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The Dependence between the Structural-Morphological Features Mixes $0.8SiO_2/0.2Al_2O_3$ from the Time of Mechanical Treatment

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This paper highlights the relationship between changes in structural and morphological features, electronic structure and expanding of time mechanical treatment at microbraker (MBT). Scanning electron microscopy revealed a change in the morphological features of nanoscale powders. From the comparison of SEM images of $0.8SiO_2/0.2Al_2O_3$ mixture before and after MBT, it is established that due to MBT, the agglomerates of the initial components are simultaneously crushed with perfect mixing particles of oxides between each other and the formation of new agglomerates with a denser structure. The increase in processing time leads to an increase in the density of the nanocomposite. The effect of time of mechanical treatment on the structural parameters and phase composition of mixtures of silicon dioxide and alumina oxide were studied using the method of X-ray structural analysis. The established agglomeration is accompanied by a change in the lattice parameter c with a change in the regions of coherent scattering of crystalline Al_2O_3. Ultra-soft X-ray emission spectroscopy was used to study the distribution of Op-, Sisd- and Alsd- valence electrons in $0.8SiO_2$ / $0.2Al_2O_3$ powder mixtures after the different time of mechanical treatment. An increase in atomic charges has been measured and can be explained by the transfer of electrons from Si and Al to O atoms in split Op_π-binding states.

Keywords: mechanical treatment at microbraker, morphology, XRD distribution of valence electrons, coherent scattering field, spectra.

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Introduction

Oxides of transition and semi-transition metals have a wide range of special properties, which are widely used in the field of semiconductor electronics, information storage, solar and renewable energy, etc. [1-5]. Among the wide range of nanooxides of transition metals used in such areas, SiO_2 and Al_2O_3 should be distinguished. It is well known that during the transition of materials from the macro- to nanoscale state, these properties can be radically different from the initial ones [6]. Namely, as a result of such a transition, quantum effects are very often observed, which in some cases improve certain characteristics of the product, and in others can significantly worsen them. Therefore, methods that provide new useful properties are undoubtedly relevant in today's rapid development of nanoelectronics. The most widely used methods are methods that are based on mechining, namely grinding in a planetary or ball mill. However, energy efficiency, and hence the cost-effectiveness of these methods is quite low, so it is more appropriate to use the method of shock-vibration treatment on micro-breaker, which can provide the same result, but for a shorter period of time. In previous works [7-10] it was shown that this method of processing is quite effective in the processing of nanocomposites. However, it is not known how the processing time of this method affects the energy efficiency of this method. Therefore, it is necessary to study the influence of this method on structural morphological features and electron structural properties. Therefore, it is advisable to conduct such studies for a promising mixture $0.8SiO_2/0.2Al_2O_3$, which is very promising for use as an electrode material of lithium current sources.

I. Materials and methods

1.1 Materials

The investigated samples of silicon oxide were synthesized at the Institute of Surface Chemistry Chuka National Academy of Sciences of Ukraine. The raw materials for the pyrogenic silicon dioxide were $SiCl_4$, which was fed into O_2/H_2 flames for hydrolysis / oxidation and the formation of nanoparticles of individual SiO_2 oxides with a specific surface area of 230 m^2 / g (PK300).

The fumed nanoparticles of Al_2O_3 with the specific surface area SBET = 89 m^2/g and of Si_2O with S_{BET} = 300 m_2/g were used as the initial powders. Method of synthesis (Pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine), structural and morphological characteristics of these powders were described in detail elsewhere [11].

Preparation of the initial mixture (SA-20) was performed by conventional stirring for 5 minutes, followed by stirring in a 50 Hz mechanical vibrator Ardenne (Germany) in a 25 mm diameter metal reactor using one 10 mm diameter metal ball during 3 seconds.

The mechanical treatment at microbraker (MBT) of mixtures of $0.8SiO_2 / 0.2Al_2O_3$ was performed in a mechanical vibration mill in Ardenne (Germany). MBT occurred in a metal reactor with a diameter of 25 mm using a single metal ball with a diameter of 10 mm, at a frequency of oscillation of the reactor 50 Hz. The Table 1 shows the correspondence between the processing time and the name of the sample.

