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Synthesis and properties of Cu - doped finely dispersed ceramic pigments

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The present work investigates the synthesis and properties of finely dispersed ceramic pigments from the Al_2O_3 - SiO_2 system. The synthesis of the pigments was carried out by the solid-phase sintering method. As initial materials both pure materials and waste raw materials - waste rice husks were used. In the first case, Al_2O_3 and $SiO_2.nH_2O$ were used as a pure initial material. The more active amorphous form of $SiO_2.nH_2O$ was chosen, instead of the crystalline form of silica. Rice husk is a waste product containing about 20 % SiO_2. By burning rice husk in an oxidizing environment, the amount of SiO_2 significantly increases. For the purposes of the experiment, rice husk ash (RHA) with a 94.47 % SiO_2 content, was used. The synthesis was carried out at temperatures of 1350 °C and 1400 °C with a one-hour isothermal period. In both starting compositions - from pure and waste raw materials, the amount of Cu chromophore was 5% introduced in the form of CuO. Finely dispersed gray pigments were obtained. The pigments synthesized from the Al_2O_3 - SiO_2 system were investigated by a number of methods - X-ray diffraction, scanning electron microscopy, hot-stage microscopy, thermogravimetric analysis, color measurement, etc. The results of the scanning microscopy showed that clusters of particles are formed. The color of the pigments was determined spectrally on a Lovibond Tintometer RT 100 Color. The pigments with the best color characteristics were those obtained from pure raw materials (Al_2O_3 and $SiO_2.nH_2O$) at 1400 °C for 1 hour - (a) = - 3.6 and (b) = 5.6.

Keywords: ceramic pigments, Cu - chromophore, rice husk, solid-state sintering, color characteristics

INTRODUCTION

Inorganic ceramic pigments are used to color various materials, as well as to improve one or another property of the material. The color of the pigments is due to coloring ions such as cobalt, copper, nickel, etc. [1, 2]. These materials must have excellent chemical resistance [3], as well as resistance to high temperatures [4]. In addition, the pigments must be relatively chemically inert - they must not easily react with their carriers. They must be insoluble in water, organic solvents and binders [5]. Another requirement for them is to show good coverage, high color intensity and high refractive index [6].

Nowadays, ceramic pigments are used to color various ceramic materials. They are obtained by solid-phase synthesis [7, 8] or by sol-gel technology [9, 10]. Of particular interest, both from a scientific and an applied ecological aspect, is the production of ceramic pigments not only from pure but from waste raw materials. More and more scientific studies report on the synthesis of ceramic pigments using industrial waste [11], biowaste [12], spent catalysts, etc. [13].

Scientists create more stable pigments with a higher color intensity compared to pigments from pure SiO_2 [14, 15].

The development and production of various ceramic pigments using agro-waste is poorly represented. The lack of sufficient data, especially in recent years, on the synthesis of ceramic pigments, as well as their detailed study, makes the current research timely and useful for filling the existing niche.

In connection with the above, the aim of the present study is the synthesis of ceramic pigments from the Al_2O_3 - SiO_2 system, by the solid-phase sintering method, from pure raw materials and waste ones, by using rice husk ash as a source of silicon dioxide. Also, the starting batches are studied and the characteristics of the obtained pigments are determined.

EXPERIMENTAL

Materials and methods

- *Materials.* The synthesis of finely dispersed ceramic pigments from the Al_2O_3 - SiO_2 system was carried out by the solid-phase sintering method. Both pure materials and waste raw materials - ash from burnt rice husks were used as starting materials.

Two series of pigments were synthesized. In the first case, pure starting materials were used - Al_2O_3 and $SiO_2.nH_2O$ (Sigma Aldrich) - compositions M2-5 and P2-5, Table 1. The more active amorphous form of $SiO_2.nH_2O$ was chosen instead of the

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crystalline form of silicon dioxide. Rice husk is a waste product, which is known to contain about 20% of SiO_2. By burning the rice husk in an oxidizing environment, the amount of SiO_2 significantly increases. For one of the purposes of the experiment (compositions MR2-5 and PR2-5, Table 1) ash from burnt rice husks (RHA) with a SiO_2 content of - 94.47 % was used. Since the color of most natural and synthesized mineral substances is associated with the presence in their composition of d- or f-elements of the periodic system, in both starting compositions (from pure and from waste raw materials) Cu ions were selected and introduced as a chromophore in an amount of 5 %. The copper chromophore was introduced in the form of CuO.

