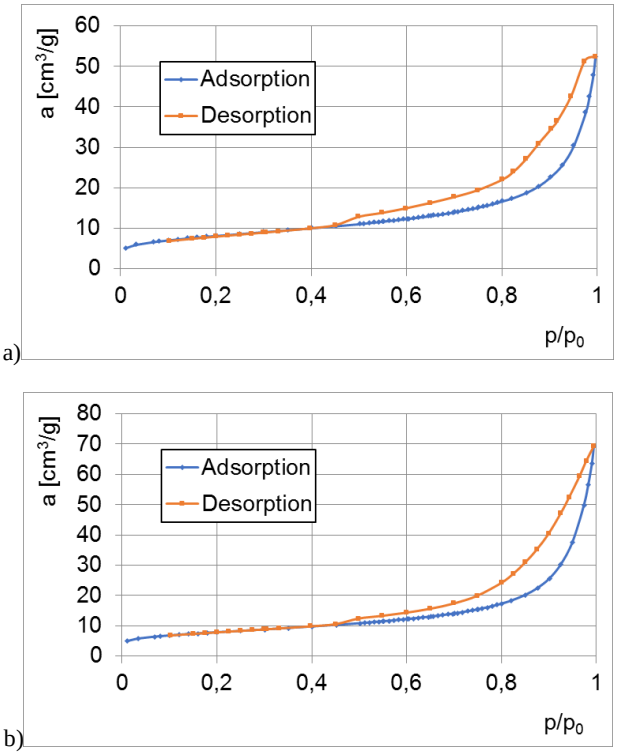
Fig. 5. SEM photographs of the tested adsorbent - structure of clinoptilolite granules under different zoom; a) x10000; b) x20,000

The parameters of the porous structure determined on the basis of nitrogen adsorption isotherms are presented in Table 3, and the low-temperature nitrogen adsorption isotherms for the tested zeolites (i.e. the amount of N_2 gas adsorbed relative to the pressure) are shown in Figure 6.

Table 3.
Textural properties of the obtained zeolite materials

Properties	crushed	grounded
S_{BET} ,m^2/g	29,24	27,87
V_t ,cm^3/g	0,0740	0,0985
V_{me} ,cm^3/g	0,0719	0,0966
V_{mi} ,cm^3/g	0,0021	0,0019
D_p, [nm]	10,1	14,1
mesoporosity	97,2%	98,1%

Markings: SBET - specific surface area of the material determined by the BET method, V_t - total pore volume for relative pressure $p/p_0 = 0.99$, V_{mi}, V_{me} - volume of micropores and mesopores based on the pore volume distribution function KJS, D_p- mean pore diameter, share mesoporosity - percentage of the mesopore volume V_{me} in the total pore volume V_t.



Markings: po - saturated vapor pressure, p - equilibrium pressure, a - size of adsorption / desorption [cm^3/g STP].

Fig. 6. Low-temperature nitrogen adsorption isotherms (i.e. the amount of N2 gas adsorbed relative to pressure) for the tested zeolites: a) crushed, b) ground

The specific surface area calculated by the BET method for crushed zeolite is 29,24 m^2/g and is higher than the milled type by about 1,27 m^2/g.

The course of adsorption isotherms for both zeolite materials - crushed and ground, indicates that they were type IV isotherms according to the IUPAC classification and had well-formed H-type hysteresis loops [11-13]. Typical H hysteresis loops confirmed the presence of homogeneous mesopores in the tested materials.

3. Results

3.1. Manufacturing process

The casting process of zeolite granules with the aluminum alloy AC-AlSi11 was carried out in accordance with the PN-EN1706 standard. Figure 7 shows photos of the produced samples.

Fig. 7. Photo of the manufactured composite

The process of manufacturing a porous structure in the conducted experiment consisted in adding to the cast aluminum alloy AC-AlSi11 at a temperature of 790°C, zeolite granules with a grain size of 4-6 mm in the amount of 20% by weight. The foaming agent in the form of zeolite granules was mixed with the liquid metal while pouring the mold - die. After solidification and cooling down to room temperature, the ready foamed element with a porosity of about 55% was removed from the mold. Upon contact with metal at elevated temperatures, water vapor is released from the hydrated aluminosilicates, leading to the formation of pores in the liquid or solidifying metal. The zeolite grains that have not decomposed due to the intense evolution of water vapor are the syntactic part of the material. The melting process was carried out in a laboratory muffle furnace at 760°C for zeolite granulate and aluminum alloy. All processes were carried out without a protective atmosphere. Cylindrical samples with a diameter of φ29 were produced for further research.

