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THE EFFECT OF THE FIRING TEMPERATURE ON THE HARDNESS OF ALUMINA PORCELAIN

VPLIV TEMPERATURE ŽGANJA NA TRDOTO PORCELANA IZ ALUMINIJEVEGA OKSIDA

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Green alumina porcelain samples containing kaolin (27 %), Al_2O_3, grog (50 %) and feldspar (23 %) were fired at temperatures between 300 °C and 1250 °C with a heating and cooling rate of 5 °C/min. The Shore hardness and the Vickers hardness of the fired samples were measured at room temperature. Both hardnesses of the green alumina porcelain samples are low and remain approximately constant up to 400 °C when dehydroxylation begins. Between 400 °C and 700 °C both hardnesses slightly increase. Above 700 °C, they increase exponentially. This is explained by sintering and high-temperature reactions in metakaolinite. The dependencies between both hardnesses, Shore and Vickers, and the firing temperature are very similar, i.e., the Shore hardness and the Vickers hardness reflect changes in the sample in the same manner. The Vickers hardness is much more sensitive to the firing temperature. Its values after firing at 1250 °C are 130 times higher than those measured at room temperature. However, the values of the Shore hardness are only four times higher. The relationship between the Young's modulus and the Shore hardness and the Vickers hardness can be fitted by power-regression functions.

Keywords: Shore hardness, Vickers hardness, alumina porcelain, Young's modulus

Surovi vzorci porcelana, ki vsebujejo kaolin (27 %), Al_2O_3 in gline (50 %) ter glinenec (23 %), so bili žgani pri temperaturah med 300 °C in 1250 °C s hitrostjo ogrevanja in ohlajanja 5 °C/min. Pri sobni temperaturi je bila pri žganih vzorcih izmerjena trdota po Shoreu in Vickersu. Obe trdoti surovega porcelana na osnovi aluminijevega oksida sta nizki in ostajata relativno konstantni do temperature 400 °C, ko se začne dehidroksilacija. Med 400 °C in 700 °C obe trdoti nekoliko narasteta. Nad 700 °C trdoti naraščata eksponencialno. To si razlagamo s sintranjem in z visokotemperaturnimi reakcijami v metakaolinitu. Odvisnosti med obema trdotama po Shoreu in Vickersu ter temperaturo žganja so zelo podobne, kar pomeni, da trdoti po Shoreu in Vickersu izražata spremembe v vzorcu na enak način. Trdota po Vickersu je bolj občutljiva za temperaturo žganja. Njena vrednost po žganju pri 1250 °C je 130-krat višja kot trdota, izmerjena pri sobni temperaturi. Vrednosti trdote po Shoreu so samo 4-krat višje. Odvisnost med Youngovim modulom, trdoto po Shoreu in trdoto po Vickersu je mogoče ugotoviti s funkcijami regresije.

Ključne besede: trdota po Shoreu, trdota po Vickersu, porcelan na osnovi aluminijevega oksida, Youngov modul

1 INTRODUCTION

The desired mechanical properties of ceramics are achieved in a relatively complex technological process in which firing is the most important part. During firing, a ceramic kaolin-based body, such as porcelain, passes from the green state to the final ceramic state through several phase transitions, during which both composition and structure change significantly. It is important to know how the mechanical properties develop during firing, so one group of research projects is focused on different mechanical properties measured during the firing.[1] Some projects deal with the same properties, but measured at room temperature after firing at chosen temperatures. This second way is experimentally simpler and is often used as a measurement of the Young's modulus, the mechanical strength, hardness, and other mechanical parameters.

