

## THE EFFECT OF THE ADDITION OF ZEOLITE ON THE PROPERTIES OF A SINTERED COPPER-MATRIX COMPOSITE

BOROWIECKA-JAMROZEK Joanna, DEPCZYŃSKI Wojciech

*Department of Applied Computer Science and Armament Engineering, Faculty of Mechatronics and Mechanical Engineering, Kielce University of Technology, Kielce, Poland, EU*

[jamrozek@tu.kielce.pl](mailto:jamrozek@tu.kielce.pl)

### Abstract

This paper presents results concerning copper-zeolite composites fabricated by powder metallurgy. It focuses on the effect of zeolite particles on the properties of the sintered material as well as the quality of the bonding between the zeolite reinforcement and the copper matrix. Before the sintering process, the zeolite morphology and composition were characterised. The zeolite powder (0.0-0.2 mm fraction) used in the experiments was ground tuff rock extracted from the Kucin Quarry (VSK PRO-ZEO s.r.o.) in Slovakia. The as-delivered material was imaged and analysed using the SEM/EDS and XRD techniques. Before sintering, the powder mixtures were compacted on one side with a hydraulic press at a pressure of 400 MPa. The sintering process was carried out in a laboratory tube furnace at 950 °C under an atmosphere of dissociated ammonia. The sintering time was fixed at 60 minutes. The resulting agglomerates were measured for density, hardness, porosity. SEM/EDS analysis was employed to observe the microstructure and composition of the metallographic sections. The addition of zeolite powder to the copper matrix (5, 10 or 20% by weight) increased the porosity and hardness of the sintered material but decreased its density.

**Keywords:** Metal composite, sintering, zeolite, copper, powder metallurgy

### 1. INTRODUCTION

Composites are a numerous and varied group of structural materials. Metal-matrix composites reinforced with ceramic particles seem to be some of the most interesting materials of this type. Recently, research has focused on developing novel composites with a metal matrix reinforced with ceramic particles that exhibit high hardness and good thermal conductivity. The addition of ceramic particles to a metal matrix results in higher compressive strength and higher resistance to abrasive wear [1].

The literature on the subject shows that only recently has some research been devoted to copper-matrix materials fabricated by sintering in which volcanic tuff is used as the reinforcement particles. The addition of volcanic tuff leads to a decrease in the density and porosity of the sintered compacts and an increase in their hardness [2-4]. Taking the above findings into consideration, the authors of this paper undertook research on the application potential of zeolite particles as the reinforcement phase in copper-matrix composites. There are not many publications on the physical and chemical properties of this mineral and its applications.

Zeolites are a large group of natural hydrated aluminosilicate minerals varying in composition and properties. The most common are sodium and calcium aluminosilicates. The least frequent are barium, strontium, potassium, magnesium and manganese aluminosilicates. Zeolites were first described in 1756 by the Swedish mineralogist Axel Frederik Cronstedt [5-7]. Over millions of years, they were formed through high temperature and pressure during volcanic eruptions by the reaction of volcanic lava or ash with salty sea water. The reaction of volcanic ash with salts present in lakes resulted in the conversion of the ash into various aluminosilicates, with each group characterised by unique physical and chemical properties. The properties are due to a specific crystalline structure, i.e. the occurrence of isolated and/or connected voids with certain molecular dimensions. The basic units constituting the zeolite backbone are  $(\text{SiO}_4)^{4-}$  and  $(\text{AlO}_4)^{5-}$  tetrahedra bonded by means of

shared oxygen atoms. Some of the silicate atoms are replaced by  $(\text{AlO}_4)^{5-}$  aluminium atoms. In this way, a characteristic spatial structure with a large number of voids containing metal cations or water molecules is formed. The voids constitute 24-32% of the total volume. Zeolites are commonly used in a wide variety of applications, including ion exchange, catalysis, oil processing, construction, treatment of water or fumes, because of their unique properties, for instance, a crystalline structure, a negative charge of the lattice, easy exchange of valence lattice cations, a uniform size of micropores and thermal and hydrothermal stability [5].

