

The structural studies of aluminosilicate gels and thin films synthesized by the sol-gel method using different Al_2O_3 and SiO_2 precursors

ANNA ADAMCZYK*

AGH University of Science and Technology, Faculty of Materials Science and Ceramics,
al. Mickiewicza 30, 30-059 Kraków, Poland

Aluminosilicate materials were obtained by sol-gel method, using different Al_2O_3 and SiO_2 precursors in order to prepare sols based on water and organic solvents. As SiO_2 precursors, Aerosil 200TM and tetraethoxysilane TEOS: $\text{Si}(\text{OC}_2\text{H}_5)_4$ were applied, while DisperalTM and aluminium secondary butoxide ATSB: $\text{Al}(\text{OC}_4\text{H}_9)_3$ were used for Al_2O_3 ones. Bulk samples were obtained by heating gels at 500 °C, 850 °C and at 1150 °C in air, while thin films were synthesized on carbon, steel and alundum (representing porous ceramics) substrates by the dip coating method. Thin films were annealed in air (steel and alundum) and in argon (carbon) at different temperatures, depending on the substrate type. The samples were synthesized as gels and coatings of the composition corresponding the that of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ mullite because of the specific valuable properties of this material. The structure of the annealed bulk samples and coatings was studied by FT-IR spectroscopy and XRD method (in standard and GID configurations). Additionally, the electron microscopy (SEM) together with EDS microanalysis were applied to describe the morphology and the chemical composition of thin films. The analysis of FT-IR spectra and X-ray diffraction patterns of bulk samples revealed the presence of $\gamma\text{-Al}_2\text{O}_3$ and $\delta\text{-Al}_2\text{O}_3$ phases, together with the small amount of SiO_2 in the particulate samples. This observation was confirmed by the bands due to vibrations of Al–O bonds occurring in $\gamma\text{-Al}_2\text{O}_3$ and $\delta\text{-Al}_2\text{O}_3$ structures, in the range of 400 to 900 cm^{-1} . The same phases ($\gamma\text{-Al}_2\text{O}_3$ and $\delta\text{-Al}_2\text{O}_3$) were observed in the deposited coatings, but the presence of particulate ones strongly depended on the type of Al_2O_3 and SiO_2 precursor and on the heat treatment temperature. All thin films contained considerable amounts of amorphous phase.

Keywords: *sol-gel method; aluminosilicate materials; FT-IR spectroscopy; XRD method; SEM*

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1. Introduction

Although the structure of the aluminosilicate materials has been described in many scientific articles, the studies of bulk samples or coatings of $\text{Al}_2\text{O}_3\text{--SiO}_2$ system still become the subject of many projects. Especially, the mullite and mullite-like materials have properties which allow them to find the applications in many branches: medicine (coatings on different type implants [1]), a space technology (surface and parts of space ships), in devices working in extremely high temperatures [2] or as substrates in solar cells [3] and electronic packages [4]. The presence of the mullite phase is valuable because of its remarkable physical and chemical properties, such as the good thermal and

chemical stability, the thermal shock resistance, the low thermal expansion and the conductivity. Thus, the deposition of mullite-like anticorrosive coatings on different types of substrates could improve the chemical and thermal resistance and stability of all the materials and enable one to find wider application possibilities [5]. The protecting activity of the mullite-like thin film strongly depends on its structure and morphology which is connected not only with the synthesis conditions but also with the type of Al_2O_3 and SiO_2 precursors applied [6].

The aluminosilicate thin films can be deposited by different methods: dip-coating, spin-coating, CVD, PVD and others [7–11]. In this work, aluminosilicate coatings were synthesized by sol-gel method and deposited by a dip-coating on different materials, which can find applications in many

*E-mail: aadamcz@agh.edu.pl

branches (mentioned above), as medicine (coatings on a steel), electronics (coatings on alundum) or technologies, where elevated temperatures are applied (coatings on carbon fibres or their composites).

The main target of this work was to investigate and compare the structures of bulk samples and thin films synthesized by the sol-gel method in relation to different types of Al_2O_3 and SiO_2 precursors. Also the studies of structures of the coatings synthesized from the obtained sols were conducted. Additionally, thin films were deposited on different types of substrates, depending on the further possible applications.

2. Materials and methods

Alumina and silica one-component sols as well as alumina-silica mixed sols can be prepared using different types of Al_2O_3 and SiO_2 precursors. In this work, the following precursors were applied: Disperal P-2TM: AlOOH and aluminium secondary butoxide, ATSB: $\text{Al}(\text{OC}_4\text{H}_9)_3$ for introducing Al_2O_3 . In addition, tetraethoxysilane TEOS: $\text{Si}(\text{OC}_2\text{H}_5)_4$, tetramethoxysilane TMOS: $\text{Si}(\text{OCH}_3)_4$ and AerosilTM (SiO_2) were used for SiO_2 . Four different suspensions were prepared basing on the precursors mentioned earlier, as is given in Table 1.

There are two main methods of the synthesis of sols used for coating deposition: first – to prepare a colloidal suspension, and second – to carry out the hydrolysis and the polycondensation reactions between alkoxides and alkoxysilanes dissolved in non-aqueous solvents. Both of these methods have been applied in the present work.

