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Diffusion of copper ions into kaolinite layers

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Abstract

Kaolinite transforms to mullite at 1200 °C temperature. The additive copper oxide decreases this temperature by approximately 200 °C. The aim of present paper is to analyze how copper oxide, as additive, influences the high-temperature processes of kaoline. In this article we present the investigations for diffusion of copper ions into the kaolinite matrix. At the work pressed tablets of kaolinite were weighted into powders of crystal copper oxide during heating at 900, 950 and 1000 °C temperatures for 6.5 and 13 h, respectively. Influence of temperature and exposition time at the maximum temperature on the thickness of diffusive layer, formed structures, and dependence of these formed structures from the depth of penetration of copper ions into the kaolinite matrix has been reported using a combination of optical microscopy, SEM, X-ray diffraction and microanalysis.

Keywords: Calcination; X-ray methods; Mullite; CuO; Kaolinite

1. Introduction

Due to its excellent high temperature stability, mechanical properties, low creep rate, low thermal expansion coefficient, low thermal conductivity mullite is an important material for sintering refractories, white-wares, structural clay products, ceramic-matrix composites.[1–5] The transformation of kaolinite to mullite requires a high thermal input. Mullite from kaolinite forms at 1200 °C temperature. This process has been investigated by many scientists. The mechanism for mullite formation has not been adequately explained. Some authors affirm that mullite forms through an intermediate spinel-type phase, others suggest that mullite forms direct from metakaolinite.[6–14]

The literature suggests that copper oxide is one of the most effective additivities for reducing the formation temperature for the conversion of kaolinite to mullite. From our and other researchers' previous investigations it has been detected, that the effect of copper oxide addition results in an exothermal reduction of the transformation temperature in some 150–200 °C.[14–19] The explanation of the mechanism for such temperature lowering differs between our previous and other researchers' investigations and it is not clear until now.

We have noted that active Cu^{2+} ions form the solid solution with $[SiO_4]$ layer and destabilize the matrix of metakaolinite.[14,15] CuO is not stable and decomposes around 1050 °C to Cu_2O. This results in Cu^+ formation, which can diffuse and react with the metakaolinite matrix. Bond energy of Cu–O is not relatively large (187 kJ/mol).[18]

Segnit and Gelb[16] investigated a mixture of kaolinite and CuO (1:1 molar ratio). They noticed that at 900 °C formed a copper spinel phase and quartz type structure. Above this temperature cristobalite began to replace the quartz structure. Špokauskas and Kičas[17] also investigated the same system (1:1 kaolinite:CuO molar ratio). They noted that copper oxide reacts with kaolinite at 800 °C by forming quartz-type phase. Authors called this phase as "q-quartz-type" phase. At higher temperature this phase decomposes, amorphous SiO_2

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and quartz crystallize to cristobalite, and finally mullite is formed.

MacKenzie[18] reports that a little amount of Cu^{2+} (0.5%) exchanges into clay structure and strongly facilitates mullite formation – probably by disruption of the Si–O and Al–O bonds in the precursors phases.

Maslenikova and Konesova link the formation of mullite at a lower temperature to the formation of copper aluminate.[19] After dehydration of kaolinite metakaolinite reacts with copper oxide (20 wt.%) and a copper aluminate $CuAl_2O_4$ is formed. The matrix of metakaolinite loses its stability and the diffusion of the structure elements increases. Therefore, finally, mullite is formed at the lower temperature.

In our previous investigations[14,15] we have noted that copper aluminate forms only with concentration of CuO above 20%. However, we also noted that the 5% CuO has the most influence on mullite and cristobalite formation (see Fig. 2 in ref.[14]). The amount of copper aluminate was not detected in this sample. However, this sample, heated at 1000 °C, had green color, characteristic of copper silicate glasses in which bonds Cu–O–Si exist. In the literature it is not confirmed that the copper silicate forms during the kaolinite heating time. Probably, this color indicates a formation of silicon oxide–copper oxide solid solution – copper oxide intervenes between $[SiO_4]$ layer. The amount (<5%) of CuO was not detected by X-ray diffraction. The peaks of tenorite appears only in the samples with CuO concentrations >10% (heated at 1000 °C).

CuO interaction with silicon oxide aggregates has been widely studied.[20–27] According to Cordoba et al.,[20] copper(II) ions existed in two different environments in the samples from silicon oxide and CuO: one isolated copper(II) species incorporated into the silica network and the other clustered on the silica surface. For samples, where the amount of CuO was 1% or lower the copper(II) ions trapped in the surface were monomolecularly dispersed, and for samples with copper loadings above 1%, small aggregates that are highly dispersed were formed. In the work by Perez-Robles et al.,[22] it was found that some of the copper formed the colloidal CuO crystalline particles and either molecular complexes such as $[Cu^{2+}O_2^{-}]$ or copper substituted Si in the SiO_2 matrix.

The mechanism of CuO influence on kaolinite high-temperature conversion is not clear until nowadays. Authors used various minerals of kaolinite with different impurities; also the influence of CuO concentration on kaolinite transformation into mullite was not investigated. To clarify this mechanism we present the diffusion of copper oxide into the kaolinite layers. Results of these experiments may be useful in explanation of CuO effect on the mullite formation. The sequence of formed crystal phases in the diffusive layer models the CuO treatment in the powder mixture of CuO and kaolinite. It is presumed that the sequence of the reactions that going on at the heating time of kaolinite with CuO is bound with sequence of phases in the diffusive layer depending from depth of CuO penetration – this diffusion models the interaction between powders of CuO and grains of kaolinite.