The hardness is an important property of the ceramic body that often determines its application. For example, the hardness of porcelain determines whether this material is suitable for floor tiles. There are different kinds of hardness, which is more a technical parameter than physical, and consequently different methods are used for their measurement. A quick and simple method, the Shore method, uses an indenter that falls down vertically on a sample.[2] This type of hardness is related to the material's elasticity. A measure of the Shore hardness is the maximum height reached by the indenter after the rebound off the sample. The principle of this method is simple and can be used at elevated temperatures. Although the Shore hardness is mostly measured on elastomers, this parameter is also used for rocks[3–5] as well as for ceramics and metals in high-temperature conditions.[6] If a steel ball is used as the indenter, it is necessary to obtain an accurate horizontal position of the sample as well as an optical measurement of the maximum vertical position of the indenter after the rebound.[7] Another mechanical arrangement is exploited in[6], where the steel ball falls on a tilted sample and the hardness is determined from the time between two impacts, recorded by electromechanical receivers. One of them is placed on the sample and the other on a metallic reflector situated above it.

Another hardness test that is often used for ceramics is the Vickers hardness.[8] Its principle is based on the load of a diamond-pyramided indenter over the sample surface for the dwell time. The Vickers hardness is calculated from the loading force and indentation area. For example, the Vickers hardness of ceramic floor tiles was measured in[9] and alumina composites were tested in[10]. It was found that the Vickers hardness increases with the sintering temperature.

Since the macroscopic hardness as well as the Young's modulus are generally determined by interatomic bonds inside the crystals and interface forces between the crystals in a polycrystalline body, one may expect a close relationship between these quantities. This can be exploited for an estimation of the Young's modulus through a hardness measurement, which is simpler. For example, it is known that the Shore hardness is related to the elasticity and there are formulae that link the Young's modulus and the Shore hardness of elastomers.[11,12] A power relationship between the Young's modulus and the hardness (obtained from the Schmidt hammer test, which is also a rebound method) was found in[13] for different rocks. A logarithmic relationship between them was derived in[14]. A linear as well as an exponential relationship between the values of the Young's modulus and the hardness were presented.[3,4,15,16] Our findings imply that no unambiguous relationship exists between the Young's modulus and the hardness for the measured material. Experimental points in the plots of the hardness vs. Young's modulus are usually very scattered, which makes these relationships questionable. We did not succeed in finding such a relationship for ceramic materials.

The aim of this work is to measure the Shore hardness and the Vickers hardness at room temperature on ceramic samples fired at different temperatures and to compare the Shore hardness with the Vickers hardness.

2 EXPERIMENTAL

The samples for the hardness test were cut from a green alumina porcelain plastic blank (diameter 300 mm) intended for high-voltage insulators. The blank consists of kaolin (27 %), Al_2O_3, milled fired waste (50 %), and feldspar (23 %). Its chemical composition is in **Table 1**.

Table 1: The chemical composition of the green sample material in mass fractions, *w*/%

Tabela 1: Kemijska sestava surovega materiala vzorcev v masnih deležih, *w*/%

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	L.O.I.
40.22	48.99	0.81	0.20	0.23	0.27	3.60	0.59	4.93

The blank was cut into samples with dimensions of 10 mm × 30 mm × 30 mm. The samples were dried in the open air and both 30 mm × 30 mm faces were smoothed with fine sandpaper. After that the sets of three samples were fired at (300, 400, 425, 450, 475, 500, 550, 600, 700, 800, 900, 1000, 1100, 1200, and 1250) °C with a heating and cooling rate of 5 °C/min.

To measure the Shore hardness, we designed an apparatus where the indenter (a steel ball Ø = 4 mm) hits a sample, tilted by an angle between the sample and the horizontal plane of 22.5°, and falls down on a soft plasticine surface. Here the indenter creates a circular imprint. The hardness was calculated from the geometrical quantities denoted as h_1 (the vertical distance between the initial position of the indenter and the sample), h_2 (the vertical distance between the sample and the plasticine surface), and l (the horizontal length of the indenter's trajectory after the rebound). Since the distances $h_1 = h_2 = 0.25$ m are fixed, only l is measured. The Shore hardness (HSC) is defined as HSC = 10^4 $h_3/65h_1$, where h_3 is the maximum vertical height reached by the indenter after the rebound.[2] When the vertical rebound is expressed through l as $h_3 = l2/[2(l + h_2)]$, we obtain HSC = 10^4 $l_2/[130h_1(l + h_2)]$ and after substituting numerical values we have:

$$HSC = \frac{307.7l^2}{l + 0.25} \tag{1}$$

where l is in metres.