Sol 1 (Table 1) was prepared as a mixture of one-component silica and alumina sols. The silica sol was obtained from TEOS diluted in ethanol with water addition at a molar ratio of $\text{TEOS}/\text{H}_2\text{O} = 4:1$ and HCl , applied as a catalyst with $\text{HCl}/\text{TEOS} = 1:40$ molar ratio. This procedure allowed us to obtain the silica sol with 7 % SiO_2 mass fraction [12]. The alumina sol was prepared by applying sonocatalysis method for obtaining Disperal P-2TM dispersed in distilled water.

Both sols were then mixed in a molar ratio proper to obtain a suspension of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ mullite composition.

Sol 2 was prepared as a mixture of two colloidal suspensions, one obtained with Disperal P-2TM (similar procedure as in case of sol 1), and the other one: using AerosilTM. To mix and homogenize both sols up to $\text{Al}_2\text{O}_3/\text{SiO}_2 = 3:2$ molar ratio, the sonocatalysis was once more applied.

Sol B1 was synthesized with TEOS and ATSB as SiO_2 and Al_2O_3 precursors, respectively. Silica sol was obtained in the same way as in the case of sol 1 but with a higher SiO_2 concentration (15 % mass fraction). To prepare boehmite sol, ATSB, 2-butanol, distilled water and HNO_3 were mixed (by slow stirring) in a proper order. The synthesis was conducted in an argon atmosphere, according to the procedure described in Yoldas' work [13]. The mullite composition of the final suspension was obtained by mixing a proper amount of alumina and silica sols.

In sol B2, ATSB and TMOS as Al_2O_3 and SiO_2 precursors, respectively, were mixed carefully in the same ratio as in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ mullite and then dissolved in 2-butanol, with distilled water and HNO_3 as a catalyst, in a molar ratio of $\text{H}_2\text{O}/\text{HNO}_3 = 1:0.07$. The whole synthesis was also carried out in an argon atmosphere [14].

The samples were obtained as a bulk material and in a form of coatings deposited on different substrates, such as the carbon composite (or in some cases on the incompact fibres), on steel and on alundum, representing the porous ceramics. All bulk samples were prepared by annealing (in air) of the gels obtained from sol 1, sol 2 as well as B1 and B2 sols. The temperatures of the heat treatment were chosen so as to achieve the level at which the mullite phase was possible to be obtained (1150 °C), and to go through temperatures at which the particulate coatings are heat treated (500 °C and 850 °C) after deposition.

All coatings were deposited by the dip-coating method, using a dip coater with the stable speed of 0.02 m/s during dipping. They were then annealed

Table 1. The components of suspensions: sol 1, sol 2, B1 and B2.

sol	sol 1	sol 2	B1	B2
basic components	TEOS Disperal P-2™	Aerosil™ Disperal P-2™	TEOS ATSB	TMOS ATSB
solvents	ethanol, water	water	ethanol, butanol, water	ethanol, butanol, water

in air at 850 °C or 1150 °C, or in argon at 500 °C, depending on the type of substrate.

All samples were studied by XRD method using X'Pert Panalytical Diffractometer (with CuK α radiation). The X-ray diffraction patterns were measured in a standard or GID (Grazing Incidence Diffraction, $\omega = 1.5^\circ$) configuration. The phase analysis was carried out using HighScore Plus software and PDF2 database.

FT-IR spectra were obtained with a FTS-60V BIO-RAD spectrometer. They were measured as the absorption spectra of samples in a form of KBr pellets, also in case of thin films. All spectra were collected in the range of 400 to 4000 cm $^{-1}$, with 4 cm $^{-1}$ resolution.

To study the morphology and the chemical composition of the coatings, SEM imaging together with EDS microanalysis were carried out using FEI NOVA SEM microscope.

3. Results and discussion

3.1. Bulk samples

3.1.1. XRD measurements

In samples obtained from sols 1 and 2, different forms of Al $_2$ O $_3$ were crystallizing from the very beginning of the annealing process, whereas the samples of sols B1 and B2 remained amorphous up to 500 °C (Fig. 1a – 1d). In the diffraction patterns of sol 1 sample, the first peaks due to γ -Al $_2$ O $_3$ (4-0880 – γ -Al $_2$ O $_3$ Identification Card Number) were observed at 500 °C, then at 1050 °C the presence of δ -Al $_2$ O $_3$ (46-1131) was confirmed. At 1150 °C, both phases remained in the annealed sample, without any other phase transformation. In the diffraction patterns of sol 2 sample, reflections assigned to the cubic γ -Al $_2$ O $_3$ were first observed at 500 °C, then at 850 °C, tetragonal δ -Al $_2$ O $_3$ was

detected, whereas at 1050 °C also θ -Al $_2$ O $_3$ was noticed. The sample heat treated at 1150 °C consisted of three crystalline phases: γ -Al $_2$ O $_3$, δ -Al $_2$ O $_3$ and θ -Al $_2$ O $_3$ (9-0440) with a very slight amount of silica (Identification Card No. 47-1301, not marked in Fig. 1b).