3.2. Density and porosity investigations

The produced samples were subjected to density measurements by weighing in air and in water using a WPA120 hydrostatic balance in accordance with the PN EN ISO 2738: 2001 standard. The results of density measurements are shown in Table 4.

Table 4.
The results of density measurements

Cast AC-AlSi11 [g/cm³]	Foam (AC-AlSi11+ zeolite) [g/cm³]
2,68±0,03	2,25±0,02

The measurement of porosity of the manufactured composites was determined by the Cavalier-Hacquert method. In order to assess the degree of porosity of the tested samples, quantitative image analysis was performed using the NIS 4.x software included (OM) Nikon MA 200 ECLIPS. In the quantitative analysis according to the Cavalieri-Hacquert principle, the porosity was measured by the surface pore content: the ratio of the sum of the pore area to the total area of the analyzed cut. In the research, the ratio of the sum of the pore area to the total area of the analyzed grinding was measured. Due to the difficult preparation of the produced materials, there was a need to perform multiple measurements on

each sample. Analyzes were performed in three randomly selected places on each sample. ROI frames were set up to binarize and analyze porous areas, omitting any artifacts. The results were averaged. The results of porosity together with pictures of the microstructure of the tested sinters are presented in Figures 8a,b and Table 5.

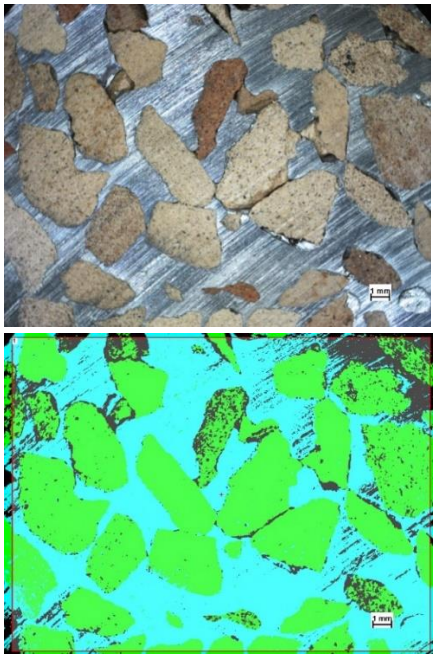


Fig. 8. Microstructure of foam zeolite, measurements of porosity, light microscopy

Table 5.
Results of porosity measurements of AC-AlSi11 + zeolite cast samples

Foam (AC-AlSi11+ zeolite)	Porosity, %
	58,2±1,87

3.3. XRD analyses of fabricated material

The phase analysis of the porous sample was carried out after casting the zeolite granulate with the AC-AlSi11 aluminum alloy by the powder method (DSH) in the Bragg-Brentano geometry using the D8 Discover diffractometer by Bruker, using the same test parameters and the same standards as during the study of zeolite rock (as above).

The performed XRD tests of the sample showed the following phase composition: aluminium (Al), clinoptilolite-Ca(Na, K, Ca)(Al, Si)Si_8O_{18}·$7H_2O$, quartz (SiO_2), silicon (Si), cristobalite (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), feldspars (potassium $K[AlSi_3O_8]$), iron (Fe), amorphous substance.

Due to the surface tests, it is not possible to perform quantitative tests in relation to the above-mentioned crystalline phases. However, it is possible to estimate the content of amorphous substance on the scanned surface, the amount of which is approx. 32-35%.

The presence of an amorphous substance in the sample is indicated by the characteristic elevation of the line diffractogram in the angular range 15-40° 2θ (Fig. 9). The occurrence of the identified mineral phases in the surface analysis of the sample is shown in the figure that includes the diffraction pattern with explanations. Due to the large number of mineral phases, the strongest reflections of the marked crystalline phases were marked on the diffractogram.

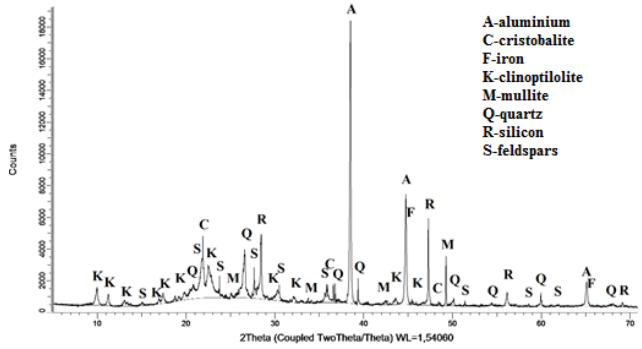


Fig. 9. Diffractogram of the tested AC-AlSi11 sample with zeolite

4. Discussion and conclusions

Studies of the chemical composition of zeolite as delivered have shown that the main elements present in zeolite are: aluminum, silicon, potassium, calcium and iron. This study confirmed that the tested rock is an aluminosilicate mineral.