First, the main aim of the present paper is to analyze how ions of copper intervenes into the kaolinite layers, which crystal phases form, and how these phases depend from the depth of Cu ions penetration. Second, we will compare our results of this article with our and other researches' works and explain the influence of CuO on the mullite formation from kaolinite.

2. Experimental

2.1. Sample materials

In this research mineral kaolin from Prosianov (Ukraine) was used. The mineralogical impurities were quartz, little amounts of anatase and montmorillonite. The chemical composition of this kaoline was as follows (wt.%): SiO_2 (46.78), TiO_2 (0.15), Al_2O_3 (37.52), Fe_2O_3 (0.82), CaO (0.18), MgO (0.15), K_2O (0.42), Na_2O (0.06), loss on ignition 13.8%. Copper oxide was p.a. (Fluka).

2.2. Sample synthesis

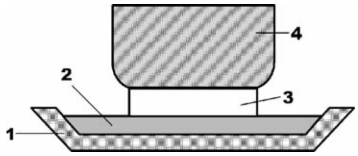
Tablets of 3 mm thickness from kaoline powders were pressed at 230 kg/cm^2 pressure. Pressed tablets were heated at 900, 950, and 1000 °C temperatures (heating rate 25 °C/min) in the chamber furnace at the air atmosphere with exposition at the maximum temperature for 6.5 and 13 h. To increase the contact surface between starting materials, the tablets of kaolinite were weighted on CuO powders at 0.88 N/cm^2 pressure during heating. The schematic diagram of experimental set-up is shown in Scheme 1 (**1**, corundum dish; **2**, powders of CuO; **3**, pressed tablet of kaolinite; **4**, special weight).

The cross-section of heated tablets was investigated by optical microscopy and X-ray microanalysis. The surface of tablets (longitudinal section of tablets) was polished until necessary depth and investigated by XRD.

2.3. Investigation methods

Prepared samples have been investigated by optical microscopy (Olympus BH2 optical microscope), pictures have been obtained by Nikon Coolpix-4500 digital camera (several pictures with the polarized light).

X-ray microanalysis has been investigated by JEOL JXA-50A electronic microscope with beam energy 25 keV. The samples were coated in vacuum with carbon. Microanalysis data were received from 20 μm^2 probe area. Weight percents of Cu were recalculated using ZAF correction.



Scheme 1.

XRD analysis was carried out using D8 Advance (Bruker AXS) difractometer with Cu Kα radiation ($I = 25$ mA, $U = 36$ kV, $\lambda = 1.5405$ Å) in the 5–70° (2θ) range with step size 0.05° and step time 5 s (20–40° 2θ patterns are shown in the article).

3. Results

3.1. Optical microscopy

At the beginning of our experimental work, samples of kaolinite (pressed tablets) were weighted on CuO powders (0.09 kg/cm^2) in the chamber furnace during heating time at 900, 950, and 1000 °C temperatures for 6.5 and 13 h length in maximum temperature. Powders of copper oxide contacted with only one face of tablets of kaolinite (see Scheme 1).

Optical microscopy photos of diffuse layers (cross-section of tablets) between CuO and kaolinite of these heated samples are shown in Fig. 1. Top and bottom parts of figure show photos of samples with respectively, 6.5 and 13 h exposition at the max. temperature [maximum temperature: (a and d) 900; (b and e) 950; (c and f) 1000 °C]. Layer of kaolinite (yellow) is shown at the top of photos, CuO – at the bottom. The diffusive layer is placed between CuO and kaolinite layers. The bound of diffusive layer is placed at the boundaries of kaolinite tablet (it was established from optical microscopy and X-ray microanalysis). An interaction interface is bound with the CuO diffusion into the kaolinite layers. Elements of kaolinite (Al_2O_3 and SiO_2) do not diffuse into the CuO layer (or the degree of diffusion of Al^{3+} and particularly Si^{4+} into CuO is very small and it does not makes considerable influence on the diffusive layer). We can make a presumption that this process was not interdiffusional process. This presumption was also confirmed by X-ray microanalysis: there were no amount of Al and Si detected by X-ray microanalysis (data not shown).

Photos of these diffusive layers also show the depth of Cu^{2+} ions penetration – the bound between diffusive and kaolinite layers is very clearly visible. The depths of Cu^{2+} ions penetration into kaolinite layers (or the thickness of diffusive layer) were 83, 158, 1022 and 199, 1091, 1133 μm in the samples heated at 900, 950, and 1000 °C temperatures with 6.5 and 13 h heating time at the max. temperature, respectively. To compare photos of the samples, heated with 6.5 and 13 h exposition, the exposition at the temperature 950 °C has the greatest influence on the depth of Cu^{2+}-ions penetration. The most intensive transformation of phases was going on at the 950 °C temperature (the thickness of diffusive layer increases about six times in the sample with 13 h to compare with 6.5 h exposition sample). The exposition time has not so great influence on depth penetration at 1000 °C temperature, the difference between the layers of 6.5 and 13 h samples is only about 100 μm. It confirms our previous investigations[14,15] that the most intense phase transformation was going on at the 950 °C temperature.