The plausibility of the results obtained using the described apparatus was verified by Vickers sclerometer Indentamet 1105 Buehler (Germany). For the Vickers hardness (HV) measurement a loading force of 10 N and a dwell time of 10 s were used.

We used three samples for every firing temperature and the measurement was repeated five times at different places of the sample, so we had 15 sets of experimental data of the hardness for each firing temperature.

Young's modulus was measured at room temperature using the sonic resonant method[17] with cylindrical samples of dimensions Ø 11 mm × 150 mm fired at temperatures between 300 °C and 1250 °C.

3 RESULTS AND DISCUSSION

The dependence of the Shore hardness on the firing temperature is depicted in **Figure 1**. As noted above, the Vickers hardness was also measured (**Figure 2**) to find the similarities between both the results. The Vickers hardness is more sensitive to changes in the sample structure developed during heating from room temperature to 1250 °C. In contrast to the Shore hardness, which increased by only ≈4 times, the Vickers hardness increased by ≈130 times. Both the Shore hardness and the Vickers hardness reflect the main processes in the samples in the same manner.

During the heating from room temperature up to 400 °C, the hardness is approximately the same as the green sample hardness. This supports the idea that no structural and compositional changes in the sample occur in this temperature interval.[18,19]

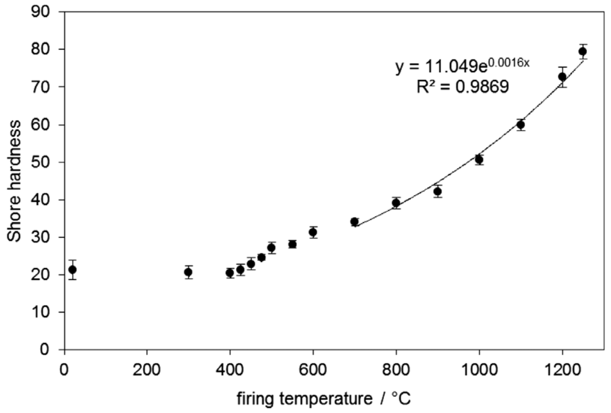

Figure 1: The Shore hardness versus firing temperature
Slika 1: Trdota po Shoreu v odvisnosti od temperature žganja

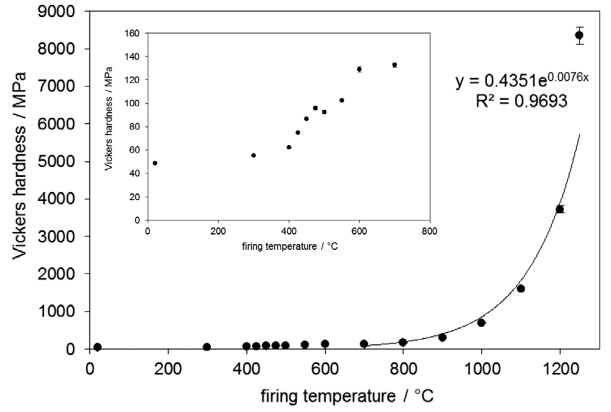

Figure 2: The Vickers hardness versus firing temperature
Slika 2: Trdota po Vickersu v odvisnosti od temperature žganja

Another interesting occurrence is found between 400 °C and 600 °C, where dehydroxylation runs in the kaolinite component. Dehydroxylation creates the highly defective porous metakaolinite,[18–20] which represents ≈ 23 % of the sample mass. Consequently, the mechanical properties of the metakaolinite crystals are weaker, and these properties must also be weaker for the porcelain mixture containing metakaolinite. The total porosity of the sample (consisting of metakaolinite, alumina, feldspar, and grog) increases by 3–4 % after dehydroxylation.[18,21] In spite of these facts, we do not observe a significant decrease in the hardness, as would be logically expected, but an increase occurs instead. We observe only a very low decrease of the Vickers hardness in **Figure 2** and a decelerating of the increase of the Shore hardness above 500 °C in **Figure 1**. We note that similar results were obtained in the dehydroxylation region using a measurement of the Brinell hardness on the green quartz porcelain samples that contained 50 % of kaolin, 25 % of feldspar, and 25 % of quartz.[21] Such behaviour can be explained only by an improvement of the crystal interfaces, because the crystal interiors remain unchanged.