Table 1

The correspondence between the name of the samples and time of their mechanical treatment

Name of the sample	Processing time, min
SA-20	0
SA-20-3	3
SA-20-5	5
SA-20-10	10
SA-20-15	15
SA-20-20	20

1.2. Methods of research

The crystalline structure of the powder mixture was studied using a Ultima IV (Rigaku, Japan) diffractometer with monochromatic CuKα radiation. XRD patterns of the powder mixture were analyzed using Power Cell 2.4 program. The analysis of XRD profiles and the allocation of true physical broadening of peaks was carried out using an approximation method. The separation of the broadening effects of the XRD peaks associated with the size of the coherent-scattering region and the tensions of the second kind was carried out using the Holl-Williams approximation. The crystallinity of the investigated powders was determined by the normalization of the integral intensity of the amorphous halo to the value of the intensity of the diffuse maximum corresponding to the completely amorphous sample with similar composition.

The morphology of the nanoparticles before and after MBT was studied by scanning electron microscopy (SEM) PEM-106.

The energy distributions of valence Op, Si_{sd} and Al_{sd} electrons were studied using ultra-soft X-ray emission spectroscopy (USXRES) applied to the OKα, SiLα and AlLα emission bands. The study was carried out in a X-ray spectrometer with monochromator PCM-500 in vacuum (5×10^{-6} Pa) with an energy of electron 5 KeV and an intensity of 6×10^{17} electrons per cm^2 (el/cm^2). The spectrometer has oil-free pumping system and a liquid-nitrogen trap placed directly in the vicinity of the sample to allow an additional freezing of vapors. The equipment distortions in the 510 - 535 eV range of energies, in which the OKα band is located, were $\Delta E = 0.3$ eV, and in the region of energies corresponding to the SiLα and AlLα emission bands, it was $\Delta E = 0.2$ eV.

To avoid the overlap of the OKα band of the studied powder mixtures with the OKα of CuO the spectra were measured in the energy region hν = 510 - 535 eV.

II. Results

Based on the assumption that any treatment is accompanied by energy transfer, and the processing time may correlate with the amount of this energy provided to the system, it was decided to determine the optimal time of MBT, which will give the best results of electrochemical analysis.

Figure 1 shows the SEM image of the samples after different machining times.

The initial mixture of nanoxides $0.8SiO_2 + 0.2Al_2O_3$ (Fig. 1, a) has the form of blurred agglomerates of amorphous SiO2 and crystalline Al_2O_3, preferably separated from the cloud-like amorphous phase. After three minutes of MBT, the blurred cloud-like component of the mixture basically disappears and the sizes of agglomerates from 20 - 5 µm to 100 - 350 µm (Fig. 1, b) with rather clear boundaries increase sharply. The agglomerates are most dense where alumina crystals have been detected.

Increasing the processing time to 5 min is accompanied by the growth of dense agglomerates with clearly delineated boundaries (Fig. 1, c) and both large (400 - 500 µm) and small particles separated from each other. A further 10-minute treatment results in the particles being combined into very large grain combinations and the number of fine particles reduced. Increasing the processing time to 15 min and 20 min leads to the destruction of these groups into smaller grains, and the number of which increases and they all become the densest at 20 minutes MBT.

From the images presented in (Fig. 2), obtained at magnifications of 2500 times, it is seen that the nature of the agglomeration of nanoparticles with changing processing time remains the same and confirms the