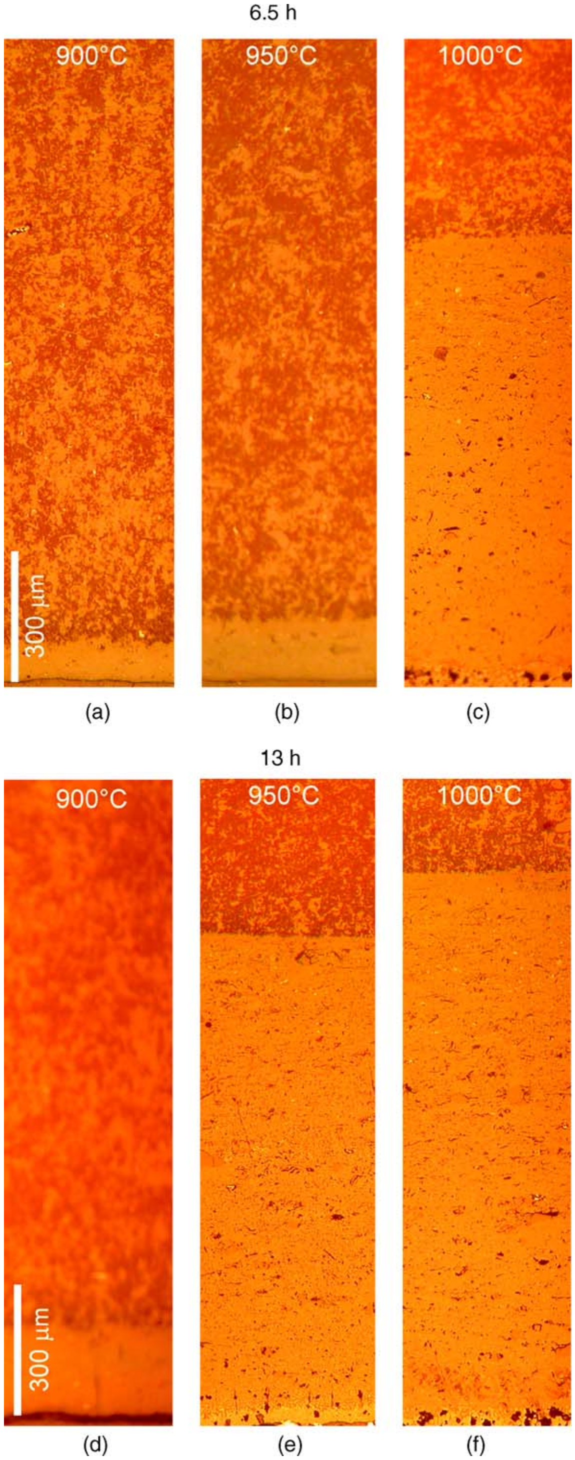


Fig. 1. Optical microscopy photos of diffusive layers (samples heated at 900, 950, and 1000 °C temperatures for 6.5 and 13 h heating length at the maximum temperatures).

Parts a–f of Fig. 2 shows photos of optical microscopy with polarized light of diffusive layers of samples heated at 900, 950, and 1000 °C for 6.5 and 13 h at the maximum temperature, respectively. There are different zones well visible on these pictures. The color of these zones provides information about the phases, which form during heating. A green color indicates a formation of silicon oxide–copper oxide solid solutions, a dark brown color is characteristic of tenorite (copper(II) oxide); red, copper(II) aluminate ($CuAl_2O_4$); a yellow color, copper(I) aluminate ($CuAlO_2$). Colors, depending on the depth of copper ions' penetration, are distributed from brown (CuO layer), red (the middle of diffusive layer) to light green color (boundaries of kaolinite and diffusive layers), and yellow (kaolinite).

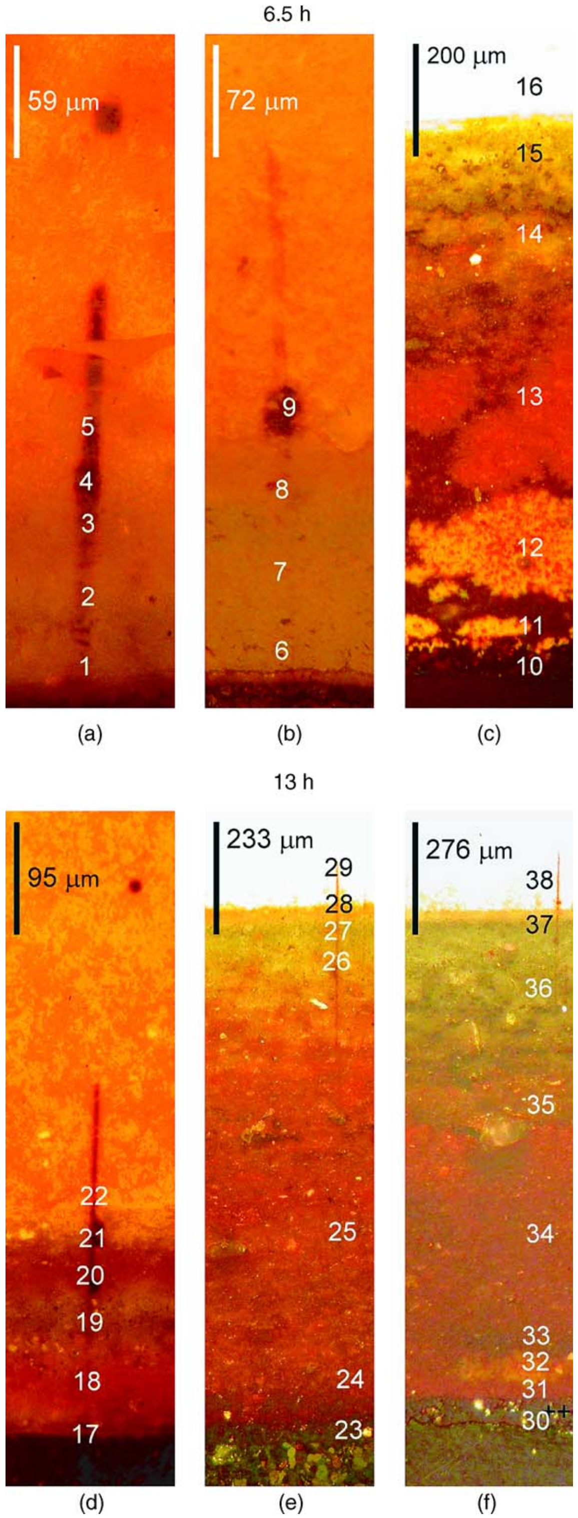


Fig. 2. Optical microscopy photos of diffusive layers with polarized light (samples heated at 900, 950, and 1000 °C temperatures for 6.5 and 13 h heating length at the maximum temperatures).