Diffractometric tests performed with the powder method (DSH) in the Bragg-Brentano geometry using the D8 Discover diffractometer by Bruker, showed that the mineral composition was clinoptilolite in the amount of 34-36%, potassium feldspar in the amount of 28-30%, quartz in the amount of 11-12%, illite in an amount of 1-3%, kaolinite in an amount of less than 2% and amorphous substance in an amount of 20-21%. It should be concluded that the low content of clinoptilolite in zeolite is caused by the grinding process of the rock, which damages its structure. The rock should be broken up by crushing, not by grinding. XRD analysis showed that all major peaks in the diffraction pattern (Figure 4) are from the $KAlSi_8O_{18}$ and SiO_2 phase. The parameters of the porous structure determined on the basis of nitrogen adsorption isotherms showed that the crushed zeolite material has a larger specific surface area and total pore volume. The specific surface area calculated by the BET method for crushed zeolite is 29,24 m^2/g and is higher than the milled type by about 1,27 m^2/g. The differences in the determined values of the textural properties are so insignificant that zeolite materials of both crushed and ground zeolite samples are mesoporous materials (effective pore radius 2-50 nm. The characteristics of adsorption/desorption isotherms indicate (Fig. 6) that these are type IV isotherms for crushed and ground zeolite (IV type according to IUPAC). This type of isotherm is characteristic of mesoporous materials. Types IV and V isotherms correspond to type II and III curves. They differ from them only in that the maximum of adsorption is achieved at a pressure lower than the pressure of saturated vapor, along a certain section of the isotherm they run parallel to the pressure axis. The reason for this is that only a limited number of adsorption layers

are formed in the pores of the adsorbent due to the pore width. It is believed that they reflect the phenomenon of capillary condensation [8-13], i.e. sudden filling of all pores with the same shape and diameter with adsorbate. Optimal parameters of the sintered production technology were selected on the basis of previously conducted own research and it is satisfactory to repeatedly produce a porous structure in the experiment. As a result of the experiment, a casting with a density lower than that of a casting made in a solid mold was obtained. Figure 8 and Table 5 show the results of the sintered porosity measurements. The highest porosity obtained for the composite was 58%. The results of the total porosity test for the produced foams made of aluminum alloy with zeolite allow for the conclusion that the introduction of zeolite particles increases the porosity of composites. The macrostructures of composites based on an aluminum alloy with the participation of zeolite particles are presented in Figures 8. As a result of the observations, no discontinuities were found at the interface between the matrix and zeolite particles. A very good combination of zeolite particles with an aluminum matrix was obtained, without the occurrence of voids, only the pores present in the composite are visible in the photomicrographs. The zeolite particles are clearly visible in the fractures in the form of irregular precipitations. Fig. 9 shows the results of the phase analysis carried out on foams obtained with the matrix of an aluminum alloy with the participation of zeolite particles, produced at a temperature of 790°C. Phase analysis revealed a number of changes due to the temperature effect on clinoptilolite, feldspars and clay minerals present in the sample. The changes consisted in the formation of new phases, i.e. mullite and substances $Na_2Ca_2(SiO_3)_3$. Mullite in the tested sample is probably present in two varieties. The first is formed after the temperature transformation of clay minerals, illite and kaolinite. The second form of mullite is probably a synthetic form from the reaction of hot aluminum on silicates and quartz. The differentiation of these types of mullite results from the intensity of the reflections on the diffractogram (Fig. 4). This indicates the following genesis of mullite, probably formed with a greater proportion of aluminum and the presence of iron in its structure.

On the basis of the conducted research, it was assessed that the optimal parameters of the technology for the production of the porous structure on the matrix of the AC-AlSi11 aluminum alloy with the participation of zeolite particles were correctly selected and it is satisfactory to repeatedly obtain the above-mentioned porous structure in accordance with the proposed technology. Acoustic tests planned at a later date will confirm whether the produced porous composite can be used for elements intended to dampen sounds and vibrations.

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