To explain this peculiar behaviour of the hardness in the dehydroxylation region, we propose a mechanism based on additional electrostatic forces between electrically charged defects on the surfaces of the metakaolinite crystals that fortify the sample.[19] The idea is based on the fact that dehydroxylation is a source of the electrically charged defects inside the crystals.[20,22] Many of them are supposedly located on the crystal faces, and, consequently, they become a source of the additional attractive electrostatic forces between metakaolinite crystals. We may also suppose a solid-state sintering as another source of the fortification of the samples.

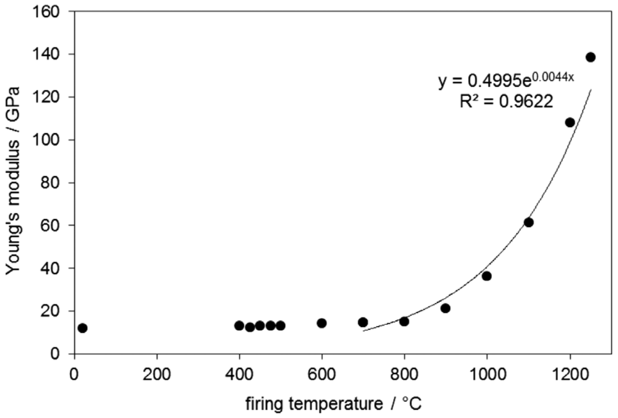

Figure 3: The Young's modulus versus firing temperature
Slika 3: Youngov modul v odvisnosti od temperature žganja

At temperatures of 700–1250 °C, the relationships between the hardness and the firing temperature can be expressed by exponential functions, HSC = 11.049 exp(0.0016t) and HV = 0.435 exp(0.0076t). This can be explained by sintering.[23–25]

As follows from **Figure 3**, the relationship between the Young's modulus and the firing temperature is very similar[25] to those of the Shore hardness and the Vickers hardness (**Figures 1** and **2**). The comparison between the Shore hardness and the Vickers hardness is depicted in **Figure 4**. It is clear that the dependence between them is not linear. Nonlinearity is probably caused by multiple processes that take place in the material during measurement. To create an imprint in the Vickers test, the irreversible crush and redisposition of the crystals

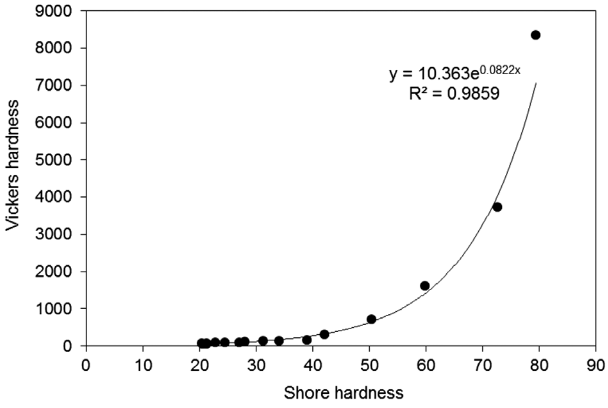

Figure 4: Comparison of the Shore and the Vickers hardnesses
Slika 4: Primerjava trdot po Shoreu in Vickersu