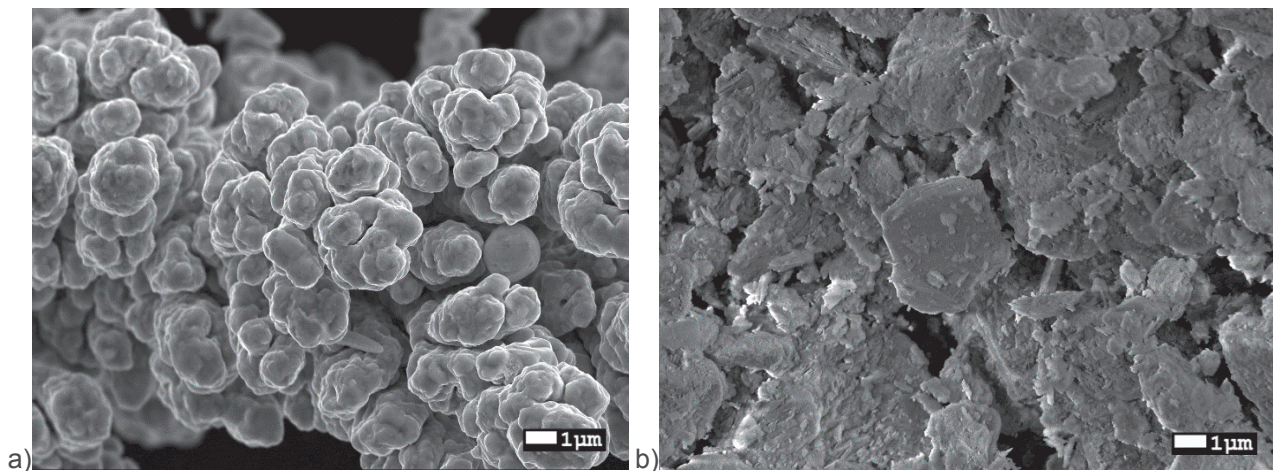
This study is focused on the fabrication of a copper-zeolite composite containing zeolite using powder metallurgy. The zeolite powder used in the tests was produced by VSK PRO-ZEO s.r.o from zeolite rocks extracted from the Kucin Quarry situated in Slovakia. The abundance and high purity of the mineral makes the deposit some of the best in the world. The rock extraction methods fully satisfy the requirements and regulations of today's industry.

The aim of this study was to fabricate copper-matrix composites with different amounts of zeolite, assess the quality of their bonding, determine the influence of the zeolite particles on the properties of the sintered compacts and, finally, analyse the application potentials of the materials.

## 2. MATERIALS AND METHODS

The study was conducted on electrolytic 99.9% Cu powder with particles varying in size (40-65  $\mu\text{m}$ ) combined with finely ground natural zeolite (0.0-0.2 mm fraction) from a deposit in Kucin, Eastern Slovakia.

The shapes and arrangements of the powder particles used in the experiments are shown in **Figure 1**.