In the diffraction patterns of B1 and B2 samples, the first reflections of γ -Al $_2$ O $_3$ were observed for the samples annealed at 850 °C, while at 1050 °C and 1150 °C only reflections characteristic of the mullite (79-1452, 79-1455) and the cristobalite (71-0785, 75-0923) phases were noticed [15]. The intensity of these peaks increased with the rising temperature which confirmed the increasing crystallization of the samples. The parallel existence of mullite and cristobalite in both samples points out that the crystallized mullite phase is probably poor of silica in comparison to the raw 3Al $_2$ O $_3$ ·2SiO $_2$ mullite composition because of the concurrent crystallization of cristobalite phase.

To observe structural changes and phase transformations in the system free of silica, the pure AlOOH was subjected to heat treatment at the same temperatures as the aluminosilicate samples. Basing on the diffraction patterns of AlOOH (Fig. 1e), one can observe the presence of γ -Al $_2$ O $_3$, at 500 °C, which at 850 °C transforms partly into δ -Al $_2$ O $_3$ and finally at 1050 °C, into three co-existing γ -Al $_2$ O $_3$, δ -Al $_2$ O $_3$ and θ -Al $_2$ O $_3$. At 1150 °C, only pure α -Al $_2$ O $_3$ (corundum 77-2135) as a final product is noticed. The peak at about 42.5°(2 θ) of the changing intensity, observed in particular diffraction patterns, is due to the sample holder of the diffractometer.

3.1.2. FT-IR measurements

In the spectra of all raw samples, the bands at about 1650 cm $^{-1}$, due to the molecular water bending vibrations, and at 3440 cm $^{-1}$, assigned to