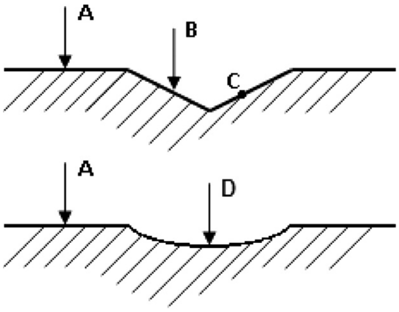

Figure 5: Positions of the sample points visualized by SEM
Slika 5: Položaji točk na vzorcu, prikazani s SEM

occur in the area closest to the sharp pyramidal indenter. This is visible in SEM pictures taken from different points (**Figure 5**) of the sample fired at 950 °C. The sample surface out of the imprint (point A) is shown in **Figure 6**. The surface inside the imprint (point B in **Figure 5**) is clearly ordered: the plate-like crystals are placed and pressed in the plane parallel to the faces of the Vickers pyramid (**Figure 7**). Then the sample was broken to show a fracture surface close to the imprint (point C in **Figure 5**). The thickness of the ordered layer (under the arrows in **Figure 8**) can be estimated, its magnitude being ≈ 3 μm.

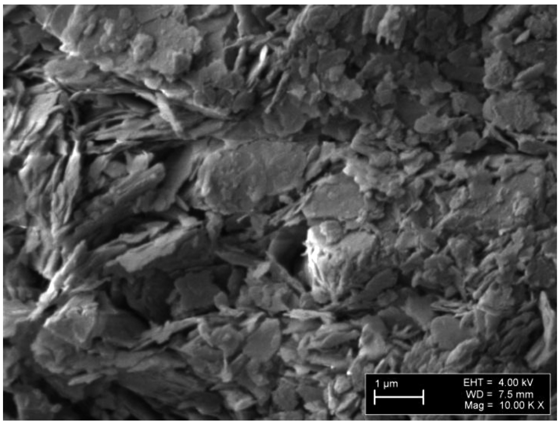

Figure 6: A view of the sample surface at the point A
Slika 6: Videz površine v točki A

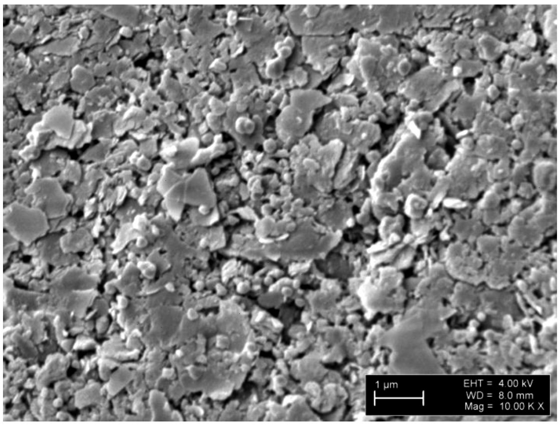

Figure 7: A view of the surface inside the imprint at the point B
Slika 7: Videz površine v vtisku v točki B

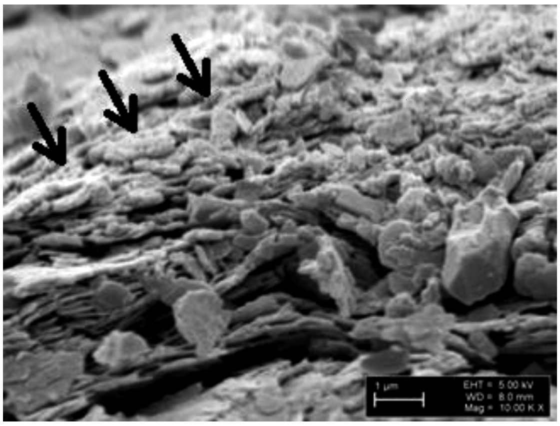

Figure 8: View of the pressed layer (under arrows) at the point C
Slika 8: Videz stisnjene plasti (pod puščicami) v točki C

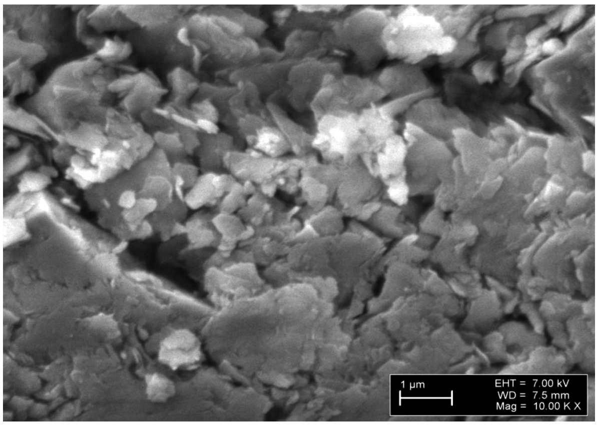

Figure 9: A view of the surface inside the imprint at the point D
Slika 9: Videz površine v vtisku v točki D