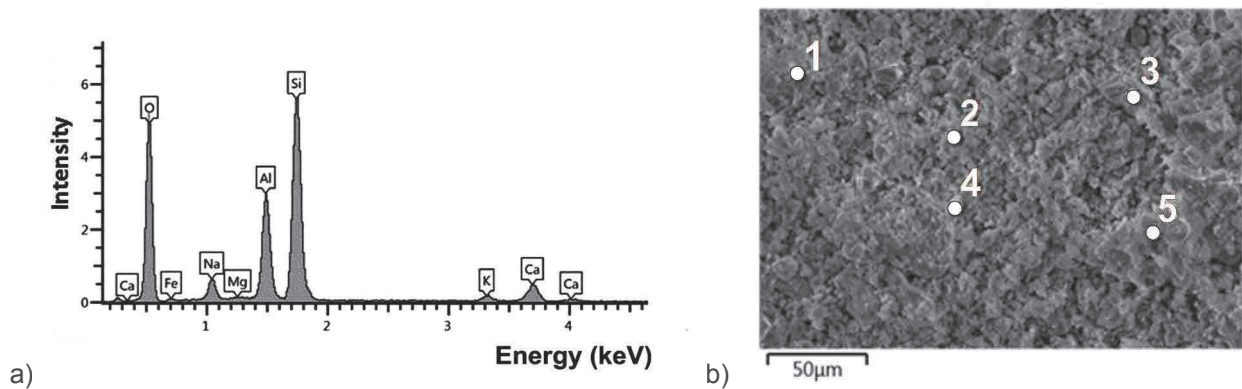


**Figure 1** Images of the powders tested: a) electrolytic copper powder, b) zeolite powder

Before the consolidation, the powders were observed and characterised using a JEOL JSM-7100F field emission scanning electron microscope fitted with OXFORD INSTRUMENTS EDS X-Max AZtec software for elemental microanalysis. The surface composition of the zeolite particles is illustrated in the X-ray diffraction pattern in **Figure 2** and in **Table 1**.

**Table 1** Major elements found in the zeolite (wt.%)

Al	Si	K	Ca	Fe	Oxygen
5-14	23-32	2-14	1-2.5	0.0-1.5	40-50



**Figure 2** X-ray spectrum (a) obtained for the zeolite particles (b)

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 CuK $\alpha$  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 the X-ray diffraction (XRD) analysis, **Table 2**.

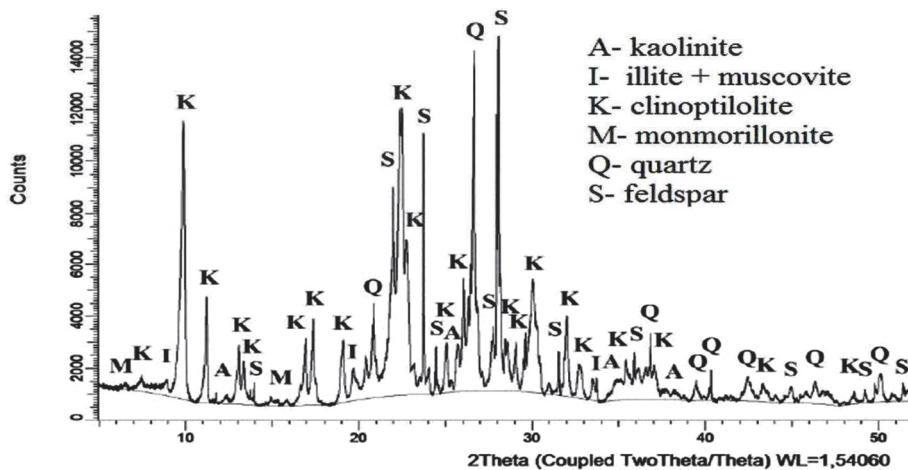
**Table 2** Phase composition of the as-delivered zeolite

Phases	Percentage (%)
Clinoptilolite-Ca (Na, K,Ca)(Al,Si)Si <sub>8</sub> O <sub>18</sub> ·7H <sub>2</sub> O	34 - 36
Feldspars (potassium feldspar K[AlSi <sub>3</sub> O <sub>8</sub> ] + plagioclase feldspars Na[AlSi <sub>3</sub> O <sub>8</sub> ] (albite) - Ca[Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ] (anorthite)	28 - 30
Quartz (SiO <sub>2</sub> )	11 - 12
Illite + muskovite KAl <sub>2</sub> [AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> ]	1 - 3
Kaolinite Al <sub>4</sub> [Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub> ]	< 1 - 2
Amorphous substance	20 - 21

After the powders were characterised, powder mixtures containing 5, 10 or 20% of zeolite were prepared. The powders were dry mixed with a Turbula shaker-mixer for 60 minutes. The sintering process was preceded by single pressing with a hydraulic press at a compaction pressure of 400 MPa. The sintering was performed using a laboratory tube furnace at a temperature of 950 °C in a dissociated ammonia atmosphere. The sintering time was 60 minutes. Finally, the material was cooled in the furnace. The tests were conducted on cylindrical specimens with dimensions  $\phi$  20x10 mm.