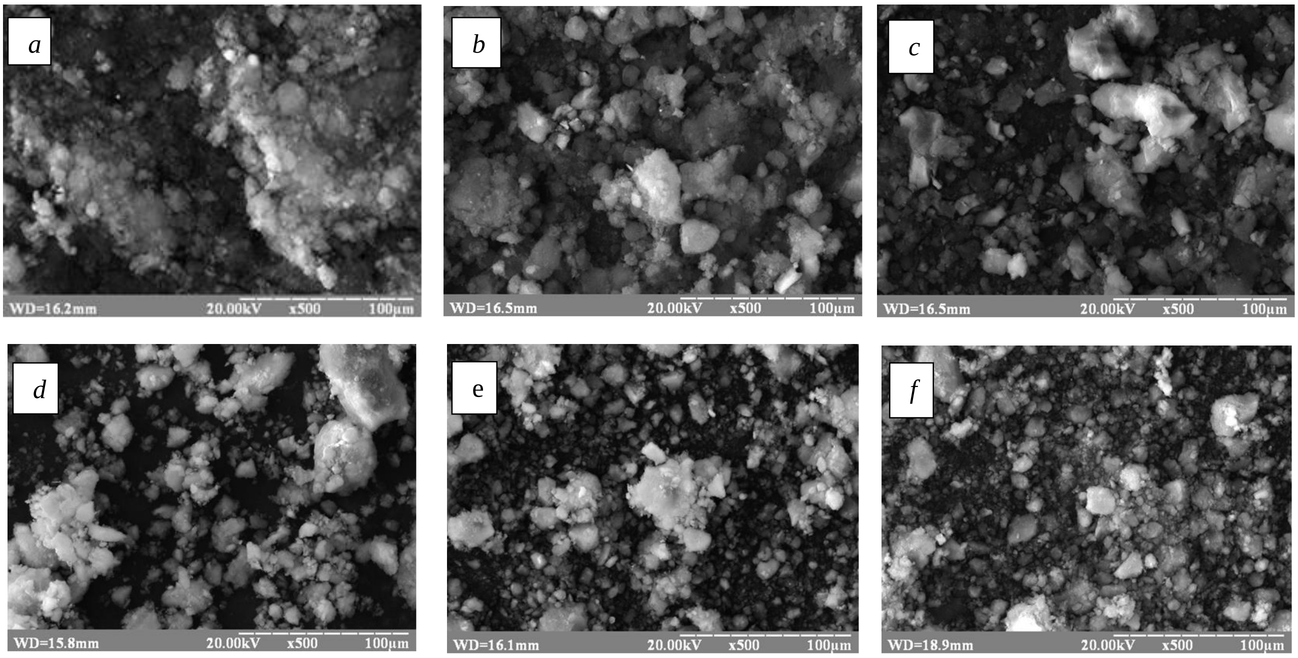

Fig. 1. SEM images of nanocomposites: *a* - SA-20; *b* - SA-20-3; *c* - SA-20-5; *d* - SA-20-10; *e* - SA-20-15; *f* - SA-20-20, x500 times.