In contrast to this, in the Shore test the irreversible changes in the impact area are not so extensive as in the case of the Vickers test, as is shown in **Figure 9** where a sample fired at 950 °C is depicted. The surface inside the imprint (point D in **Figure 5**) is partly ordered: the plate-like crystals are placed and partly pressed in the plane parallel to the spherical imprint. However, a part of the change is reversible. Here the material is partially

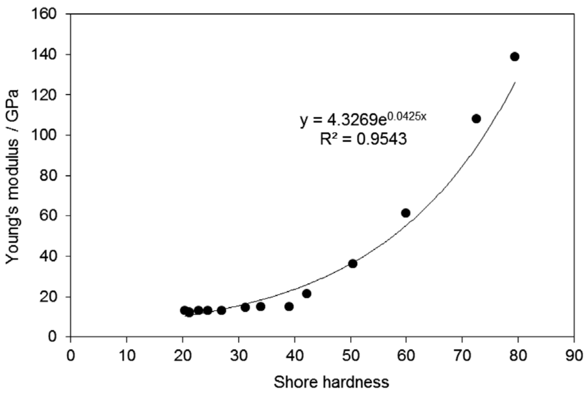

Figure 10: Relationship between the Young's modulus and the Shore hardness
Slika 10: Odvisnost med Youngovim modulom in trdoto po Shoreu

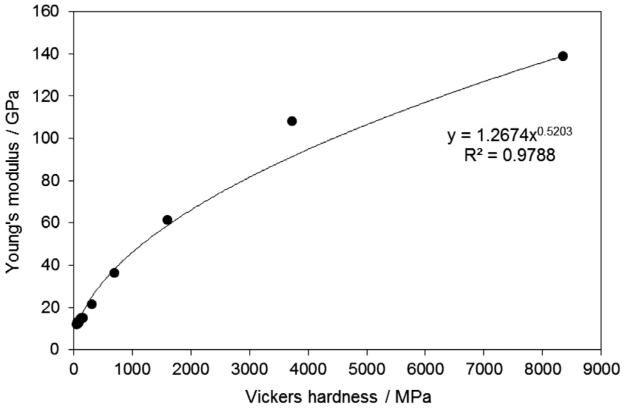

Figure 11: Relationship between the Young's modulus and the Vickers hardness
Slika 11: Odvisnost med Youngovim modulom in trdoto po Vickersu

compressed and decompressed like an elastic spring at the collision between the indenter and the sample.

As noted in the Introduction, we made attempts to find a relationship between the hardness and the Young's modulus. The relationships between the Shore hardness and the Young's modulus as well as between the Vickers hardness and the Young's modulus are shown in **Figures 10** and **11**. They were derived from the results presented in **Figures 1**, **2** and **3**. The experimental data in **Figure 10** can be fitted with an exponential function and the experimental data in **Figure 11** can be fitted with a power function. Both functions have relatively high coefficients of determination.

4 CONCLUSIONS

From the results obtained by the measurement of the hardness on alumina porcelain samples fired at different temperatures we can conclude the following.

The dependencies of the Shore hardness and the Vickers hardness types of hardness on the firing temperature exhibit the same patterns within the three temperature ranges 20–400 °C, 400–700 °C, and 700–1250 °C.

The hardness of the samples fired at temperatures less than 400 °C is approximately the same as the green hardness. This supports the fact that no structural or compositional changes in the sample occur in the 20–400 °C interval.