Table 1. Compositions of ceramic pigments from the Al_2O_3 - SiO_2 system, synthesized from pure or waste raw materials (rice husk ash RHA) with 5 % of Cu chromophore.

№	Composition	Synthesis temperature	SiO_2 introduced in the form of:
1	M2-5	1350 °C	$SiO_2.nH_2O$
2	MR2-5	1350 °C	RHA
3	P2-5	1400 °C	$SiO_2.nH_2O$
4	PR2-5	1400 °C	RHA

The initial components were dry-mixed and homogenized in a planetary ball mill. The synthesis of ceramic pigments was carried out at temperatures of 1350 °C and 1400 °C, and to ensure the completeness of the reactions that occur during solid-phase sintering, at the corresponding maximum temperature, a one-hour isothermal hold in a Nabertherm high-temperature furnace in an air environment was performed at the final stage of the process. The preparation of ceramic pigments including all procedures during the technological process, is schematically presented in Figure 1.

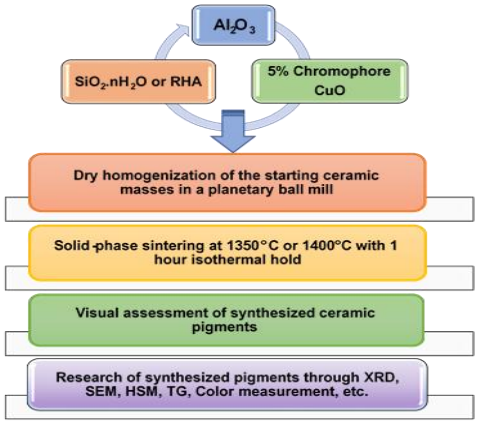


Figure 1. Scheme of the production of ceramic pigments from pure or waste raw materials by solid-phase sintering.

- *Methods.* The initial mixtures and the synthesized pigments were examined using the methods of:

- *X-ray structural analysis.* X-ray diffraction analysis was performed on a Bruker D8 Advance automatic powder X-ray diffractometer with CuKα radiation (Ni filter) and registration by a LynxEye solid-state detector. The X-ray spectrum was recorded in the angular range from 5.3 to 80° 2θ with a step of 0.03° 2θ. Qualitative phase analysis was performed using the PDF-2 (2009) database of the International Center for Diffraction Data (ICDD). Quantitative analysis was performed with the Topas 2 program.

- *Scanning electron microscopy (SEM).* The SEM observations were carried out on an apparatus TESCAN, SEM/FIB LYRA I XMU at 30 kV accelerating voltage. The observations were accompanied by energy-dispersive X-ray spectroscopy (EDS) carried out with a detector of Bruker.

- *Hot-stage microscopy (HSM)* High-temperature microscope ESS Misura HSM - 1400 ODHT, model 1600/80, Italy (IFH-BAS) was used. The sample was heated to 1400 °C at a rate of 10 °C min^{-1}, and the graph reflects the changes occurring with it during heating.

- *Thermogravimetric analysis (TG).* Thermogravimetric analysis was performed on a complex thermal analysis apparatus (STA 449 F3 Jupiter), Netzsch, Germany, by heating to 1100 °C at a rate of 10 °C min^{-1}.

- *Color measurement.* The color of the pigments was spectrally determined on a Lovibond Tintometer RT 100 Color.

RESULTS AND DISCUSSION

Two series of finely dispersed ceramic pigments of the Al_2O_3 - SiO_2 system were synthesized by the solid-phase sintering method at temperatures of 1350 °C and 1400 °C. In the synthesis of the first series of pigments, pure starting materials were used - compositions M2-5 and P2-5. In the second series, a waste raw material was utilized - ash from rice husks burnt in air (RHA), as a source of silica - compositions MR2-5 and PR2-5.

The color of pigments is most often determined by d-d electron transitions or charge transfer and occurs only in compounds of transition elements since their electronic structure allows such a transition. That is why, in the syntheses carried out, in both starting compositions (from pure and from waste raw materials) 5% of Cu chromophore was introduced as CuO.