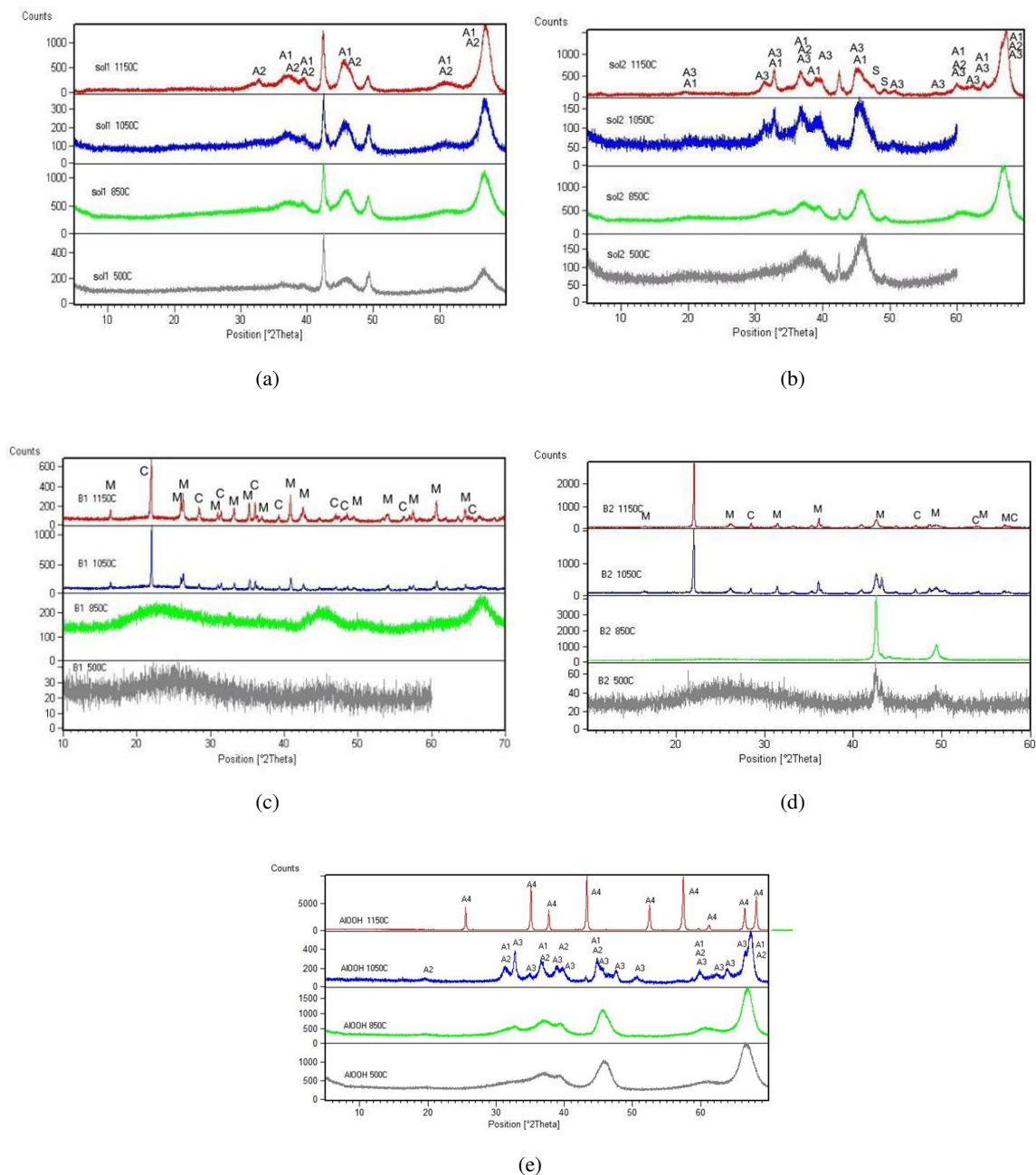


Fig. 1. The diffraction patterns of bulk samples synthesized with: (a) sol 1; (b) sol 2; (c) sol B1; (d) sol B2 and (e) the pure AlOOH annealed at different temperatures. Letters in the pictures of the diffraction patterns mean proper phases according to the description: A1 – γ - Al_2O_3 ; A2 – δ - Al_2O_3 ; A3 – θ - Al_2O_3 ; A4 – α - Al_2O_3 (corundum), S – SiO_2 ; M – mullite and C – cristobalite.

the stretching vibrations of –OH groups and of the molecular water, are observed (Fig. 2 – 6). After annealing of the samples, these bands changed their intensity but were still present in the spectra of all sol 1 and sol 2 samples though they disappeared

in the spectra of gels B1 and B2 annealed over 1000 °C.

Besides, one can distinguish two main groups of bands, one in the range of 900 to 400 cm^{-1} , where the bands due to Al–O bond vibrations

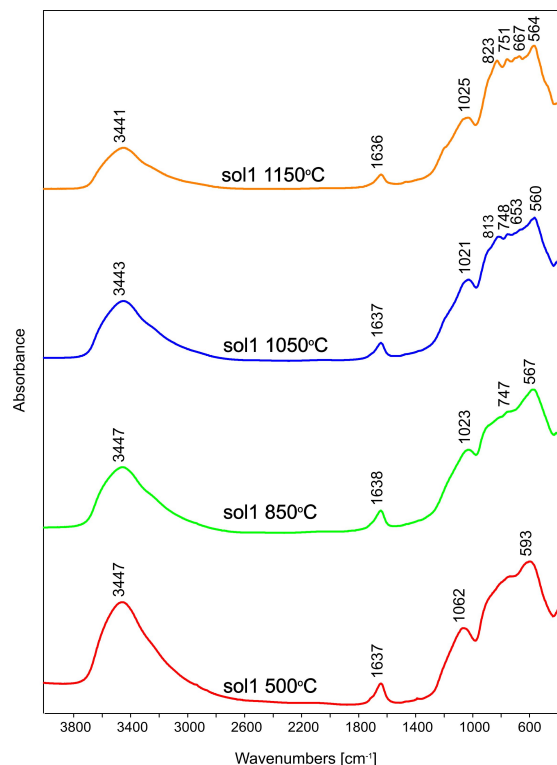


Fig. 2. FT-IR spectra of sol 1 bulk sample annealed at 500 °C, 850 °C, 1050 °C and 1150 °C.

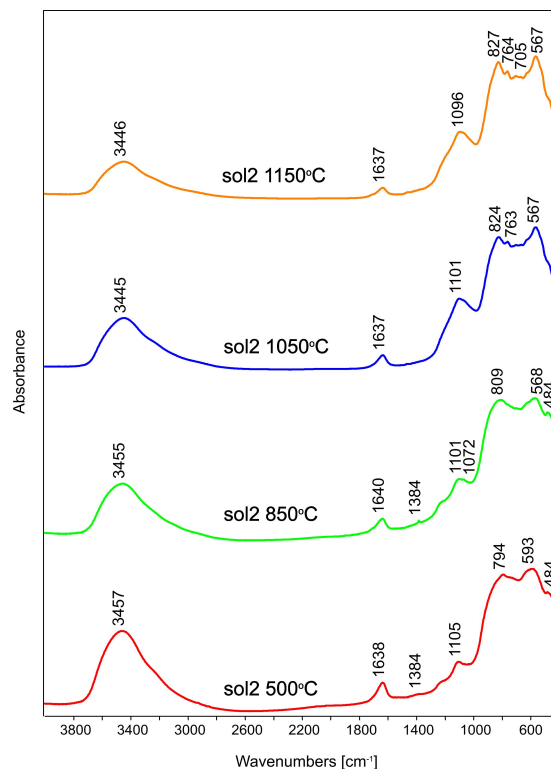


Fig. 3. FT-IR spectra of sol 2 bulk sample annealed at 500 °C, 850 °C, 1050 °C and 1150 °C.

of octahedrally coordinated Al are present, and the second, in the range of 950 to 1100 cm^{-1} , where the bands originating from the asymmetric stretching vibrations of Si–O–Si and/or Si–O–Al linkages are observed. The presence of Al in octahedral coordination is confirmed by the band at about 560 cm^{-1} , due to the bending vibrations of Al–O in AlO_6 units, observed in almost all spectra (Fig. 2 – 4), except those of the samples of sol B2 annealed at 1050 °C and 1150 °C (Fig. 5). Only in case of the sample of sol 1 heat treated over 850 °C there is a possibility of the concurrent existence of Al atoms in both octahedral (the earlier mentioned band at 560 cm^{-1} in the spectrum of this sample) and tetrahedral coordinations. This fourfold coordination of Al is confirmed by the presence of the band at 1020 cm^{-1} assigned to the asymmetric stretching vibrations of Si–O–Al linkage, where Al is fourfold coordinated (Fig. 2) [16].