The crystalline phases obtained by XRD are illustrated in **Figure 3**.

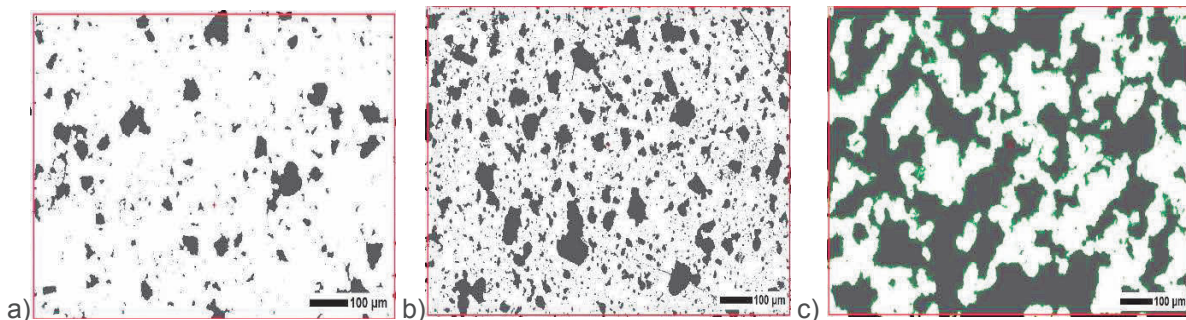
The sintered compacts were measured for density and hardness. The density was determined by weighing the specimens in air and water using WPA120 hydrostatic scales in accordance with the PN EN ISO 2738:2001 standard. The hardness of the material was measured using the Brinell method (with a steel ball 5 mm in diameter at a load of 250 kg) in line with the PN EN ISO 6506-1:2014 standard.



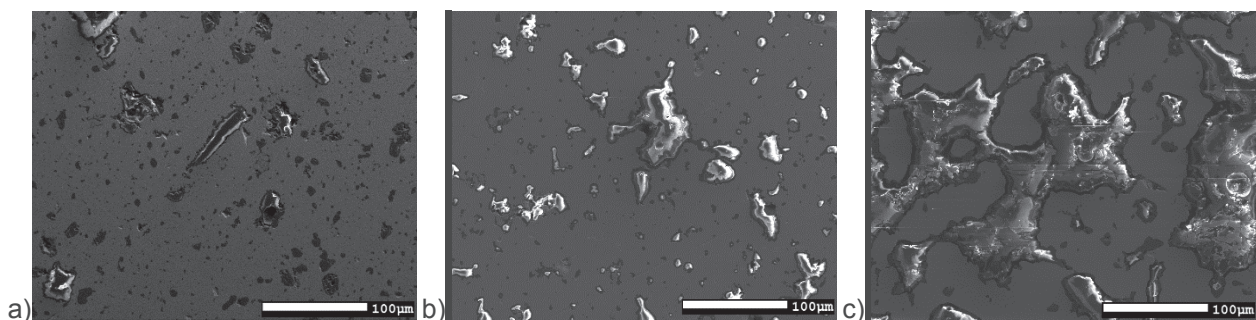
**Figure 3** X-ray diffractogram of the as-delivered zeolite rock

The microstructure and porosity of the composites produced were observed and characterised using the Cavalieri-Hacquet method. The porosity of the samples was determined with NIS-Elements ver. 4.x software incorporated in the Nikon ECLIPSE MA200 using a quantitative analysis of the images obtained.