The optical microscopy gives us primary results – the influence of the depth of Cu^{2+} ions penetration on the formation of different crystal phases. From the CuO to kaolinite layers the phase distribution in the diffusive layer follows: brown zone, tenorite; yellow and red, copper aluminates; green, solid solution of $CuO–SiO_2$. Tenorite mostly formed at the bound of CuO-difussion layer. Deeper, considerable amount of cuprite and cupper(I) aluminate formed. The middle of the diffusion layer was red, there a great amount of copper(II) aluminate formed. At the bound of diffusive-kaolinite layers formed a solid solution of $CuO–SiO_2$. A green color of surface confirms this fact. The formation of solid solution should increase an amount of formed mullite at this zone.

3.2. X-ray microanalysis

Table 1 describes separate zones in the diffusive layer (the same zones are numbered in Fig. 2a–f). These separate zones were investigated by X-ray microanalysis to determine the amount of copper in the diffusive layer. The data of X-ray microanalysis in these points are reported in the third and sixth columns.

Fig. 3 shows Cu distribution in diffusive layers. Samples heated at 900 °C 6.5 h, 900 °C 13 h, 950 °C 6.5 h and 950 °C 13 h, 1000 °C 6.5 h, 1000 °C 13 h have similar thickness of diffusive layers; X-ray microanalysis of these samples is shown in Fig. 3a and b, respectively. The bound between CuO-diffusive layer is shown by dotted line. Arrow indicates the bound between diffusive and kaolinite layers.

The amount of copper, depending from the depth of diffusive layer, should evenly decrease. However, X-ray microanalysis data of samples heated at lower temperatures (900 and 950 °C) show the increase of copper amount not only at the copper oxide layer, but also at the bound of diffusive-kaolinite layers [see curves in Fig. 3a, points **3**, **8**, and **21**; see also Table 1 data (wt.% of Cu) at the same points]. This increase of amount at the bound of diffusive-kaolinite layers was small in the samples heated at the higher temperature (1000 °C) [see curves in Fig. 3b, points **15**, **27**, and **28** and Table 1 for amount of Cu (wt.%)]. No increase of this amount was detected in the sample heated at 1000 °C for 13 h (see Fig. 3b, points **36** and **37**).

Curve of sample, heated at 950 °C for 6.5 h, has two peaks near the **6** point. First peak is bound with CuO layer, the second – with diffusion of CuO in the fracture of kaolinite layer. Other samples also contain several small peaks in the diffusive layer – probable through formation of conglomerations of copper oxide combinations and small fractures in the diffusive layer.

It is difficult to explain the increase of copper amount at the boundary of kaolinite-diffusive layer. It may to explain

Table 1
X-Ray microanalysis data in the zones described in Fig. 2

6.5 h Exposition time			13 h Exposition time		
Number of point	Description of points	Cu (wt.%)	Number of point	Description of points	Cu (wt.%)
900 °C			900 °C		
1	10–15 μm depth of diffusive layer (brown zone)	2.07	**17**	10 μm depth of diffusive layer	2.64
2	The middle of the diffusive layer	2.80	**18**	Red zone	2.24
3	Near the bound of diffusive layer	3.04	**19**	Middle of diffusive layer	2.41
4	Kaolinite near the diffusive layer	0.39	**20**	Brown zone	3.37
5	Kaolinite; 15 μm from diffusive layer	0.25	**21**	Near the kaolinite layer	3.15
			22	The kaolinite layer (20 μm from diffusive layer)	0.21
950 °C			950 °C		
6	15 μm depth of diffusive layer	3.85	**23**	Copper oxide layer	34.27
7	The middle of diffusive layer	2.98	**24**	100 μm depth of diffusive layer	33.18
8	Diffusive layer near the kaolinite layer	4.73	**25**	Middle of diffusive layer (red zone)	8.98
9	Kaolinite layer (20 μm from bound of diffusive layer)	0.10	**26**	Green zone	3.18
			27	Yellow zone	3.33
			28	Border with kaolinite	3.22
			29	Kaolinite layer (20 μm from diffusive layer)	0.21
1000 °C			1000 °C		
10	Copper oxide layer	39.43	**30**	Edge of diffusive layer	33.11
11	Yellow zone	6.80	**31**	Brown zone	7.40
12	Spinel zone	8.09	**32**	Yellow zone	6.40
13	Middle of diffusive layer	5.89	**33**	Brown zone	5.55
14	The green color zone (80 μm from kaolinite layer)	2.64	**34**	Middle of diffusive layer	4.71
15	Different layer, 15 μm from kaolinite	2.74	**35**	Ruddy brown zone	3.60
16	Kaolinite (20 μm from diffusive layer)	0.47	**36**	Green zone	3.39
			37	Border with kaolinite	3.17
			38	Kaolinite layer (20 μm from diffusive layer)	0.22

that some diffusion barrier forms at this boundary. At higher temperature this barrier decreases. To compare the distribution of samples heated at 950 °C for 6.5 and 13 h, the decrease of above mentioned CuO amount at kaolinite-diffusive layer considerably differs (compare curves of samples heated at 950 °C for 6.5 and 13 h). It concludes, that the longer heating at maximum temperature decreases this barrier.