The starting batches and the ceramic pigments obtained by us were studied and characterized using the methods of XRD, SEM, HSM, and TG, and the color characteristics of the pigments were spectrally determined with a Lovibond Tintometer RT 100 Color.

Studies on initial mixtures

Fig. 2 presents the results from the hot-stage microscopy (HSM) of a mixture obtained from pure raw materials - Al_2O_3 and $SiO_2.nH_2O$.

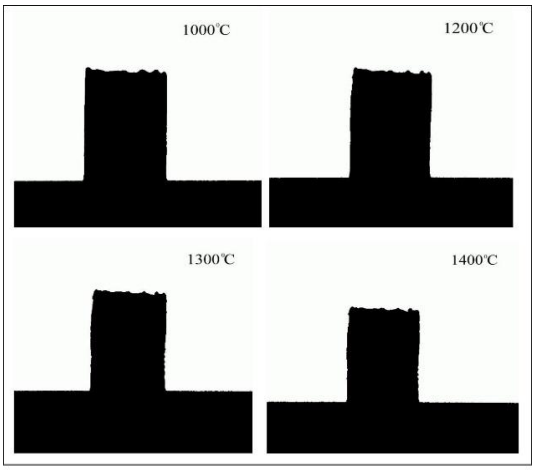


Figure 2. Hot-stage microscopy (HSM) of mixtures obtained from pure raw materials - composition P2-5.

The results indicate an extremely high thermal stability of the studied samples, even at a temperature of almost 1400 °C. This shows that the synthesized pigments are highly refractory and will not decompose during the firing of ceramic products covered with glazes colored with the pigments obtained by us. Therefore, the pigments could be used in real production conditions.

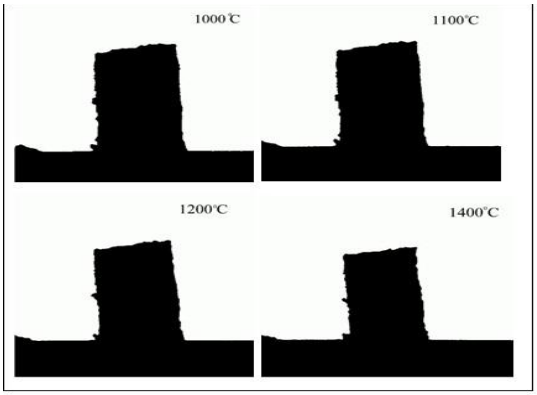


Figure 3. Hot-stage microscopy (HSM) of mixtures obtained from Al_2O_3 and waste RHA - composition PR2-5.

Fig. 3 presents the results of hot-stage microscopy (HSM) of batches composed of Al_2O_3 and air-burnt rice husk ash (RHA). It can be seen that the introduction of RHA, as a source of SiO_2 into the starting compositions, also gives high-temperature resistant batches. No spillage or shape change are observed up to almost 1400 °C.

The starting mixtures, consisting of Al_2O_3 and pure or waste raw materials, were also studied by means of thermogravimetric analysis. The complex thermal analysis shows that the process consists of several main stages of mass loss. DSC and DTG thermograms are presented in Figs. 4 and 5. Until a stable regime is reached in the complex thermal analysis apparatus, adsorption processes of moisture in the dry samples prevail, due to which the mass increases, after which the desorption process takes priority and the mass decreases. The first two low-temperature endothermic stages in both charges proceed with mass loss, consisting mainly of water physically adsorbed on the surface of the material. The next stage is characterized by the endothermic peak in the range of 500 - 550 °C (Fig. 4), which corresponds to the dehydration of $SiO_2.nH_2O$. In Fig. 5 a large endothermic effect is observed between 400 - 500 °C, both in height and area. Here the mass loss is the greatest, which is probably a result of the combustion of unburnt particles in the RHA.