The bands at 800 cm^{-1} and 1100 cm^{-1} indicate the presence of silica in an amorphous form in all

samples and in a form of cristoballite in particular case of sol B1 and B2 specimens annealed over 1000 °C , which is also confirmed by the XRD measurements. The temperature 850 °C is the barrier for the creation of crystalline phases and the transformation from the homogeneous to heterogeneous form of samples. The sharpening of the bands in correlation with the rising temperature points out the enhanced crystallization of all samples.

The changes in the shape and the position of the band at 1020 cm^{-1} in the spectra of sol B1 and B2 samples (Fig. 4 and Fig. 5) annealed over 850 °C , assigned so far only to the asymmetric stretching vibrations of Si–O–Si and Si–O–Al bridges, could also indicate the formation of the mullite phase in these samples [17–19].

In the same way as in case of XRD measurements, the spectra of pure AlOOH annealed at the same temperatures as aluminosilicate samples were collected and are shown in Fig. 6. The presence of the bands at about 580 cm^{-1} and 820 cm^{-1} points

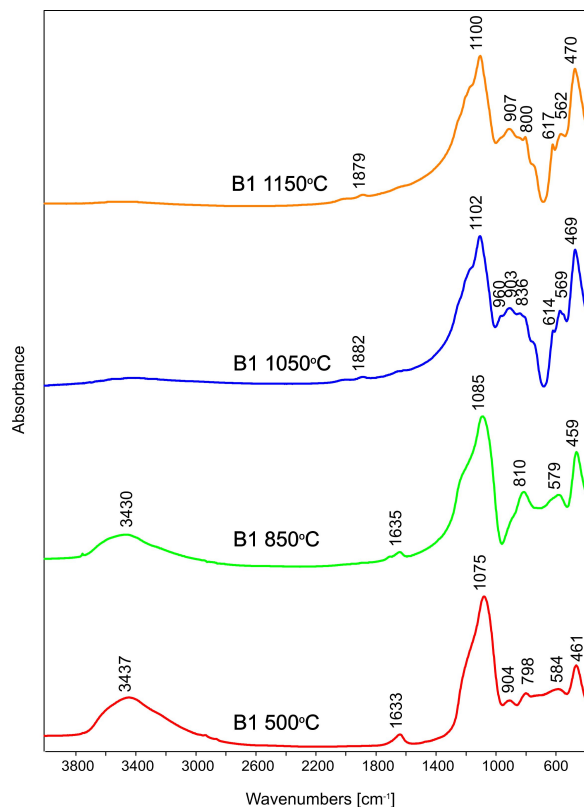


Fig. 4. FT-IR spectra of bulk sample of B1 sol annealed at 500 °C, 850 °C, 1050 °C and 1150 °C.

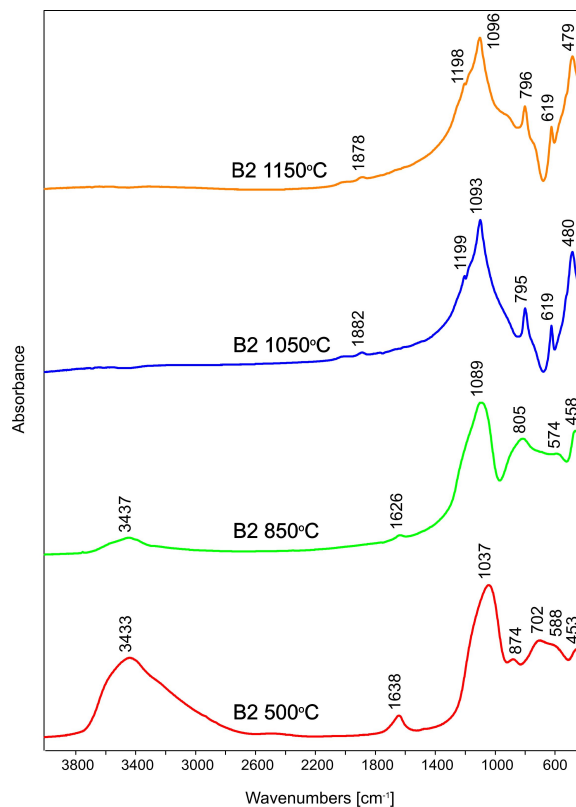


Fig. 5. FT-IR spectra of B2 bulk specimen annealed at 500 °C, 850 °C, 1050 °C and 1150 °C.

out the co-existence of octahedrally and tetrahedrally coordinated Al atoms, respectively. The disappearance of the band at 830 cm^{-1} and the increase of the intensity of the band at 594 cm^{-1} in the spectrum of AlOOH annealed at $1150\text{ }^{\circ}\text{C}$ indicates the presence of one-type octahedrally coordinated Al in this alumina structure.