This increase of amount may be explained also by the process of sintering. The diffusive layer was more sintered than heated kaolinite layer. Also, the formation of stable phase –

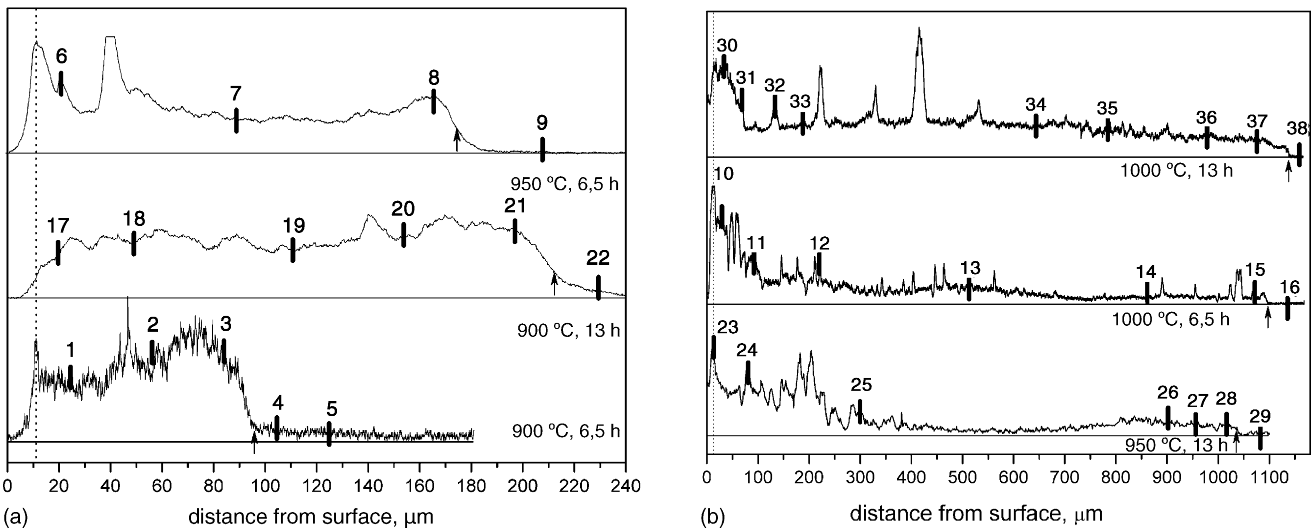


Fig. 3. Distribution of Cu in the diffusion layers in the samples conducted by X-ray microanalysis. Points (typed in boldface) are explained in Table 1 and Fig. 2.