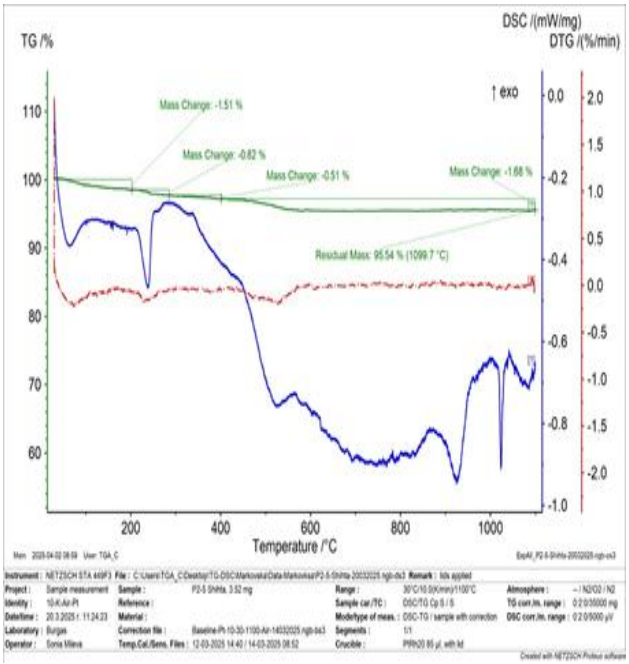


Figure 4. DSC/DTG thermogram of the mixture obtained from pure raw materials: Al_2O_3 and $SiO_2.nH_2O$.