3.2. Coatings

3.2.1. FT-IR measurements

In all spectra of the coatings (example spectra are shown in Fig. 7), the bands similar to those in the spectra of bulk samples are observed. First of all, the bands due to the molecular water vibrations at 1639 cm^{-1} and at 3450 cm^{-1} together with the bands assigned to the vibrations of $-\text{OH}$ groups at about 3450 cm^{-1} are present. More structurally important bands characteristic of silica, at about 470 cm^{-1} , 800 cm^{-1} and $1044\text{ to }1100\text{ cm}^{-1}$ are also observed.

The bands at 470 cm^{-1} are due to the bending vibrations of O-Si-O linkage, whereas the bands at 800 cm^{-1} and $1044\text{ to }1100\text{ cm}^{-1}$ can be assigned to the symmetric and asymmetric stretching vibrations of Si-O-Si bridges, respectively. All the bands are broad and with a profile characteristic of the existence of high amount of an amorphous phase in the coatings.

The bands assigned to the vibrations of Al-O bonds of octahedrally coordinated Al are observed in the region of $400\text{ to }900\text{ cm}^{-1}$, with the characteristic of this coordination band at about $560\text{ to }590\text{ cm}^{-1}$. There are no changes in the shapes or positions of these bands indicating the mullite phase crystallization, like in the spectra of bulk samples [17–19]. It is difficult to distinguish the bands which can be due to the vibrations of Al-O connections of tetrahedrally coordinated Al, located usually at 1020 cm^{-1} in the spectra of the studied thin films. As was mentioned earlier,

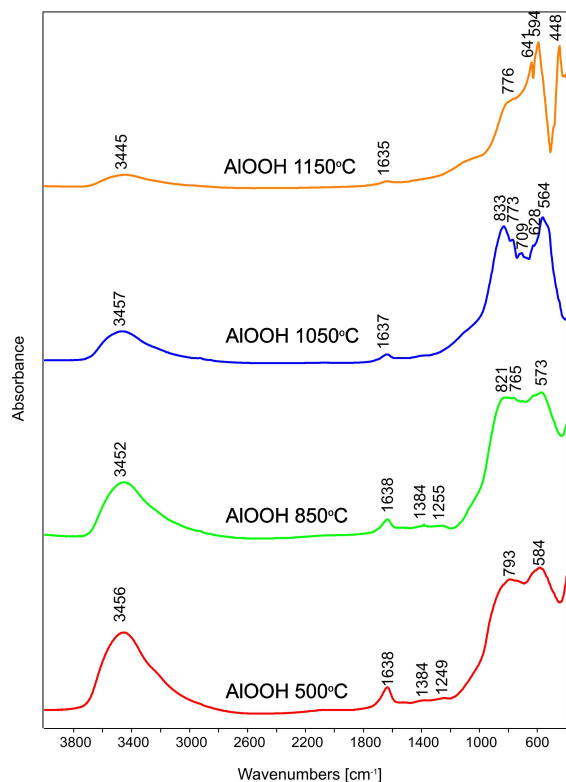


Fig. 6. FT-IR spectra of Dispersal-2™ specimen annealed at 500 °C, 850 °C, 1050 °C and 1150 °C.

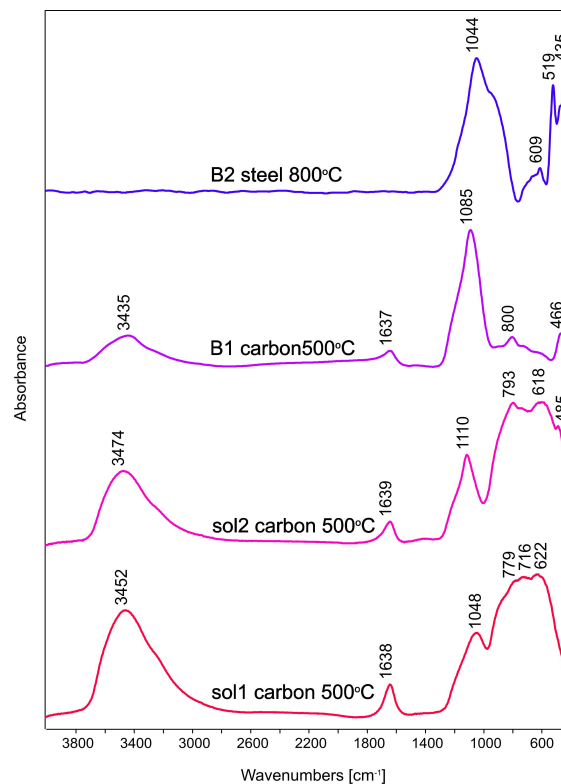


Fig. 7. FT-IR spectra of coatings prepared from different sols, on steel and carbon composites, deposited and annealed at different temperatures.

the observed bands at about 1040 to 1100 cm^{-1} are more typical of Si–O–Si bridges vibrations than of the vibrations of Si–O–Al connections, where Al is fourfold coordinated.