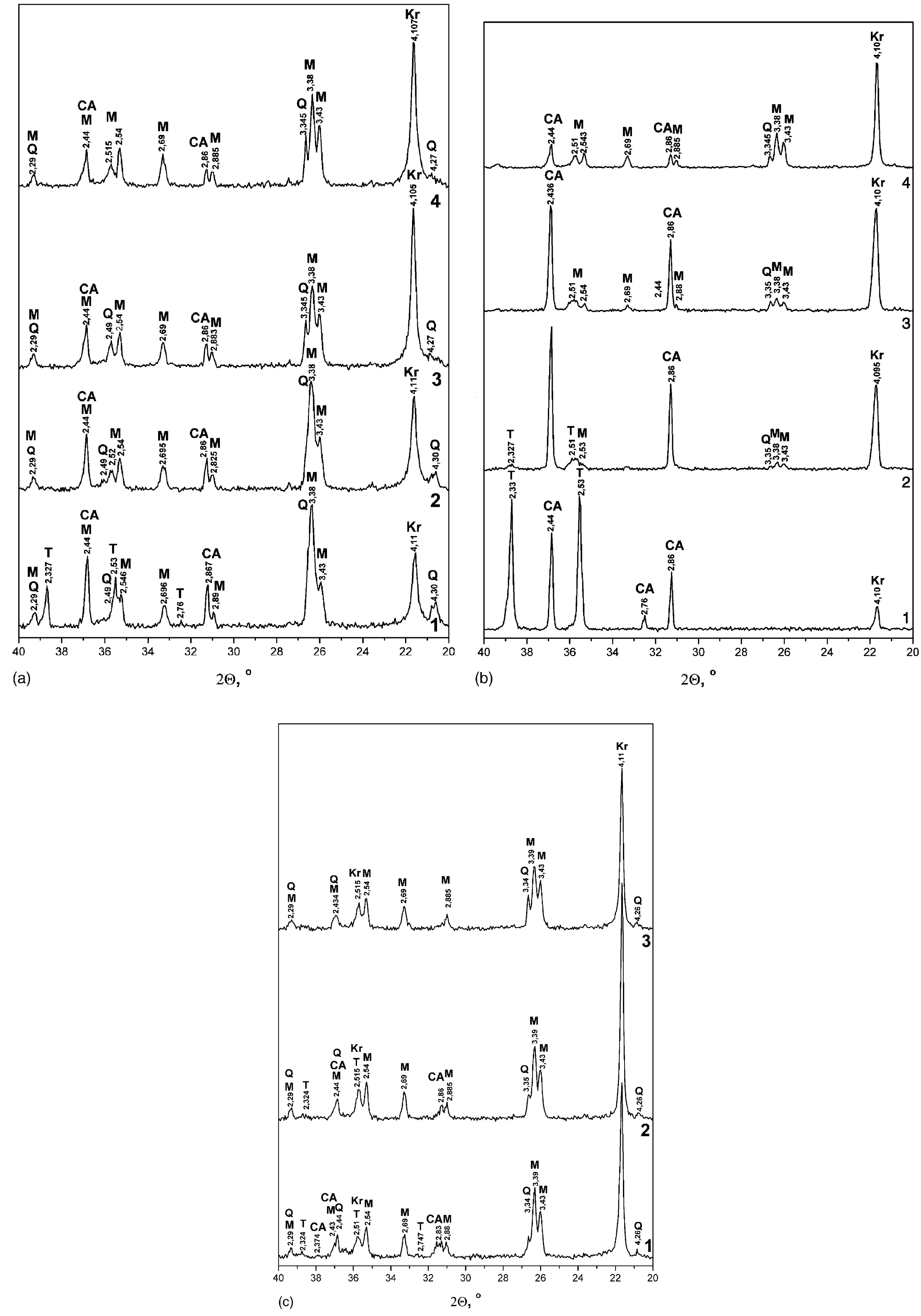


Fig. 4. XRD peaks of samples heated at 900 (a), 950 (b), 1000 °C (c) temperatures for 13 h (M, mullite; Kr, cristobalite; Q, quartz; T, tenorite; CA, copper aluminate).

mullite, may trouble the further diffusion of copper ions into the kaolinite layers.

3.3. X-ray diffraction analysis

The cross section of tablets was polished until the change of color and investigated by XRD. Fig. 4a shows X-ray diffraction peaks of the sample heated at the 900 °C (13 h time length) in following depths of diffusive layer: graph 1–0 μm (near zone **17**, see Fig. 2 and Table 1); graph 2–93 μm (near zone **19**); graph 3–120 μm (between zones **19** and **20**) and graph 4–183 μm (near zone **21**). Fig. 4b shows X-ray data of the sample heated at 950 °C temperature (13 h time length): graph 1–0 μm (near zone **23**); graph 2–75 μm (near zone **24**); graph 3–93 μm (between zones **24** and **25**); graph 4–700 μm (between zones **25** and **26**); and Fig. 4c, 1000 °C (13 h time length): graph 1–400 μm (between zones **33** and **34**); graph 2–800 μm (near zone **35**); graph 3–1160 μm (near zone **37**).

X-ray patterns shows that at the boundary of copper oxide-diffusive layers mostly tenorite and copper aluminate forms. See graphs 1 in Fig. 4a and b.

The pictures of optical microscopy show that the middle of diffusive layer has a red color; that is the characteristic color for the copper aluminate (see red color in the middle of diffusive layer in Fig. 2). Copper oxide reacts to aluminum oxide and amorphous SiO_2 crystallizes into cristobalite. The formation of copper aluminate and cristobalite is also confirmed by X-ray diffraction analysis. Diffraction patterns of copper aluminate appear in the middle of diffusive layer (see Fig. 4a and b, graphs 2, 3; c, graph 2). Mostly copper aluminate forms at 950 °C temperature. The amount of copper aluminate was lower in 1000 °C sample than in 950 °C.

Mostly mullite forms near the bound of diffusive-kaolinite layers; see diffractions patterns in Fig. 4a and b, graphs 4; and c, graph 3. The amount of copper aluminate decreases in this zone.

From X-ray diffraction data it is concluded that at the boundary of copper oxide-diffusive layers mostly formed tenorite and copper aluminate. Mostly cristobalite and copper aluminate formed in the middle of diffusive layers. Mostly mullite formed at the bound of kaolinite-diffusive layers.

We noted that copper aluminate forms only with >20% CuO in our previous investigations. As we have expected by X-ray microanalysis (Fig. 3), the amount of CuO in the middle layers was 3–7% (Cu amount recalculated to CuO). So, it may be possible, that the primary formed mullite interacts with copper ions. Copper oxide reacts with alumina, destroy mullite; and, finally, copper aluminate forms. With decomposition of mullite, amorphous SiO_2 exudes and crystallizes into cristobalite. X-ray investigations (Fig. 4) show that mostly crystobalite crystallizes in the middle of diffusive layer (Fig. 4a, graph 3; b, graph 3; c, graph 2).

To confirm our preposition we have investigated the change of contact surface between kaolinite and copper oxide with the increasing of temperature. Samples from kaolinite were weighted into CuO powders during heating time for 2 h at 850, 900, and 950 °C temperatures. Fig. 5 shows the X-ray analysis of this contact surface. The contact surface of samples, heated at 850 and 900 °C, had a green color, at 950 °C – a red color. Mullite was formed at the contact surface in the samples heated at 850 and 900 °C temperatures, cristobalite and copper aluminate crystallized only at the 950 °C temperature. These results also confirm our previous presumption that formation of copper aluminate results in interaction between copper ions and formed primary mullite. First of all, Cu^{2+} ions destroy matrix of silicon oxide layer, green color $CuO–SiO_2$ solid solution was formed. It destabilizes the matrix of metakaolinite; mullite began to form. After this process, with increasing of CuO amount, copper oxide interacts with primary formed mullite – red-color copper aluminate and cristobalite form at this time.