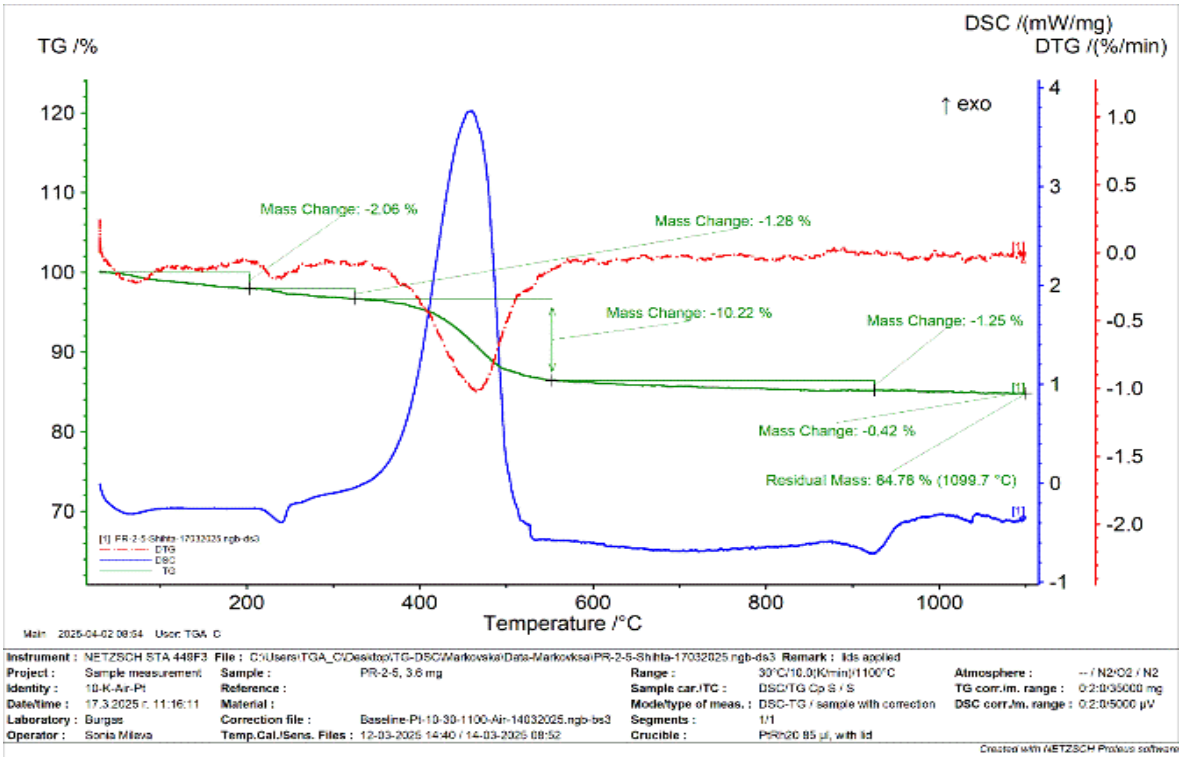


Figure 5. DSC/DTG thermogram of the batch obtained from Al_2O_3 and waste RHA

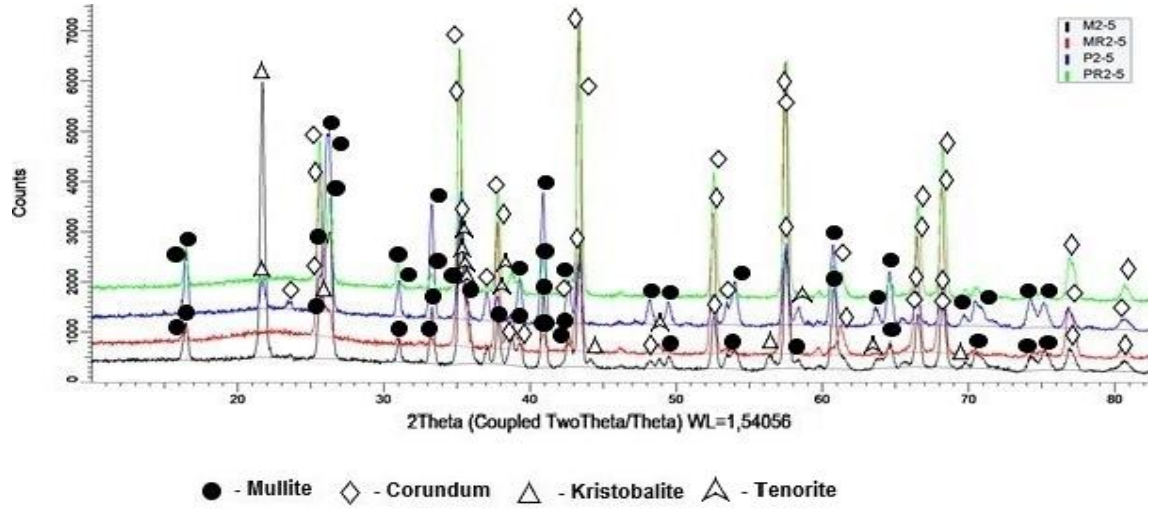


Figure 6. X-ray diffraction patterns of synthesized pigments in the Al_2O_3 - SiO_2 system

Table 2. Phase composition of pigments from the Al_2O_3 - SiO_2 system, synthesized from pure or waste raw materials, with a Cu chromophore in the amount of 5%. Mass content and crystal size

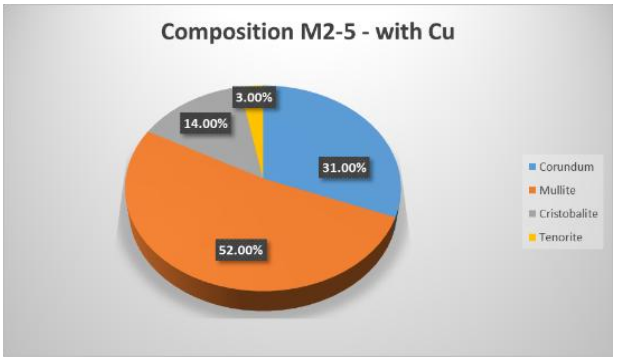
Sample	Corundum mass%, crystal size	Cristobalite mass%, crystal size	Mullite mass%, crystal size	CuO mass%, crystal size
M2-5	31%, 47nm	14%, 32nm	52%, 38nm	3%, 29nm
MR2-5	86%, 55nm	-	11%, 44nm	3%, 36nm
P2-5	17%, 54nm	3%, 22nm	78%, 44nm	2%, 34nm
PR2-5	71%, 57nm	-	27%, 46nm	2%, 52nm

Studies on pigments synthesized at temperatures of 1350 °C and 1400 °C

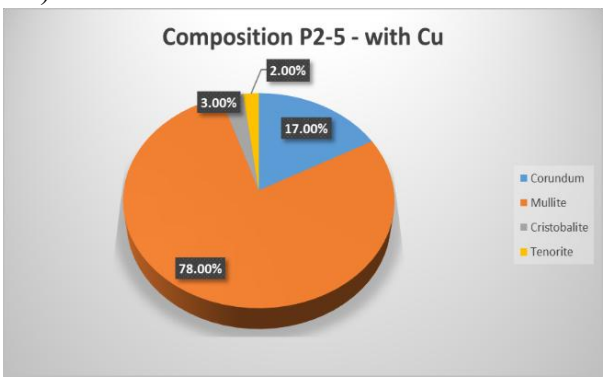
X-ray diffraction patterns of ceramic pigments synthesized by the solid-phase sintering method from pure or waste raw materials (rice husk ash RHA) with 5% of Cu chromophore are presented in Fig. 6. The sizes of the formed crystals vary between 22÷57 nm (Table 2).