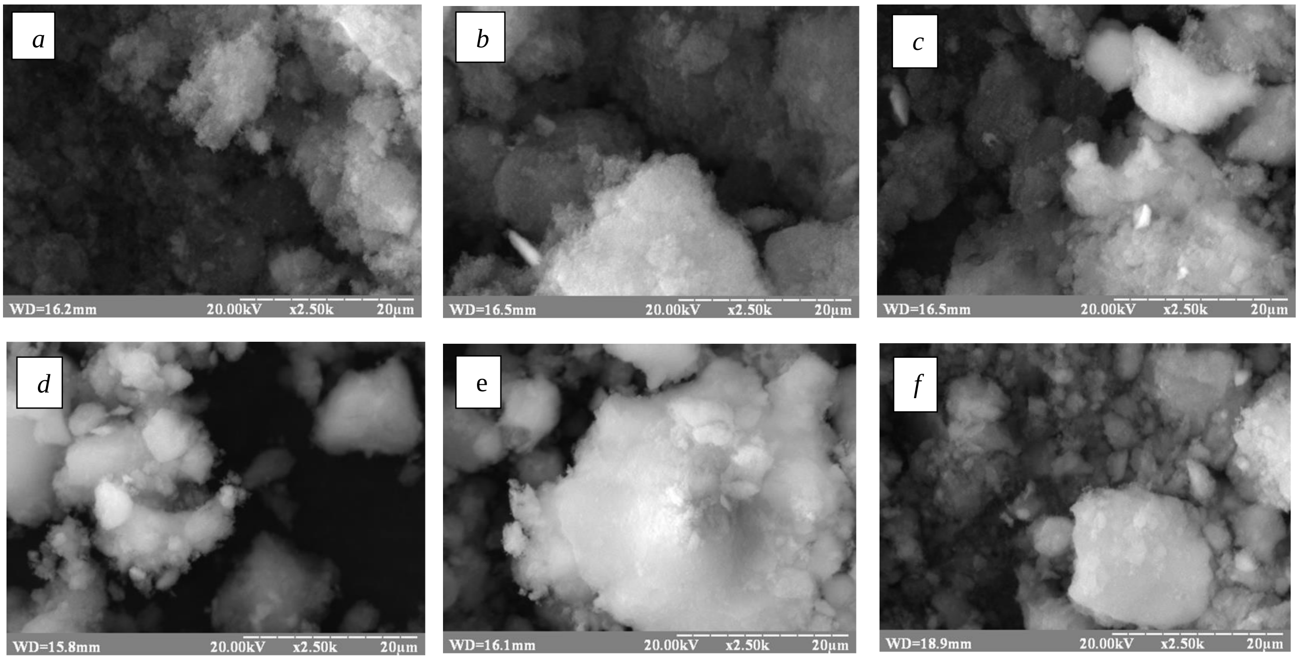

Fig. 2. SEM images of nanocomposites: *a* - SA-20; *b* - SA-20-3; *c* - SA-20-5; *d* - SA-20-10; *e* - SA-20-15; *f* - SA-20-20, x2500 times.

clarity of the boundaries of the clusters, indicating their compaction.

Analysis of radiographic data (Fig. 3) showed that nanoxide mixtures contain amorphous SiO_2 and θ-phase Al_2O_3. The content of the θ-phase of Table 2 after shock-vibration treatment for 3 min increases by only 2 %, and with increasing duration of treatment from 5 to 15 min remains virtually unchanged and decreases with 20 - minute treatment. Since no new Al_2O_3 phases are detected, this difference in the phase composition of the mixtures is obviously the result of the random content of the θ-phase of Al_2O_3 in the samples taken in the study. The lattice parameters change randomly only in the third sign and can be considered constant within the error of the experiment. At the same time, the lattice parameter "c" after processing for 3 minutes increases by 0.02 Å and remains close to 5.62 Å and at longer processing times in the vibrating mill.

The region of coherent scattering of the θ-phase of Al_2O_3, which in the initial mixture is 18nm (Table 2) at MBT for 3 minutes decreases to 15 nm, obviously due to the destruction of particles. However, increasing the time

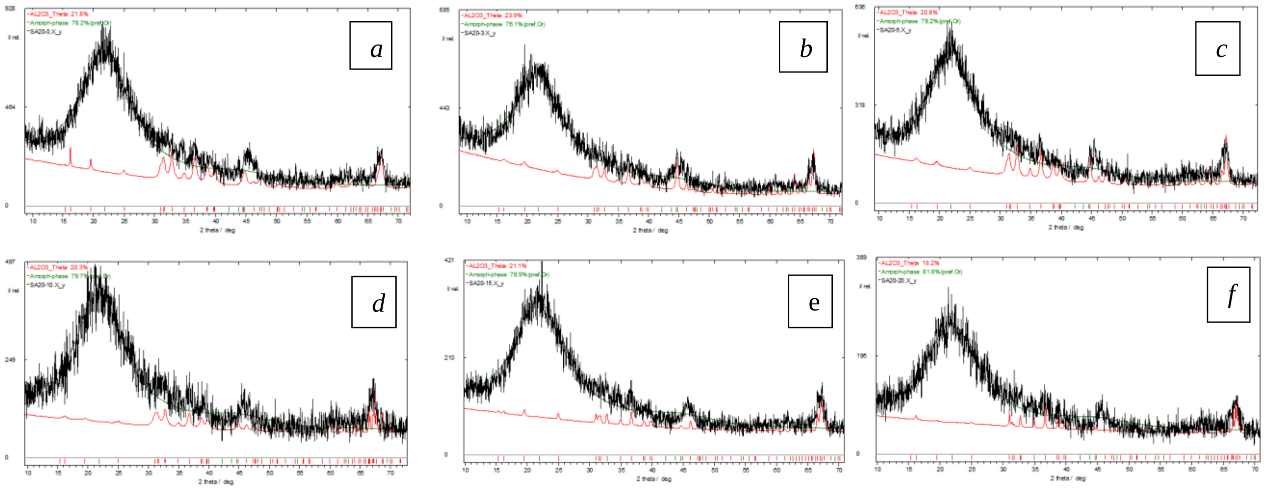

Fig. 3. XRD spectra of nanocomposites: *a* - SA-20; *b* - SA-20-3; *c* - SA-20-5; *d* - SA-20-10; *e* - SA-20-15; *f* - SA-20-20.

Table *2*

Phase composition, CSR sizes (D), the lattice parameters (a, b, c) in the initial and MBT mixtures $0.8SiO_2/0.2Al_2O_3$ with different time of treatment.