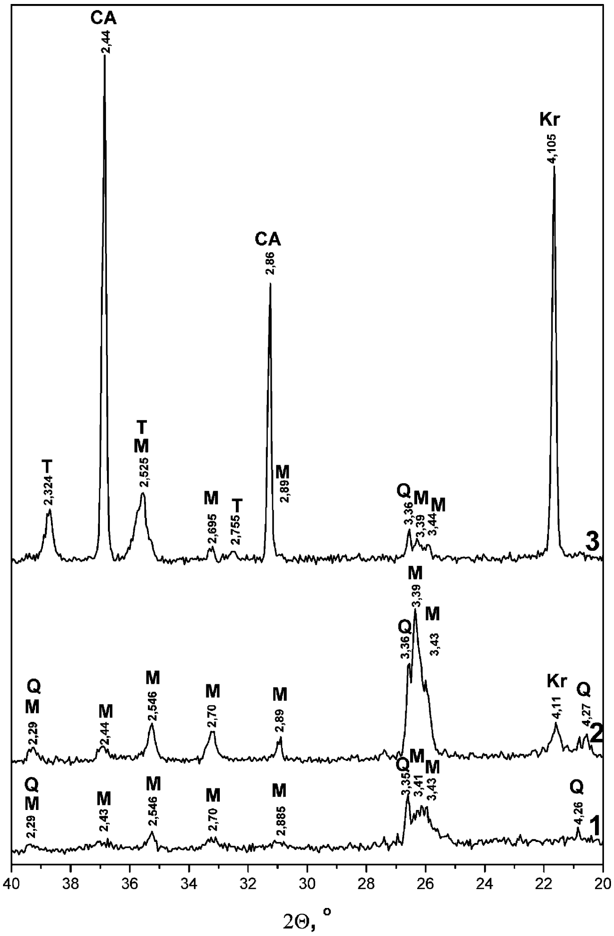


Fig. 5. XRD peaks of contact surfaces between kaolinite and copper oxide (**1**, 850; **2**, 900; **3**, 950 °C) (M, mullite; Kr, cristobalite; Q, quartz; T, tenorite; CA, copper aluminate).

4. Discussion

According to Segnit and Gelb[16] and Špokauskas and Kičas[17] a metastable quartz-type structure forms during kaolinite–mullite conversion with CuO additive (kaolinite:CuO molar ratio 1:1). This metastable phase forms together with copper spinel (copper aluminate) at 900–950 °C, and above this temperature forms thermodinamically stable phases – cristobalite and mullite. Both these works used mixtures of CuO and kaolinite with a higher concentration of CuO (1:1 molar ratio kaolinite:CuO is approximately 17 wt.% of CuO) as we have used at our previous investigations (5 wt.% CuO). Masleknikova and Konesova[19] used 20% CuO amount in the kaolinite–CuO mixture.

As we have noted in our previous investigations, copper aluminate also forms only in the samples with concentration of CuO $\geq$20%. But the most effectively mullite formation was occurred with 5% CuO and in this sample no copper–alumina spinel was detected. As we expected in experiments, described in this present article, the concentration of Cu in the diffusive layer was about 4–15% (see Table 1). However, the middle of diffusive layer has a red color and copper aluminate was also detected by X-ray diffraction (see Fig. 4). The CuO concentration in the middle of diffusive layer was 4–10% (recalculated from Cu amount). The formation of copper aluminate was unexpected at this zone (it contradict to our previous investigations that copper aluminate forms with greater CuO concentrations as 20%). Therefore, we presume that copper ions interact with primary formed mullite. Copper ions destroy primary formed mullite and copper aluminate forms. This fact has been confirmed by X-ray investigations presented in Fig. 5.

The influence of CuO on the mullite formation from kaolinite can be explained as follows. First, copper ions make a solid solution with silicon oxide in the kaolinite matrix. This fact is confirmed by formation of a green color at the bound of diffusive–kaolinite layers and by X-ray diffraction analysis: the peaks of α-cristobalite were shifted to lower diffraction angles (4.05–4.11 Å) in the X-ray diffraction patterns (Figs. 4 and 5). Second, destabilization of silica layer influences on mullite formation at the lower temperature.

The influence of CuO on mullite formation can be also explained by CuO oxide conversion to Cu_2O. As it is known from literature and our previous investigations CuO is stable in air up to 1025 °C, Cu_2O is stable phase between 1025 and 1100 °C. These changes of copper oxidation state may have a great influence on positive copper effect on mullite formation.

Segnit and Gelb and Špokauskas and Kičas explained the positive influence of copper ions by the Cu^{2+} radius size. Replacement Si^{4+} by Al^{3+} in the silicon oxygen tetrahedra requires concomitant stuffing of the open spaces to render the structure electrically neutral. Copper ions with ionic radius (87 pm) can enter in this way.

5. Conclusions

Cu^{2+} ions active diffuse into kaolinite layers. Depending from copper ions penetration copper phases in the diffusive layer distributed as follows: tenorite, copper aluminate, and copper oxide–silica solid solution.

The most intensive transformation of phases was going on at the 950 °C temperature.

Obtained results explain processes in the mixture of kaolinite and copper oxide at the heating time. First, a green color solid solution of copper and silicon oxides is formed (at the temperature 800 °C). Destabilized silicon oxide layer influences on mullite formation at the lower temperature (with additive, 1000 °C; without 1200 °C).

Primary mullite interacts with copper ions: copper reacts to alumina and finally copper aluminate forms.