The phase composition of the studied samples was determined from the X-ray diffraction analysis data. It can be seen that the main phases in the synthesized pigments are corundum (Al_2O_3) and mullite ($3Al_2O_3.2SiO_2$), and reflexes of cristobalite (SiO_2) and tenorite (CuO) are also observed. With increasing heat treatment temperature, a tendency is observed for the intensity of the peaks of the main phases to increase.

The X-ray diffraction results show that during high-temperature firing, SiO_2 almost completely reacts and mullite is formed, and the high-temperature modification of SiO_2 - cristobalite (compositions M2-5 and P2-5 with pure starting materials) is also noticeable. In pigments with the participation of waste raw materials (rice husk ash RHA), the predominant phase is corundum. For better visualization, the results presented in Table 2 are also interpreted through quantitative diagrams placed in the following figures.

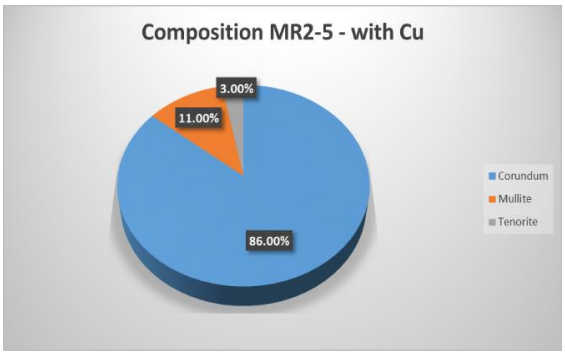


a)

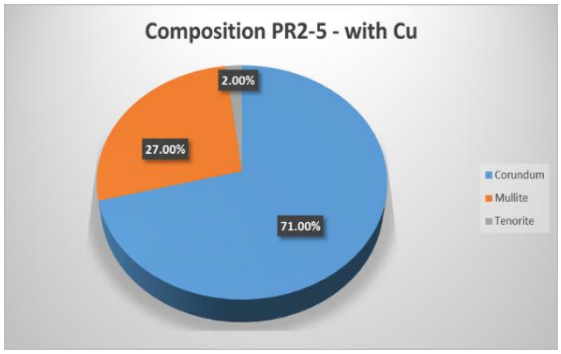


b)

Figure 7. Quantitative diagrams of the X-ray phase analysis of the compositions a)- M2-5; b) - P2-5..



a)



b)

Figure 8. Quantitative diagrams of the X-ray phase analysis of the compositions – a) MR2-5 and b) - PR2-5.

Using the CIELab system which gives a numerical expression of the visual sensation of color, the basic color characteristics of the pigments were determined - color, brightness, color hue.

In the CIELab system, the color coordinates are as follows:

- L* - brightness, L*=0 - black color, L*=100 - white color;
- a* - green color (-) / red color (+);
- b* - blue color (-) / yellow color (+).

The results of the determined color parameters of the synthesized pigments from pure or waste raw materials, with chromophore Cu (5 %), are presented in Table 3.

Table 3. Color characteristics of the synthesized pigments at temperatures of 1350 °C and 1400 °C

No	Composition	Color	L*	a *	b *
1	M2-5		56.9	-3.1	1.1
2	MR2-5		34.0	-2.4	2.5
3	P2-5		38.7	**-3.6**	**5.6**
4	PR2-5		35,8	-1.8	3.4

The pigments with the best color characteristics are those obtained from pure raw materials (composition P2-5 - Al_2O_3 and $SiO_2.nH_2O$) at 1400 °C for 1 hour - (a) = -3.6 and (b) = 5.6.

Fig. 9. presents a SEM micrograph of ceramic pigments of the Al_2O_3 - SiO_2 system, synthesized at 1350 °C from pure starting materials (composition M2-5 - Al_2O_3 and $SiO_2.nH_2O$).