Sample	Θ, %	Amorph., %	$t_{treat.}$, min	*a*, Å	*b*, Å	*c*, Å	β, °	D, *nm*
SA-20	21.79	78.21	0	11.8580	2.9150	5.6090	103.6548	18
SA-20-3	23.92	76.08	3	11.8437	2.9037	5.6269	103.7732	15
SA-20-5	20.82	79.18	5	11.8566	2.9070	5.6167	103.7710	22
SA-20-10	20.28	79.72	10	11.8589	2.9038	5.6215	103.8392	20
SA-20-15	21.09	78.91	15	11.8552	2.9054	5.6187	103.7542	25
SA-20-20	18.22	81.78	20	11.8587	2.9056	5.6208	103.7280	29

of MBT leads to a sharp increase in CSR, with 20-minute processing almost twice, 15 minutes to 29 nm. This increase in CSR cannot be explained by the fallout sintering of nanoparticles. Therefore, the only thing that is possible is the re-crystallization of one particle at the expense of another at high local pressures and temperatures, because a long processing time does not allow temperatures to decrease at the points of contact of θ- Al_2O_3 nanoparticles.

Since the nature of such changes in structural and morphological features is not known, an preparation of nanoxide mixtures for MBT requires a number of operations of heat and thermo-vacuum treatment, etc to minimize the amount of water adsorbed into the nanocomposite. In addition, it is well known that adsorbed water leads to the formation of interparticle bonds, and the transfer of additional charges to oxygen atoms. That is, molecules sorbed by water nanoxides can also provide additional negative charge. Therefore, the carried out mechano-vibration treatment of these mixtures without prior annealing can answer these questions. Since X-ray phase analysis cannot determine the contribution of sorbed water to the electronegativity of the studied system, the study of X-ray emission bands of oxygen and the influence on their parameters of MBT should be used.

It was previously shown [7] that inter-atomic bonds were formed in clad nanooxide particles, due to which the negative charge of such nanoparticles increased due to the transfer of weakly bound electrons from silicon and aluminum to the oxygen state. To determine the presence of such a transition, it is necessary to analyze the dependence of the shape and relative intensities of SiLα and AlLα emission bands on the time of MBT. OKα-emission bands obtained at minimum anode currents of 1 mA were obtained for storage of sorbed H_2O molecules in samples and at I = 10 mA for obtaining spectra from dehydrated samples.

Their comparison with the spectra obtained after thermo-vacuum treatment (Fig. 4) revealed that the width

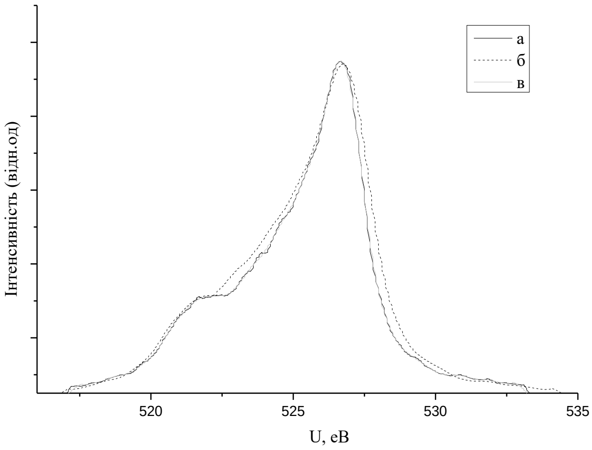

Fig. 4. OKα-spectra: SA-20 clad (*a*), obtained at an anode current of 10 mA (*b*), obtained at an anode current of 1 mA (*c*).

of the OKα band of the initial mixture is greater than the spectrum obtained from the thermo-vacuum mixture and differs from the spectra obtained earlier [7] mainly in that the expansion is observed as in high energy and low-energy area due to simple overlay. The expansion in the high-energy region is more intense, probably due to molecules that are not chemisorbed.

After MBT for 3 minutes (Fig. 5), the intensity and expansion in the high-energy region decreased, equaling that in the low-energy region. This may be a consequence of the removal of non-chemisorbed will molecules from the surface of nanoparticles, because after obtaining OKα bands at an anode current of 10 mA, it turned out to be very close to that obtained previously [7] without MBT.