The study involved determining the ratio of the sum of areas of the interparticle pores and the total surface area of the polished section. As the sample preparation procedure was difficult, it was essential to measure each sample several times. Three randomly selected areas of the polished surfaces were analysed. The regions of interest (ROIs) were defined in such a way as to enable binarisation and analysis of the porous areas while omitting potential artefacts. The results were averaged. The results of the density, hardness and porosity measurements performed to determine the microstructure of the sintered compacts are provided in **Figures 4 and 5** and **Table 3**.



**Figure 4** Microstructures of the sintered compacts observed with a light microscope; results of the porosity measurements obtained for: a) Cu+5% zeolite, b) Cu+10% zeolite, c) Cu+20% zeolite



**Figure 5** Microstructures of the sintered compacts observed with a scanning electron microscope obtained for a) Cu+5% zeolite, b) Cu+10% zeolite, c) Cu+20% zeolite

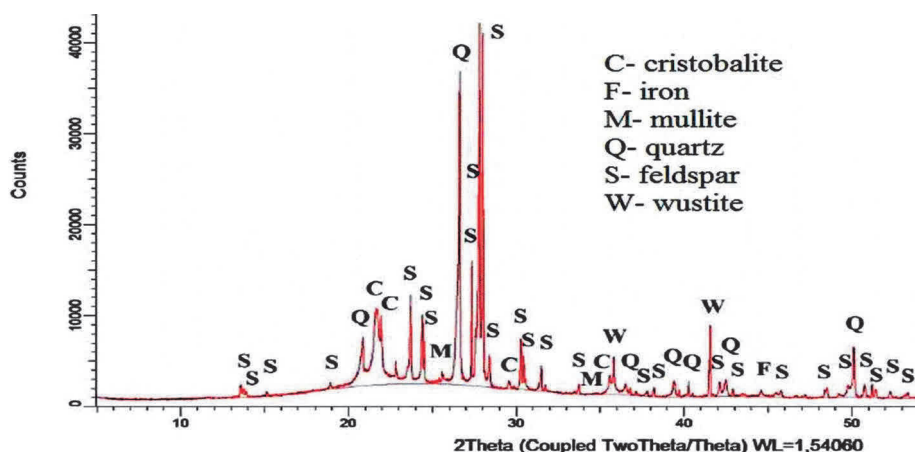
**Table 3** Results of the density, hardness and porosity measurements

Material	Density, (g/cm <sup>3</sup> )*	Theoretical density, (g/cm <sup>3</sup> )	Porosity, average value [%]	HB
Cu	7.65 ± 0.02	8.90	7.2 ± 1.5	37.14 ± 1.5
Cu + 5% zeolite	6.88 ± 0.04	8.60	11.4 ± 1.5	50.45 ± 1.8
Cu + 10% zeolite	6.27 ± 0.02	8.30	24.6 ± 1.8	51.16 ± 1.4
Cu + 20% zeolite	5.17 ± 0.03	7.70	50.2 ± 2.1	58.71 ± 1.6

\* scatter intervals estimated at the 90% confidence level

After the consolidation, the sintered compacts were crushed and the zeolite was removed for further analysis. An X-ray diffraction analysis was performed again to determine the phase composition of the zeolite after heating at a temperature of 950 °C. The analysis of the phase composition of the zeolite after heating showed the presence of 24-25% of quartz, 21-23% of potassium feldspars, 5-6% of cristobalite, 2-4% of mullite, <2 % of wustite and 43-44% of an amorphous substance.

The crystalline phases can be seen in the diffractogram in **Figure 6**.



**Figure 6** X-ray diffractogram of the as-delivered zeolite rock after heating at 950 °C

### 3. DISCUSSION

From the morphology of the as-delivered zeolite rock it is clear that agglomerates of powder particles form in the material, **Figure 5**. The powders should thus be mixed long enough before sintering to break up the agglomerates and obtain a homogeneous mixture.

The elemental analysis of the as-delivered zeolite shows that the main elements present in the zeolite are: aluminium, silicon, potassium, calcium and iron. The results confirmed that the rock studied was an aluminosilicate mineral.