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References

1. Aksay, I. A., Dabbs, D. M. and Sarikaya, M., Mullite for structural, electronic and optical applications. *J. Am. Ceram. Soc.*, 1991, **74**, 2343–2358.
2. Fernandez, E. and Baudín, C., Creep damage in different $3Al_2O_3$–SiO_2 mullites tested in 4-point bending. *J. Eur. Ceram. Soc.*, 2001, **21**, 2243–2251.
3. Slaoui, A., Bourdais, S., Beaucarne, G., Pootmans, J. and Reber, S., Polycrystalline silicon solar cells on mullite substrates. *Solar Energy Matter Solar Cells*, 2002, **71**, 245–252.
4. Peters, P. W. M., Daniels, B., Clemens, F. and Vogel, W. D., Mechanical characterization of mullite-based ceramic matrix composites at test temperatures up to 1200 °C. *J. Eur. Ceram. Soc.*, 2000, **20**, 31–535.
5. Chen, C. Y. and Tuan, W. H., The processing of kaolin powder compact. *Ceram. Int.*, 2001, **27**, 795–800.
6. Sonuparlak, B., Sarikaya, M. and Aksay, I. A., Spinel phase formation during the 980 °C exothermic reaction in the kaolinite-to-mullite raction series. *J. Am. Ceram. Soc.*, 1987, **70**, 837–842.
7. Chakravorty, A. K. and Ghosh, D. K., Kaolinite–mullite reaction series: the development and significance of a binary alumosilicate phase. *J. Am. Ceram. Soc.*, 1991, **74**, 1401–1406.
8. Lee, S., Kim, Y. J. and Moon, H. S., Phase transformation sequence from kaolinite to mullite investigated by an energy-filtering transmission electron microscope. *J. Am. Ceram. Soc.*, 1999, **82**, 2841–2848.
9. Chakraborty, A. K., DTA study of preheated kaolinite in the mullite formation region. *Thermochim. Acta*, 2003, **398**, 203–209;
Chakraborty, A. K., Resolution of thermal peaks of kaolinite in thermochemical analysis and differential thermal analysis studies. *J. Am. Ceram. Soc.*, 1992, **75**, 2013–2016.
10. Gualtieri, A., Belloto, M., Artioli, G. and Clark, S. M., Kinetic study of the kaolinite–mullite reaction sequence, Part I: kaolinite dehydroxylation; Part II: mullite formation. *Phys. Chem. Minerals*, 1995, **22**, 207–224.
11. Brindley, G. W. and Nakahira, M., The kaolinite–mullite reaction series: III. The high-temperature phases. *J. Am. Ceram. Soc.*, 1959, **42**, 319–324.
12. MacKenzie, K. J. D., Meinhold, R. H., Brown, I. W. M. and White, G. V., The formation of mullite from kaolinite under various reaction atmospheres. *J. Eur. Ceram. Soc.*, 1996, **16**, 115–119.
13. Kanka, B. and Schneider, H., Sintering mechanisms and microstructural development of coprecipitated mullite. *J. Mater. Sci.*, 1994, **29**, 1239.

14. Martišius, T. and Giraitis, R., Influence of copper oxide on mullite formation from kaolinite. *J. Mater. Chem.*, 2003, **13**, 172–176.
15. Giraitis, R., *Untersuchungen der Reaktionen von charakteristischen Alumosilikaten beim Vorhandensein der Intensivierungszusätze*. Ph.D. thesis, Institute of Chemistry, Vilnius, 1996 (in German language).
16. Segnit, E. R. and Gelb, T., Metastable quartz-type structures formed from kaolinite by solid state reaction. *Am. Mineral.*, 1972, **5**, 1504.
17. Špokauskas, A. A. and Kičas, P. V., Formation of quartz-type phases in the reaction between iron, copper, zinc, magnesium and lithium ions with metakaolinite. *Sbornik Trudov*, 1979, **12**, 136 (in Russian language).
18. MacKenzie, K. J. D., The effects of impurities on the formation of mullite from kaolinite-type minerals. *Trans. Brit. Ceram. Soc.*, 1969, **68**, 97.
19. Maslenikova, G. N. and Koneshova, T. I., The process of silicate ceramic formation. *Neorg. Mater.*, 1989, **25**, 181 (in Russian language).
20. McBridge, M., Copper(II) interactions with kaolinite: factors controlling adsorbtion. *Clays Clay Minerals*, 1978, **26**, 101.
21. Cordoba, G., Arroyo, R., Fierro, J. L. G. and Viniegra, M., Study of xerogel–glass transition of CuO/SiO_2. *J. Solid State Chem.*, 1996, **123**, 93.
22. Perez-Robles, J. F., Garcia-Rodriguez, F. J., Yandez-Limon, J. M., Esponoza-Beltran, F. J., Vorobiev, Y. V. and Gonzalez-Hernandez, J., Characterization of sol–gel glasses with different copper concentrations treated under oxidizing and reducing conditions. *J. Phys. Chem. Solids*, 1999, **60**, 1729–1736.
23. de Sousa, E. M. B., Porto, A. O., Schilling, P. J., Alves, M. C. M. and Mohallem, N. D. S., Study of the structural evolution of copper-doped porous silica gels. *J. Phys. Chem. Solids*, 2000, **61**, 853–861.
24. Altamirano-Juárez, D. C., Carrera-Figueiras, C., Garnica-Romo, M. G., Mendoza-Lopez, M. L., Ortuno-Lopez, M. B., Perez-Ramos, M. E. *et al.*, Effects of metals on the structure on the heat-treated sol–gel SiO_2 glasses. *J. Phys. Chem. Solids*, 2001, **62**, 1911–1917.
25. Manzanares-Martinez, J., Garcia-Cerda, L. A., Ramirez-Bon, R., Espinoza-Beltran, F. J., Perez-Robles, J. F. and Gonzalez-Hernandez, J., Stabilization of copper-based colloidal particles in sol–gel SiO_2 thin films. *Thin Solid Films*, 2000, **365**, 30–35.
26. Garcia-Cerda, L. A., Mendoza-Gonzalez, O., Perez-Robles, J. F. and Gonzalez-Hernandez, J., Structural characterization and properties of colloidal silica coatings on copper substrates. *Mater. Lett.*, 2002, **56**, 450–453.
27. Muhibbullah, M., Hakim, M. O. and Choudhury, M. G. M., Studies on Seebeck effect in spray deposited CuO thin film on glass substrate. *Thin Solid Films*, 2003, **423**, 103–107.