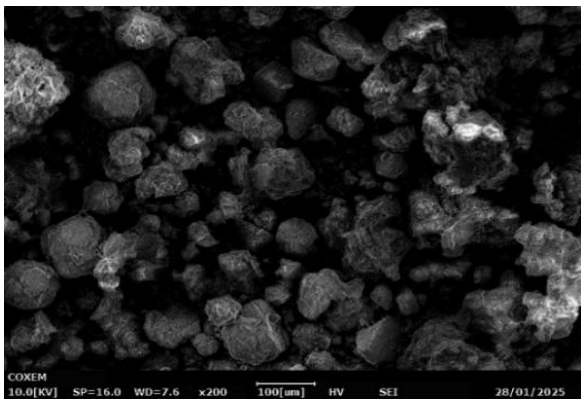


Figure 9. SEM image of pigments with composition M2-5 (Al_2O_3 and $SiO_2.nH_2O$), synthesized at 1350 °C.

SEM micrographs of pigments synthesized at 1350 °C from waste raw materials - Al_2O_3 and RHA (composition MR2-5), are presented in Fig. 10.

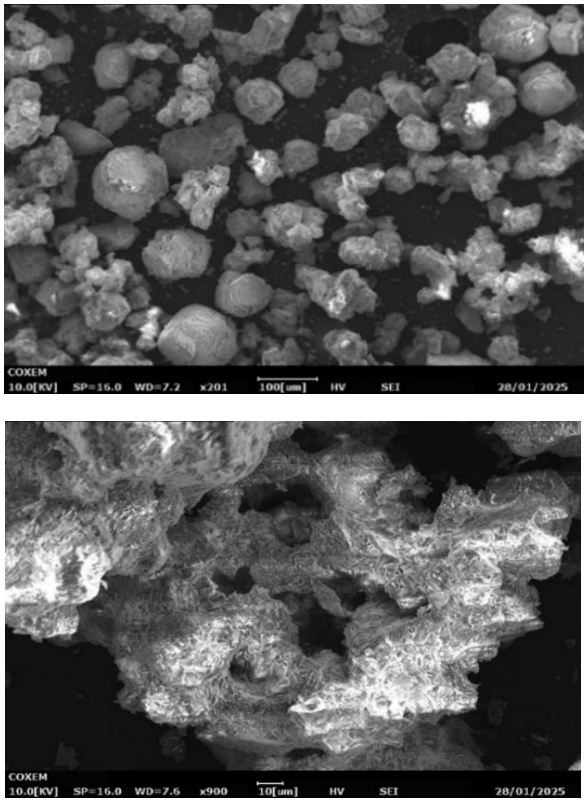


Figure 10. SEM images of pigments with composition MR2-5 (Al_2O_3 and RHA), synthesized at 1350 °C

The SEM analysis shows that clusters of particles are formed, with a size of around and below 100 nm. The coarse shape of the particles indicates the high degree of crystallinity of the obtained pigments.

CONCLUSION

The synthesis and properties of finely dispersed ceramic pigments from the Al_2O_3 - SiO_2 system were studied. The synthesis of both series of pigments was carried out by the solid-phase sintering method. In the first case, pure starting materials were used - Al_2O_3 and $SiO_2.nH_2O$, and the more active - amorphous form of $SiO_2.nH_2O$ was chosen, instead of the crystalline form of SiO_2. For the preparation of the second series of pigments, ash from burnt rice husks with a SiO_2 content of - 94.47 % was used and utilized. The syntheses were carried out at temperatures of 1350 °C and 1400 °C with 1-hour isothermal hold. In both starting compositions - from pure and from waste raw materials, the amount of chromophore was 5% Cu introduced in the form of CuO. Finely dispersed pigments in the gray color range were obtained.

The synthesized pigments from the Al_2O_3 - SiO_2 system were studied using a number of methods, such as XRD, SEM, HSM, and TG. The phase composition of the studied samples was determined from X-ray structural analysis data. It was found that the main phases in the synthesized pigments are corundum and mullite, and reflections of cristobalite and tenorite were also observed. The sizes of the formed crystals in the samples vary between 22÷57 nm. The morphology and the structure of the obtained pigments were studied by SEM which shows that clusters of particles with a crystalline structure are formed. The color characteristics of the pigments were spectrally determined with a Lovibond Tintometer RT 100 Color. The pigments with the best color characteristics are those obtained from pure raw materials (Al_2O_3 and $SiO_2.nH_2O$) and baked at 1400 °C - resp. (a) = - 3.6 and (b) = 5.6.

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