The mineral composition of the powder was analysed using the DSH method with a Bruker D8 Discover diffractometer operating in the Bragg-Brentano mode. The analysis revealed that the material contained 34-36% of clinoptilolite, 28-30% of potassium feldspars, 11-12% of quartz, 1-3% of illite, less than 2% of caolinite and 20-21% of an amorphous substance. It can be concluded that a small amount of clinoptilolite present in the zeolite, which was contaminated during the rock grinding process, damages its structure.

The optimal parameters of the sintering process were selected on the basis of the authors' previous findings and similar data available in the literature. The decrease in density with increasing amount of zeolite was due to higher porosity of the sintered compacts.

The hardness measurements revealed that the hardness of the sintered compacts could be improved by increasing the amount of zeolite. The addition of 10% by weight of zeolite improved the hardness of the composites by nearly 30%, which is a satisfactory result.

**Figure 4** shows the porosity of the sintered copper and zeolite compacts. The lowest porosity of approximately 11% was reported for the copper composite embedded with 5% of zeolite. From the analysis of the total porosity of the material it is evident that the addition of zeolite particles contributed to higher porosity of the composites.

The SEM microstructures of the metal-matrix composites with different amounts of zeolite are shown in **Figure 5**. The observations did not reveal any discontinuities at the boundary between the matrix phase and the zeolite particle phase. The bonding between the zeolite particles and the copper matrix was reported to be very good. No voids were present in the material. From the microimages it is apparent that the pores are typical of sintered metals. There was no diffusion of the elements present in the zeolite into the copper matrix. This finding is noteworthy because of the purity and electrical conductivity requirements specified for the copper matrix.

#### 4. CONCLUSION

The following are conclusions drawn from this study:

- Zeolite tuff powder dispersed into the metal matrix improves the hardness of the composite and reduces its porosity, it can be used as a reinforcing material.
- The distribution of the embedded particles is uniform and the bonding between the reinforcement and the matrix is satisfactory.
- The results of the microstructural analysis indicate that no discontinuities are present at the boundary between the matrix phase and the zeolite phase; in all the three cases studied, the bonding between the zeolite particles and the copper matrix is good.
- Zeolite particles in the form of irregular precipitates are clearly visible on the polished surfaces.

#### REFERENCES

- [1] KONIECZNY, M. The effect of sintering temperature, sintering time and reinforcement particle size on properties of Al<sub>2</sub>O<sub>3</sub> composites. *Composites Theory and Practice*, 2012, vol. 12, no. 1, pp. 39-43.
- [2] ŁACH, M. Structure of metal matrix composites with an addition of tuff. *Archives of Foundry Engineering*, 2010, vol. 10, special Issue 3, pp. 135-140.
- [3] ŁACH, M., MIKUŁA, J., HEBDA, M. Thermal analysis of the by-products of waste combustion. *Journal of Thermal Analysis and Calorimetry*. 2016, vol. 125, no. 3, pp. 1035-1045, doi 10.1007/s10973-016-5512-9.
- [4] MIKUŁA, J., ŁACH, M., KOWALSKI, J. S. Copper matrix composites reinforced with volcanic tuff. *Metalurgija*, 2015, vol. 54, pp. 143-146.
- [5] CICISZWILI, G. W, ANDRONIKASZWILI, G. N, KIROW, Ł. D. *Zeolity naturalne*. WNT, Warszawa 1990, (in polish).
- [6] GOTTARDI, G, GALLI, E. *Natural Zeolites, Mineral and Rocks*. 18. Springer-Verlag, Berlin Heidelberg, 1985, pp. 256-284.
- [7] NANBIN, H., DIANYUE, G., BEKKUM, H., FLANIGEN, E., JACOBS, P., JANSEN, J. *Introduction to Zeolite Science and Practice*. 2<sup>nd</sup> Completely revised and expanded edition, Elsevier, New York 2001, no. 137, pp.54-59.