3.2.2. XRD measurements

The XRD measurements (not shown in this work) confirmed the presence of Al_2O_3 phase in the thin films deposited on different substrates but without the possibility to distinguish the polymorph type: the reflections were of low intensities with small values of full width at half maximum, which could be caused by the weak crystallization of the samples. Concurrently, there was a lack of any traces of crystalline silica in the synthesized layers. According to the XRD measurements, all thin films contained considerable amounts of amorphous phase with a small content of crystalline phases, confirmed by the presence of weak reflections due first of all to Al_2O_3 .

3.2.3. SEM studies

SEM studies were conducted for all sols (sol 1, sol 2, B1 and B2) deposited on different type substrates: carbon (a composite or single fibers), steel and alundum. In case of the layers deposited on carbon, the thin films with the best adhesion and tight parameters were obtained from sol 2, which gave a homogenous and stable concentration of Al and Si atoms in the coatings (Fig. 8). All thin films synthesized on steel (Fig. 9) were homogenous and rather of good adhesion (basing on the surface images observation) but strongly cracked (except one obtained from sol B1) [15, 20].

The coatings synthesized on a porous material, such as alundum (Fig. 10), created the thick layer which infiltrated through the upper part of the sample. Alundum withstands high annealing temperature, thus, the infiltrating coatings on this substrate could be annealed even up to 1150 °C, which enabled obtaining the mullite phase in the

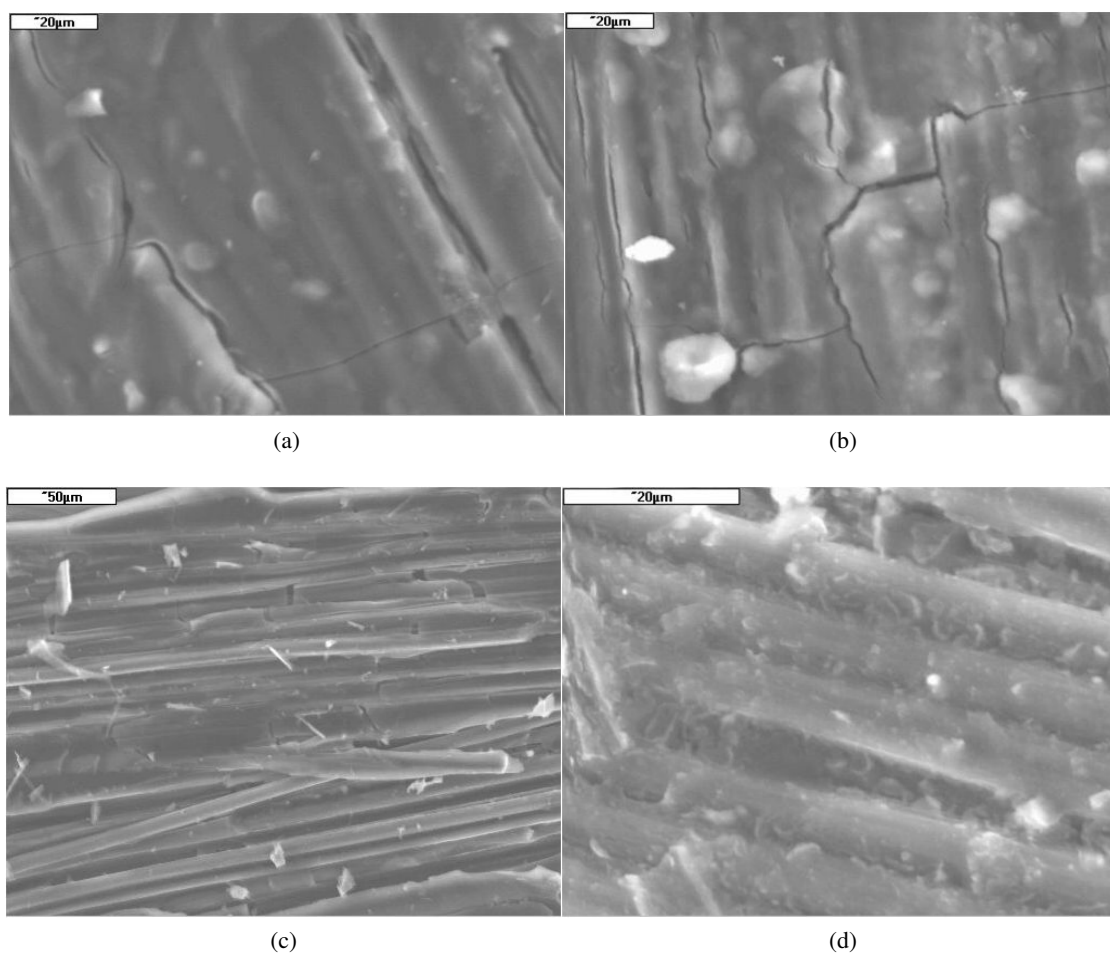


Fig. 8. SEM pictures of coatings synthesized with: (a) sol 1; (b) sol 2; (c) sol B1 and (d) sol B2 on carbon substrate.