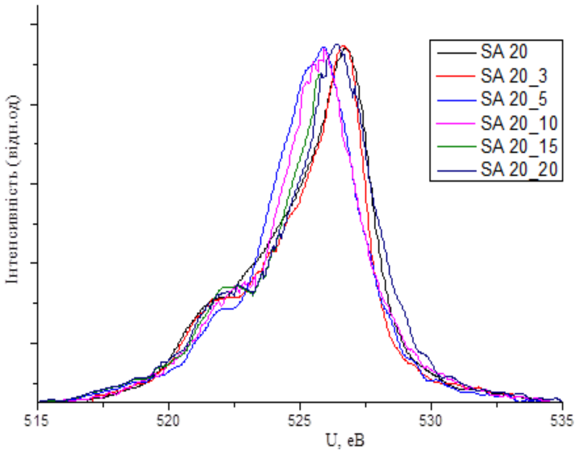

Fig. 5. OKα-spectra of mixtures with different time of MBT.

Shock-vibration treatment of the SA-20 mixture for 5 minutes led to a narrowing of the expansion of the OKα band in the high-energy branch and to a shift in the long-wave side of the low-energy circuit, as observed for clad at the same 5 minutes of processing [7]. It is obvious that it is in such modes that O-Oπ bonds are formed between the surface atoms of the contacting particles in the clad SA-20.

Increasing the MBT time to 10 minutes led to a decrease in the expansion of OKα bands in the low-energy region with the release of a fairly pronounced influx, which indicates a decrease in the contribution of Op-p_π-bonds between the surface atoms of nanoparticles. Obviously, this is a consequence of the destruction of some of the clad nanooxides. Longer treatments at 15 and 20 minutes lead to even less expansion of the OKα band in the energy range corresponding to the Orπ state, but the described expansion still remains. This indicates that not all clad nanoparticles are destroyed.

Conclusions

Studies of the effect of MBT time on the morphological features of nanocomposite SA 20 showed that during processing for 3 min there is a slight adhesion of particles to each other, and when processing more than 10 min there is only crushing of agglomerates and increase in bulk density.

From the results of X-ray diffraction analysis it was found that as a result of the Office for 15 and 20 minutes is accompanied by an increase in CSR almost twice. On the other hand, the phase composition and parameters of the crystal structure do not change as a result of processing.

From the results of USXES it is established that during processing for 3 minutes or more promotes the removal from the surface of nanoparticles of chemisorbed water molecules. When treated for 5 min, the formation of clad bonds between the nanoparticles of oxides. And when processed for 10 minutes or more, the most likely is the rupture of clad ligaments and re-crystallization processes as a result of high pressures and temperatures.

Gratitude

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Залежність між структурно-морфологічними особливостями суміші $0.8SiO_2/0.2Al_2O_3$ від часу механічної обробки

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У цій роботі висвітлено взаємозв'язок між змінами структурно-морфологічних особливостей, електронною структурою та тривалістю ударно-вібраційної обробки. Скануюча електронна мікроскопія використовувалась для виявлення зміни морфологічних особливостей нанорозмірних порошків. З порівняння СЕМ-зображень суміші $0,8SiO_2$ / $0,2Al_2O_3$ до та після ударно-вібраційної обробки встановлено, що завдяки обробці агломерати вихідних компонентів одночасно подрібнюються з ідеальним змішуванням частинок оксидів між собою та утворенням нових агломератів з більш щільною структурою. Збільшення часу обробки призводить до збільшення щільності нанокомпозиту. Вплив часу механічної обробки в ударно-вібраційному млині на структурні параметри та фазовий склад сумішей діоксиду кремнію та алюмінію вивчали методом рентгеноструктурного аналізу. Встановлена агломерація супроводжується зміною областей когерентного розсіювання кристалічного Al_2O_3 при відсутності зміни структурних параметрів компонентів. Ультрам'яка рентгенівська емісійна спектроскопія використовувалась для вивчення розподілу Op-, Sisd- та Alsd-валентних електронів у порошкових сумішах $0.8SiO_2$ / $0.2Al_2O_3$ з різним часом механічної обробки. Виявлено збільшення атомних зарядів, яке можна пояснити перенесенням електронів від атомів Si та Al до розщеплених p_π-зв'язуючих станів атомів O.

Ключові слова: ударно-вібраційна обробка, морфологія, рентгеноструктурний аналіз, розподіл валентних електронів, область когерентного розсіювання, спектр.