When dehydroxylation begins (≈ 400 °C), the hardness begins to increase. Until 700 °C the linear increase of the hardness is inhibited by dehydroxylation, which produces electrically charged defects on the surfaces of the kaolinite crystals. The van der Waals forces that act between these defects strengthen the sample structure.

Above 700 °C the hardness increases exponentially, which is related to the sintering and the high-temperature reactions in metakaolinite.

The relationship between the Shore hardness and the Young's modulus can be well fitted with an exponential function (a coefficient of determination $R^2 = 0.9543$), and the relationship between the Vickers hardness and the Young's modulus with a power function (coefficient of determination $R^2 = 0.9788$).

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5 REFERENCES

[1] I. Štubňa, A. Trník, F. Chmelík, L. Vozár, Mechanical properties of kaolin-base ceramics during firing, In: C. Sikalidis (Ed.), Advances in Ceramics – characterization, raw materials, processing, properties, degradation and healing, InTech, Rijeka, 2011, 229–244

[2] ASTM E-448, Standard practice for scleroscope hardness testing of metallic materials, 2008

[3] E. Yasar, Y. Erdogan, Eng. Geol., 71 (**2004**), 281

[4] F. I. Shalabi, E. J. Cording, O. H. Al-Hattamleh, Eng. Geol., 90 (**2007**), 138

[5] R. J. Goble, S. D. Scott, Can. Mineral., 23 (**1985**), 273

[6] J. V. Miloserdin, V. M. Baranov, High-temperature testing of reactor materials, Atomizdat, Moskva 1978

[7] J. S. Zvorono, (Dpt. of Applied Mechanics, St. Petersburg State Electrotechnical University): private information

[8] ASTM E 1327-99, Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics, 2008

[9] L. Sidjanin, D. Rajnovic, J. Ranogajec, E. Molnar, J. Eur. Ceram. Soc., 27 (**2007**), 1767

[10] N. A. Travitzky, A. Goldstein, O. Avsian, A. Singurindi, Mat. Sci. Eng. A-Struct., 286 (**2000**), 225

[11] British Standard BST 903, Methods of testing vulcanized rubber, Part 19, 1950 and Part A7, 1957

[12] H. J. Qi, K. Joyce, M. C. Boyce, Rubber Chem. Technol., 76 (**2003**), 419

[13] S. Yagiz, B. Eng. Geol. Environ., 68 (**2009**), 55

[14] O. Katz, Z. Reches, J. C. Roegiers, Evaluation of mechanical rock properties using a Schmidt hammer, Int. J. Rock Mech. Min., 37 (**2000**), 723

[15] G. Vasconcelos, P. B. Laurenco, C. S. A. Alves, J. Pamplona, Prediction of the mechanical properties of granites by ultrasonic pulse velocity and Schmidt hammer hardness, Proc. 10th North American Masonry Conference, St. Louis, Missouri, 2007, 980–991

[16] I. Yilmaz, H. Sendir, Eng. Geol., 66 (**2002**), 211

[17] I. Štubňa, A. Trník, L. Vozár, Acta Acus. united Ac., 97 (**2011**), 1

[18] F. H. Norton, Fine ceramics – technology and applications, McGraw-Hill Book Co., New York 1970

[19] V. Hanykýř, J. Kitzendorfer, Technologie keramiky, Silis Praha and Vega Hradec Králové, Praha, 2000 (in Czech)

[20] F. Freund, Ber. Deutsche Keram. Ges., 44 (**1967**), 5

[21] I. Štubňa, T. Kozík, Ceram. Int., 23 (**1997**), 247

[22] F. Freund, The defect structure of metakaolinite, In: Proc. Int. Clay Conf., Madrid, 1972, 13–25

[23] I. Štubňa, P. Šín, A. Trník, R. Veinthal, Key Engineering Materials, 527 (**2013**), 14

[24] P. Šín, R. Veinthal, F. Sergejev, M. Antonov, I. Štubňa, Mater. Sci. – Medzg., 18 (**2012**), 90
[25] I. Štubňa, A. Trník, P. Šín, R. Sokolář, I. Medveď, Mater. Tehnol., 45 (**2011**) 4, 375–378