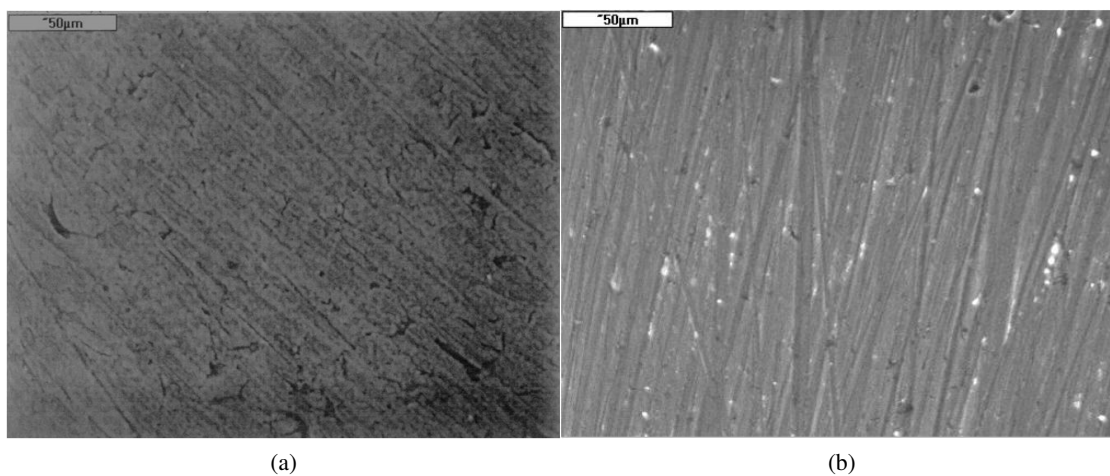
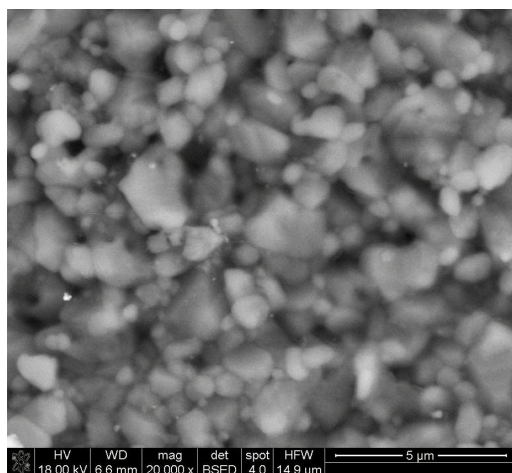
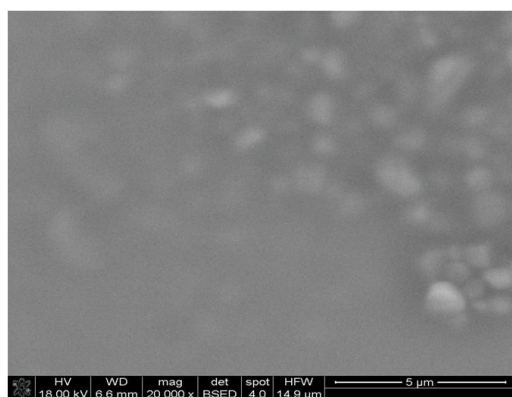


Fig. 9. SEM pictures of coatings synthesized with: (a) sol 2 and (b) sol B1 on steel substrate.

thin film synthesized from sol B2 [15]. At temperatures lower than 1150 °C and in case of other sols, those infiltrating layers were mostly amorphous or did not create continuous and tight coatings. EDS analyses conducted for all thin films (not shown in this article) confirmed the presence of Al and Si in all samples and allowed us to estimate the average thickness of the compact layer on steel as about 1 µm, by comparing the intensities of the lines due to the components of substrate in different samples.



(a)



(b)

Fig. 10. SEM pictures of coatings synthesized with: (a) sol B1 and (b) sol B2 on alundum, representing the porous ceramics.

4. Conclusions

1. There is a possibility to obtain mullite phase together with the low temperature

cristobalite in bulk samples of sols B1 and B2 annealed over 1100 °C. The presence of cristobalite means that the crystallized mullite phase is poor of silica and probably formed by the thermal dissociation, which could be connected with the low relative stability of this compound.

2. Samples obtained from annealed sols B1 and B2 have more compact structure than those obtained from sol 1 and sol 2.
3. The gels were mostly homogeneous up to 850 °C but over that temperature different crystalline phases were observed during the annealing process (mainly different polymorphs of Al_2O_3), which resulted in heterogeneity of the samples. The coatings should not be heat treated at temperatures over 850 °C to avoid their heterogeneity. Below that temperature, they remained amorphous.
4. Tetraethoxysilane TEOS: $\text{Si}(\text{OC}_2\text{H}_5)_4$ and aluminium secondary butoxide ATSB: $\text{Al}(\text{OC}_4\text{H}_9)_3$ as precursors of SiO_2 and Al_2O_3 allowed us to obtain a material with good structural and microstructural properties but the synthesis of both sols B1 and B2 demanded special conditions and was carried out in an argon atmosphere.
5. It is possible to obtain Al in both tetrahedral and octahedral coordinations in case of monolithic sample obtained from sol 1, while in all other thin films, Al is observed only in octahedral coordination, independently of the type of substrate.

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